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6. AUTHOR(S)

Dr Sanford A. Asher

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

Dept of Chemistry
University of Pittsburgh
Pittsburgh PA 15260

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13. ABSTRACT (Maximum 200 words)

The purpose of this work is to develop highly optically nonlinear CdS quantum dot-SiO₂ sphere composites useful for optical switching. The concept is to use these spheres in a BCC array formed from crystalline colloidal arrays. The spheres would normally be refractive index matched to the medium and light would freely transmit. At high light intensities the refractive index of the non-linear spheres would diverge from the medium and the array would optically "pop up" to diffract away the high intensity light. The device would act as an optical limiter. Last year's report announced the development of a successful synthesis of these SiO₂-CdS sphere composites. During this report period, we refined our process in order to obtain more homogenous and monodisperse products. We have also extended this synthesis to produce several new materials.

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Grant F49620-93-0008**

**NOVEL MATERIALS AND DEVICES FROM SELF-ASSEMBLED
PERIODIC STRUCTURES**

**Sanford A. Asher
Department of Chemistry
University of Pittsburgh
Pittsburgh, PA 15260**

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1.0 Optically Nonlinear Colloidal Silica-Cadmium Sulfide Nanocomposite Particles

Last year's report announced the development of a successful synthesis of these $\text{SiO}_2\text{-CdS}$ sphere composites. During this report period, we refined our process in order to obtain more homogenous and monodisperse products. We have also extended this synthesis to produce several new materials. We published three papers on this work.

Figure 3 shows a comparison of the UV-visible spectrum of the $\text{SiO}_2\text{-CdS}$ nanocomposites, to that of SiO_2 colloids, while Figure 4 shows the UV-visible spectrum of this nanocomposite after refractive index matching the composite to the dispersing medium. The contribution from light scattering decreases.

These functionalized SiO₂-spheres are sufficiently charged to form high quality crystalline colloidal arrays as shown in the Figure 6 UV-Visible spectrum. These silica spheres form colloidal crystalline under a wide range of colloid concentrations. We have successfully polymerized these SiO₂ crystalline colloidal arrays in a hydrogel film (Fig. 7).

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2.0 Mixed Macroionic Crystalline Colloidal Arrays

The objective of this work is to develop novel smart materials made from the polymerized crystalline colloidal arrays with tunable Bragg diffraction that can be tuned over the entire visible spectrum.

We have fabricated a new material composed of a BCC array of negatively charged polystyrene spheres (ca 100 nm diameter) polymerized in a loose polymer hydrogel. We have incorporated small positively charged polystyrene spheres (ca 30 nm diameter) into the negative lattice. (Figure 8 shows a schematic of the system.) We observe a novel phenomenon in which the diffracted wavelength dramatically decreases as the positive spheres incorporate (Fig. 9 and 10). This can be used as a switchable diffraction device which can be electronically controlled. The crystalline array film is attached to a transparent electronically conductive coating. Depending on the potential applied, positive spheres will be attracted to or repelled from the film, and the film dimension will change to alter the diffracted wavelength (Fig. 11 and 12).

We have also found that if we functionalize the acrylamide gel by hydrolyzing the gel to form carboxylate groups (Fig. 13), the gel will undergo phase transitions and change dimensions in response to an electric field. This changes the diffracted wavelength of the film (Fig. 14). This system at present responds slowly (ca. seconds), but we expect that the speed can be dramatically increased.

Since the wavelength control of both hydrolyzed and unhydrolyzed CCAs is mass transport limited, we will develop methods to make films with thicknesses less than 100 microns to increase the speed of the wavelength control. We will also study the swelling / deswelling behavior of the hydrolyzed films in detail to optimize the rate of the wavelength change in the hydrolyzed CCAs.

The obvious end use applications are laser eye protection, tunable optical filters, sensor protection, 2-D diffraction devices, and optical switches.

3.0 Crystalline Colloidal Arrays of Low Refractive Index Highly Fluorinated Polymer Colloids

The purpose of this work is to develop a synthesis for highly monodisperse colloidal particles with an extremely low refractive index which can be easily refractive index matched for use in non-linear optical limiters and switches.

The particle charge density should be inversely proportional to polymer molecular weight since the particles consist of many entangled polymer chains each of which contains a sulfonate group from the free radical initiator. Our approaches use a chain transfer agent (mercaptan) to control the particle molecular weight.

Assuming all of the sulfonate groups migrate to the surface of particles and contribute to the surface charge:

$$\sigma = 1.608 \cdot 10^3 \cdot \rho d / M_n$$

where σ is the particle surface charge density ($\mu\text{C}/\text{cm}^2$), ρ is the particle density (g/cm^3), d is the particle diameter (nm) and M_n is the number-average molecular weight.

The maximum charge density is achieved by minimizing M_n by using a chain transfer agent such as mercaptan to limit the polymer molecular weight. Table I shows a typical recipe to synthesize fluorinated highly charged colloidal spheres.

Figure 15 which shows diffraction of colloidal crystals made from a highly charged fluorinated colloid shows a narrow diffraction peak bandwidth due to the closeness between the refractive index of the fluorinated colloid and the water medium.

4.0 Colloidal Hydrogel Particles for Optical Switchable Notch Filters

The objectives of this present work are to make use of smart materials based on hydrophilic poly(*n*-isopropylacrylamide) (PNIPAAm) latex particles, and to develop switchable optical notch filters. The novel colloidal particles exhibit reversible volume changes with temperature.

We have prepared monodisperse crosslinked colloidal particles from a water soluble monomer, *n*-isopropylacrylamide, by dispersion polymerization. A typical recipe to make 200 nm diameter particles is shown in Table II. We also incorporated charged and photosensitive comonomers into these particles. As shown in Figure 16, the diameter of the PNIPAAm particles decreases by a factor of 2 and the volume decreases by a factor of 8 when the temperature is raised to 30-38 °C (the volume phase transition temperature T_v).

The particles self assembled into crystalline colloidal arrays at room temperature. These polymer colloids are electrosterically stabilized below T_v and are stabilized only by electrostatic repulsive forces above T_v . Figure 17 shows that the crystalline colloidal arrays diffract incident light much more efficiently above T_v . This is the result of an increased refractive index mismatch between the particles and the surrounding medium.

We also developed a system, consisting of particles in the presence of hydrophilic polyelectrolyte (including the comonomer sodium acrylate), that diffracts incident light only below T_v as shown in Figure 18. Above T_v , the hydrophilic polyelectrolyte dissociates from the particles and screens the repulsion between colloidal particles. This is a very good example of molecular sensing by the colloidal particles. Lowering the temperature results in a high quality crystal since the crystallization front works almost in a zone refining.

The most outstanding achievement of the present work is that the development of hydrogel membranes consisting of closely packed interconnected microspheres of PNIAAm. These membranes are prepared by drying out the colloidal dispersions. These membranes exhibit reversible volume changes in aqueous medium with temperature. We hope these will function as temperature sensitive diffraction membranes. We are in the process of optimizing the material properties for such applications.

5.0 Polymethylmethacrylate Polymerized Crystalline Colloidal Arrays for Optically Nonlinear Switchable Bragg Diffraction Devices

We have completed preliminary experiments that demonstrate a nonlinear optical response of our dyed refractive index matched crystalline colloidal arrays (CCA). These data support our proposed approach for building optical limiters. The idea was to construct an array of spheres which was refractive index matched to the medium. These spheres would, thus, not diffract light. The spheres contain absorbing dye. At high light intensities the dye would absorb sufficient light to heat the spheres and change the spheres' refractive index in the nsec time regime. This change in refractive index of the sphere array would cause diffraction to occur.

Figure 19 shows the experimental approach used where a 610 nm pump laser is coincident with a 532 nm probe beam. The array spacing would diffract the probe if the refractive indices were not matched. The diffracted light is incident on a white screen and is observed with a CCD camera. In the experiment shown here, we also record in the bottom portion a reference reflection used to normalize the diffraction intensities. For the experiment here the refractive index of the medium is slightly greater than that of the spheres. The data show that a diffracted intensity decrease in the presence of the pump beam. The diffracted intensity rides on a reflection from the polymerized crystalline colloidal array film which gives us a background intensity at the location of the diffracted light. We also see other nonlinear phenomena in the presence of dye and are presently characterizing these phenomena as well.

As part of this work we synthesized highly charged monodisperse PMMA spheres which self-assemble to form crystalline colloidal arrays, and synthesized dyed PMMA spheres and polymerized them in a polyacrylamide hydrogel matrix. We developed a new method to covalently bond dye to the PMMA spheres and demonstrated the refractive index dependence of the diffraction intensity of these films. Figure 20 shows the chemical structures of the reagents used in emulsion polymerization. Figure 21 illustrates the polymerizable monomer recipe used in preparing a hydrogel matrix, while Figure 22 illustrates the transmission spectra of the PMMA CCA in a hydrogel matrix. We published our method of polymerizing crystalline colloidal arrays in hydrogel films.

Figure 23 shows the transmission spectrum of a crystalline colloidal array formed from PMMA spheres containing covalently bonded dyed PMMA. The medium was a mixture of methyl phenyl sulfoxide and water ($n=1.513$). These PMMA colloids can be refractive index matched to the medium as indicated in Figure 24.

Personnel Working on Project:

Graduate Students Supported:	Zhenhuan Chi	33% for the year
	Guisheng Pan	100% for the year
Postdoctoral Researchers Supported:	Albert Tse	100% for the year
	Song-yuan Chang	75% for the year

Publications in Reviewed Journals:

1. "A Self Assembly Motif for Creating Submicron Periodic Materials. Polymerized Crystalline Colloidal Arrays", S. A. Asher, J. Holtz, L. Liu, and Z. Wu, J. Am. Chem. Soc. 116, 4997-4998 (1994).
2. "Creation of Templated Complex Topological Morphologies in Colloidal Silica", S.-Y. Chang, L. Liu, and S. A. Asher, J. Am. Chem. Soc. 116, 6745-6747 (1994).
3. "Preparation and Processing of Monodisperse Colloidal Silica-Cadmium Sulfide Nanocomposites", S.-Y. Chang, L. Liu, and S. A. Asher, Mat. Res. Soc. Symp. Proc. Vol. 346, 875-880 (1994).
4. "Preparation and Properties of Tailored Morphology, Monodisperse Colloidal Silica-Cadmium Sulfide Nanocomposites", S.-Y. Chang, L. Liu, and S. A. Asher, J. Am. Chem. Soc., in press (1994).

Books or Book Chapters: None

Patents:

Our patent, "Method of Making Solid Crystalline Narrow Band Radiation Filter" has just been issued by the patent office as U.S. Patent Number 5,281,370.

Technology Transfer:

We are involved in a collaboration with Mine Safety Appliances Company to develop laser eye protection from the 1.06 mm Yag laser using absorbing dyes. We are utilizing some of the equipment purchased for the AFOSR project for this work.

We are also involved in a collaboration with Westinghouse Corporation on Raman studies of growing diamond films.

Table I
Recipe for Synthesis of Highly Charged Fluorinated Colloid

<u>Reagents</u>	<u>Weight (gram)</u>
H ₂ O	20.00
CH ₂ =C(CH ₃)COOCH ₂ CF ₂ CF ₂ CF ₃	4.00
AEROSOL MA-80	VARIABLE
C ₁₂ H ₂₅ SH	VARIABLE
Na ₂ S ₂ O ₈	0.020

Reaction temperature: 50.0 °C

Reaction time: 3.0 hrs

Charge density in the range of 0.2 to 1.0 μC/cm²

Table II

Recipe for Synthesis of Thermally Responsive Colloids

N-isopropylacrylamide	3.5 g
N,N'-Methylenebis(acrylamide)	0.35g
Charged comonomer/dye	0-2 wt%
Anionic surfactant	0.1 g
Potassium persulfate	0.14 g
Deionized water	250 g

Figure 1. Synthesis of SiO_2 -CdS Nanocomposite

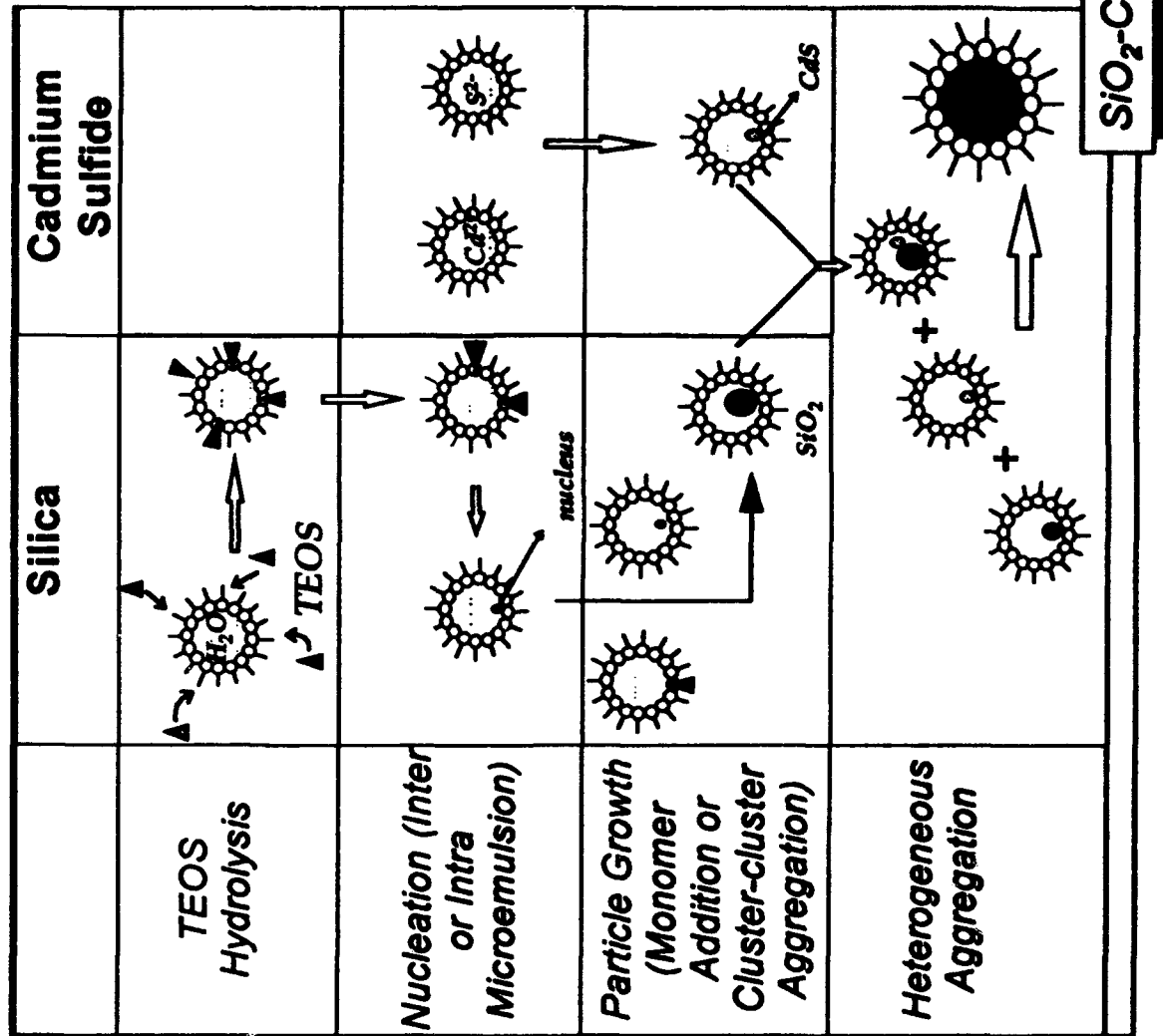


Figure 2. *Optically Nonlinear Colloidal SiO₂-CdS Nanocomposite:*

We have synthesized the nanocomposites in an unique W/O microemulsion. As shown below, the monosize nanocomposite is 110nm in diameter with ~5nm CdS dots homogeneously dispersed inside.

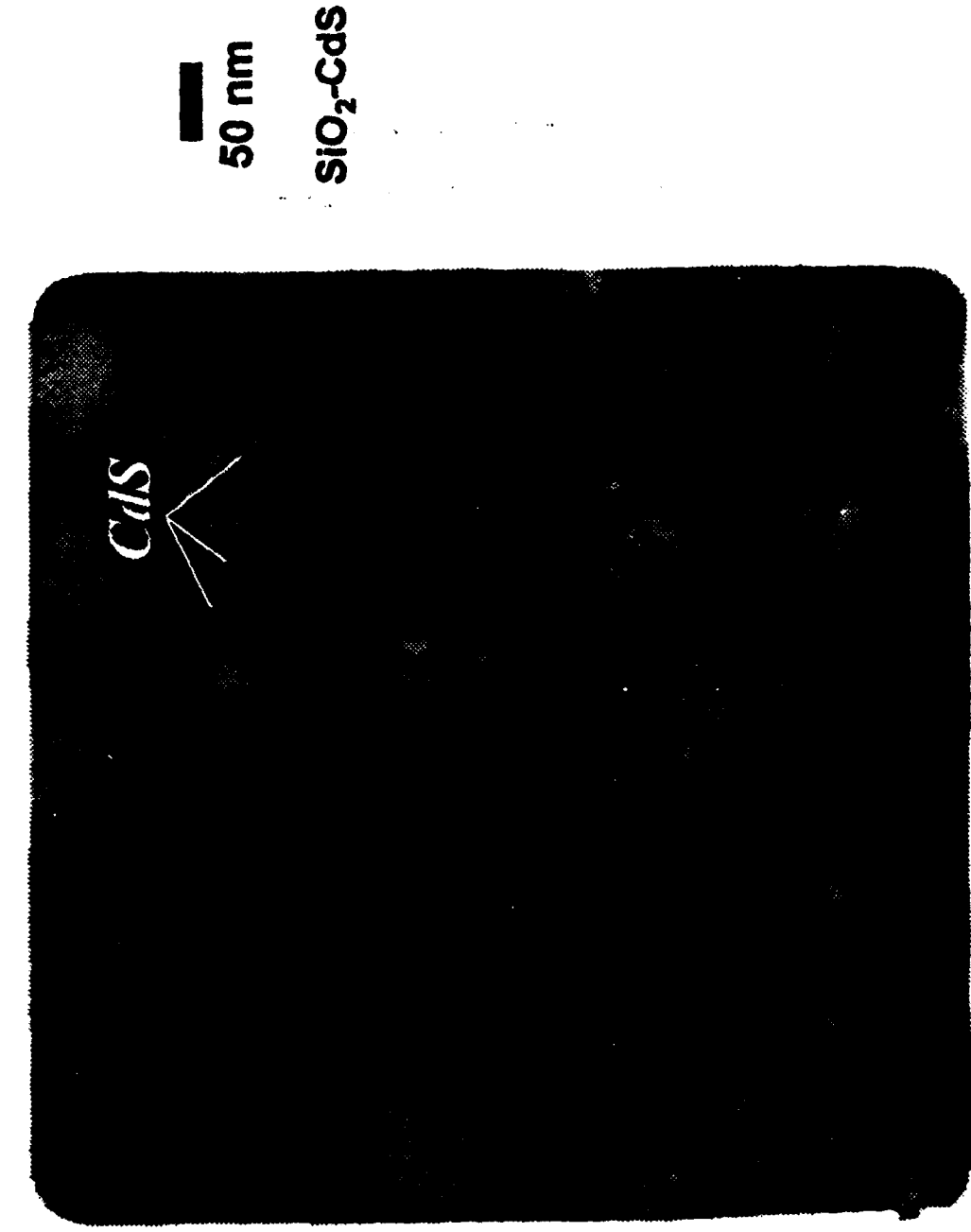


Figure 3. Quantum Confinement of Nanocomposite

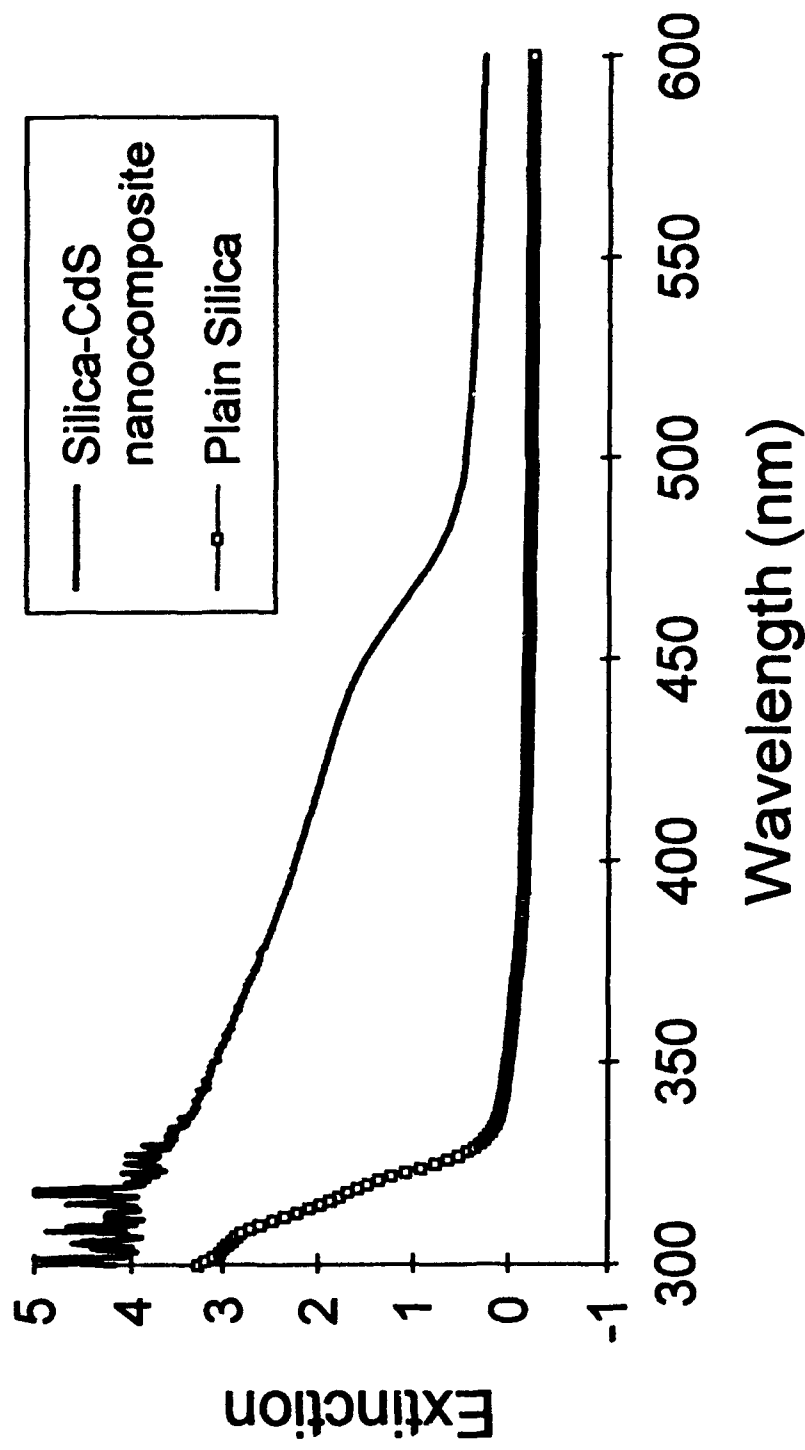


Figure 4. *Quantum Confinement Effect from a $\text{SiO}_2\text{-CdS}$ Nanocomposite:*

UV-Visible spectrum of $\text{SiO}_2\text{-CdS}$ refractive index matched nanocomposite.

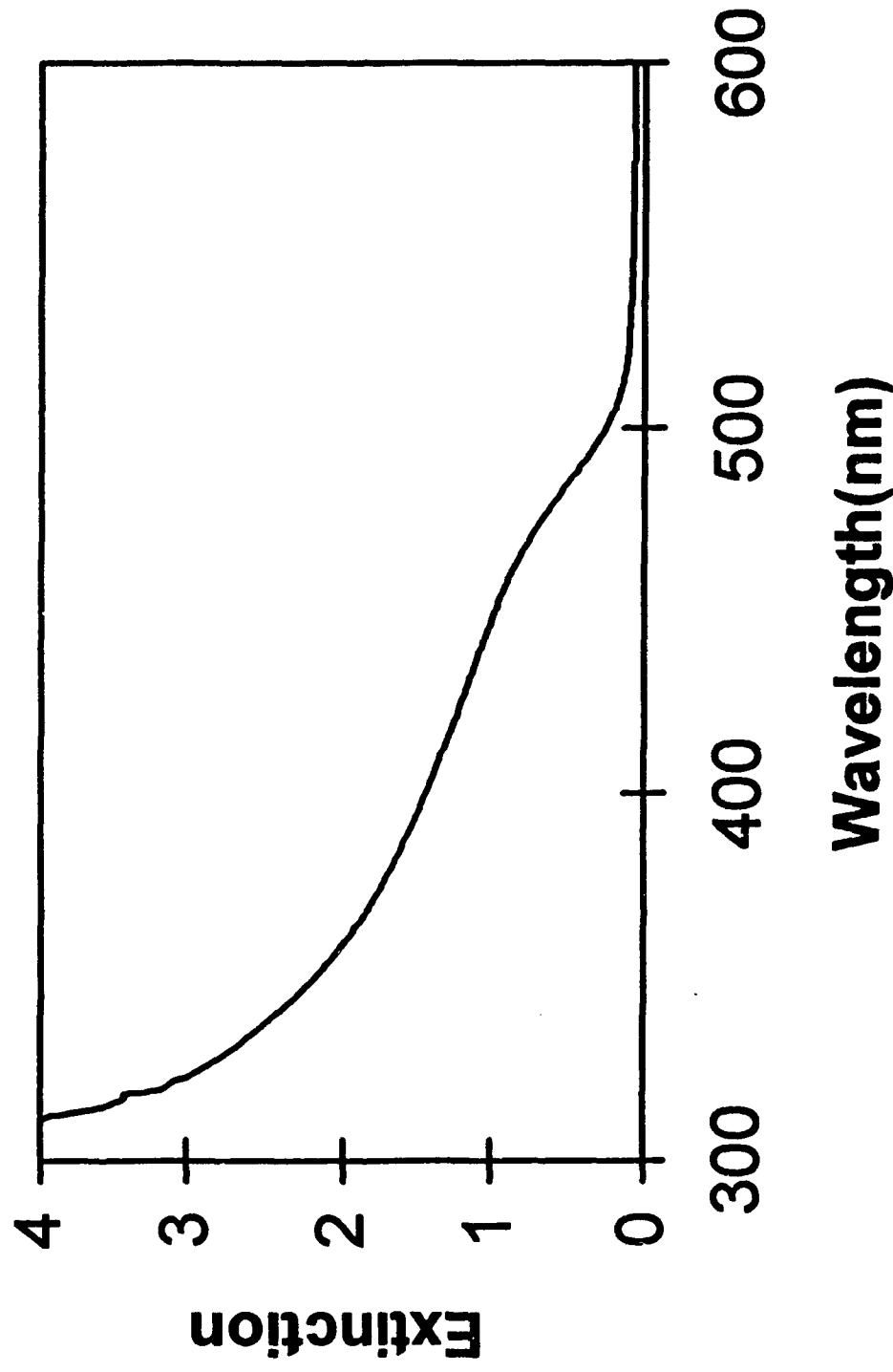


Figure 5. Charge density of silica colloids before and after surface

functionalization with (MeO)₃-Si-(CH₂)₂-(C₆H₄)-SO₂Cl.

<i>Sample ID</i>	<i>e /particle</i>	<i>μC / cm²</i>	<i>Diameter (nm)</i>	<i>Polydispersity</i>	<i>Iridescence</i>
Is38 NF*	4.24 x 10 ²	0.196	105	4.79 %	colored
Is38 F**	3.845 x 10 ³	1.78	105	4.79 %	diffracts
Is39 NF*	9.6 x 10 ¹	0.045	104	4.87 %	colored
Is39 F**	7.14 x 10 ³	3.36	104	4.87 %	diffracts

*Non-Functionalized

**Functionalized

Figure 6. Crystalline colloidal arrays(CCA) from highly charged SiO_2 colloids functionalized with $(\text{MeO})_3\text{Si}(\text{CH}_2)_2(\text{C}_6\text{H}_4)\text{SO}_2\text{Cl}$:

These colloids form CCA under a wide range of particle concentrations.

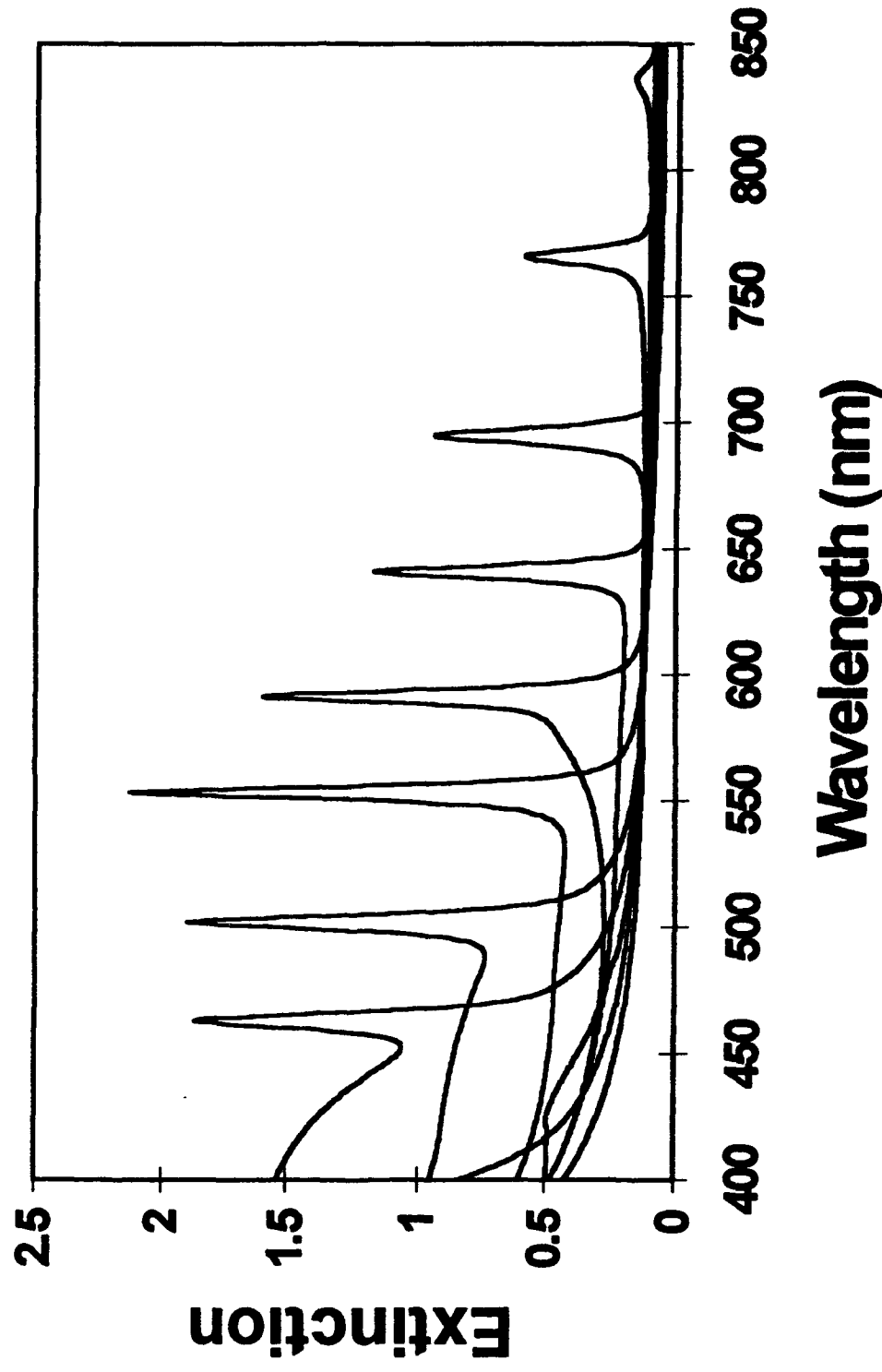
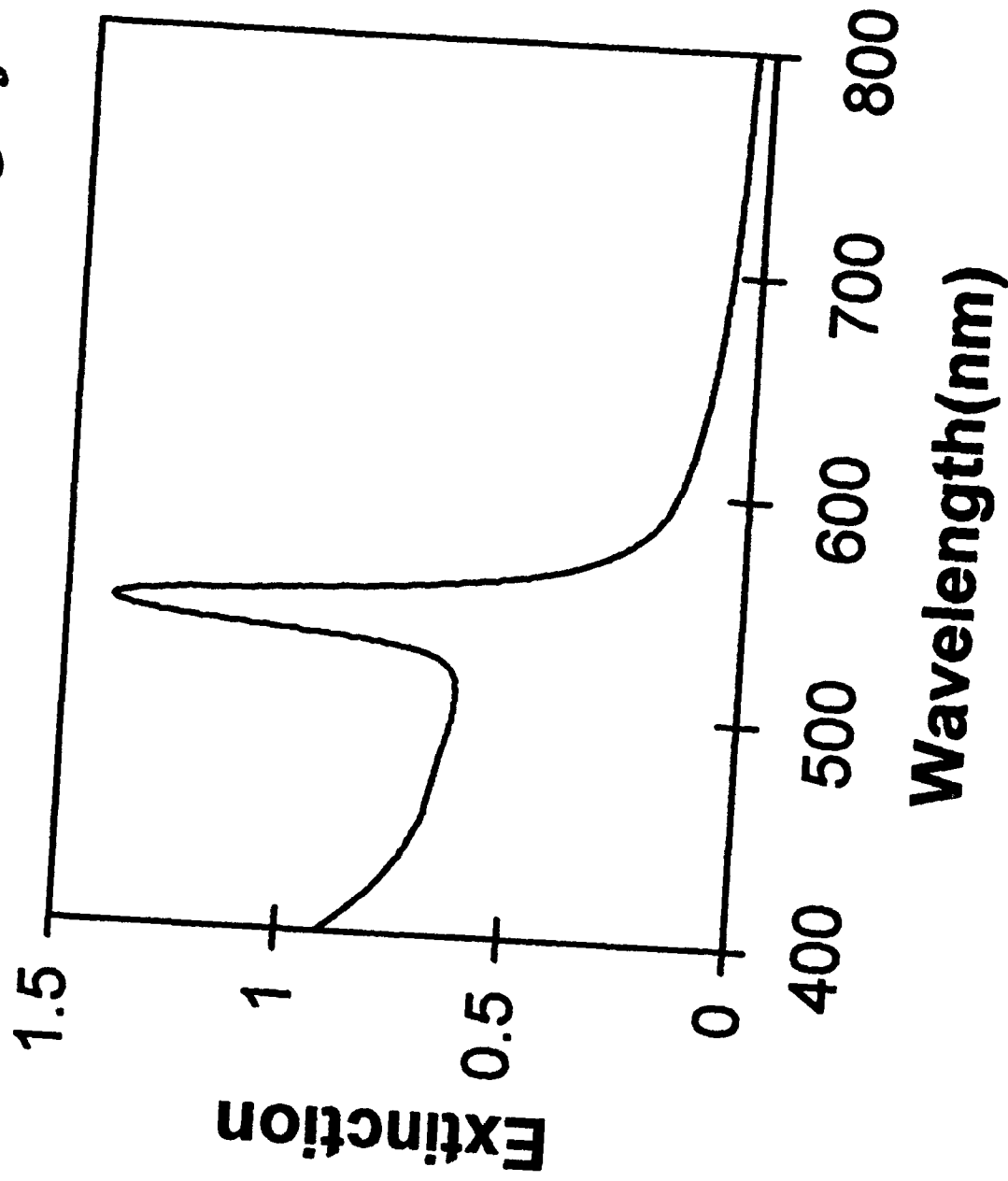


Figure 7. UV-Visible spectrum of SiO_2 crystalline colloidal arrays in a polymerized hydrogel film.



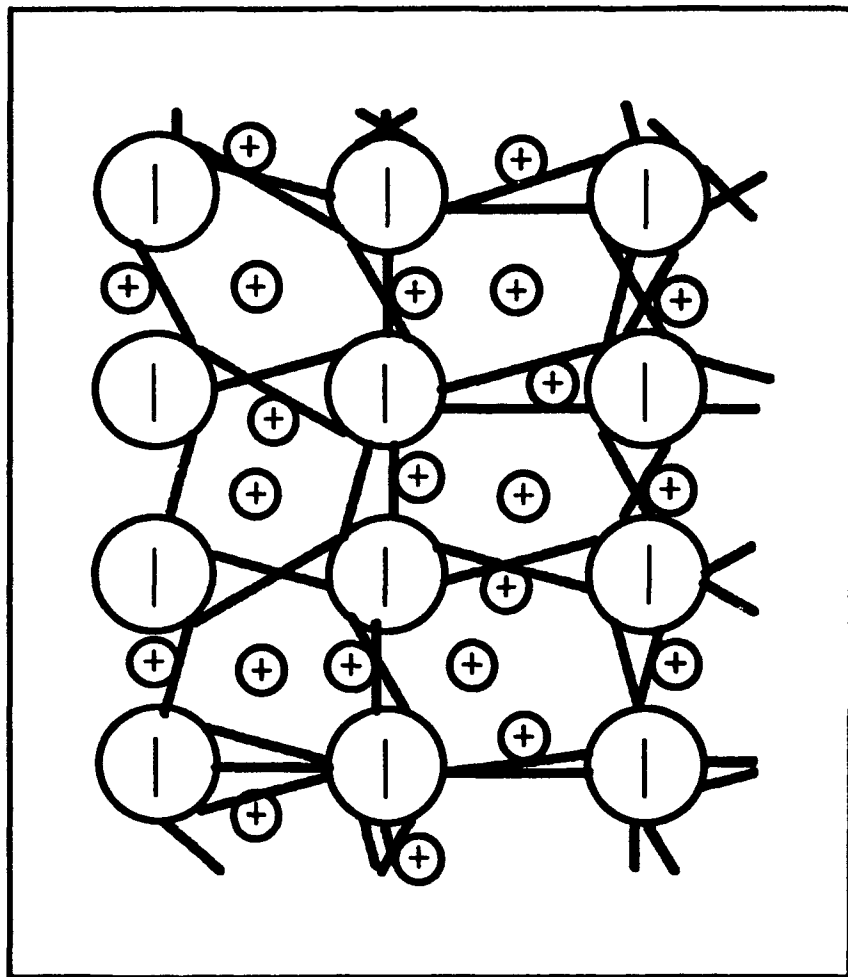
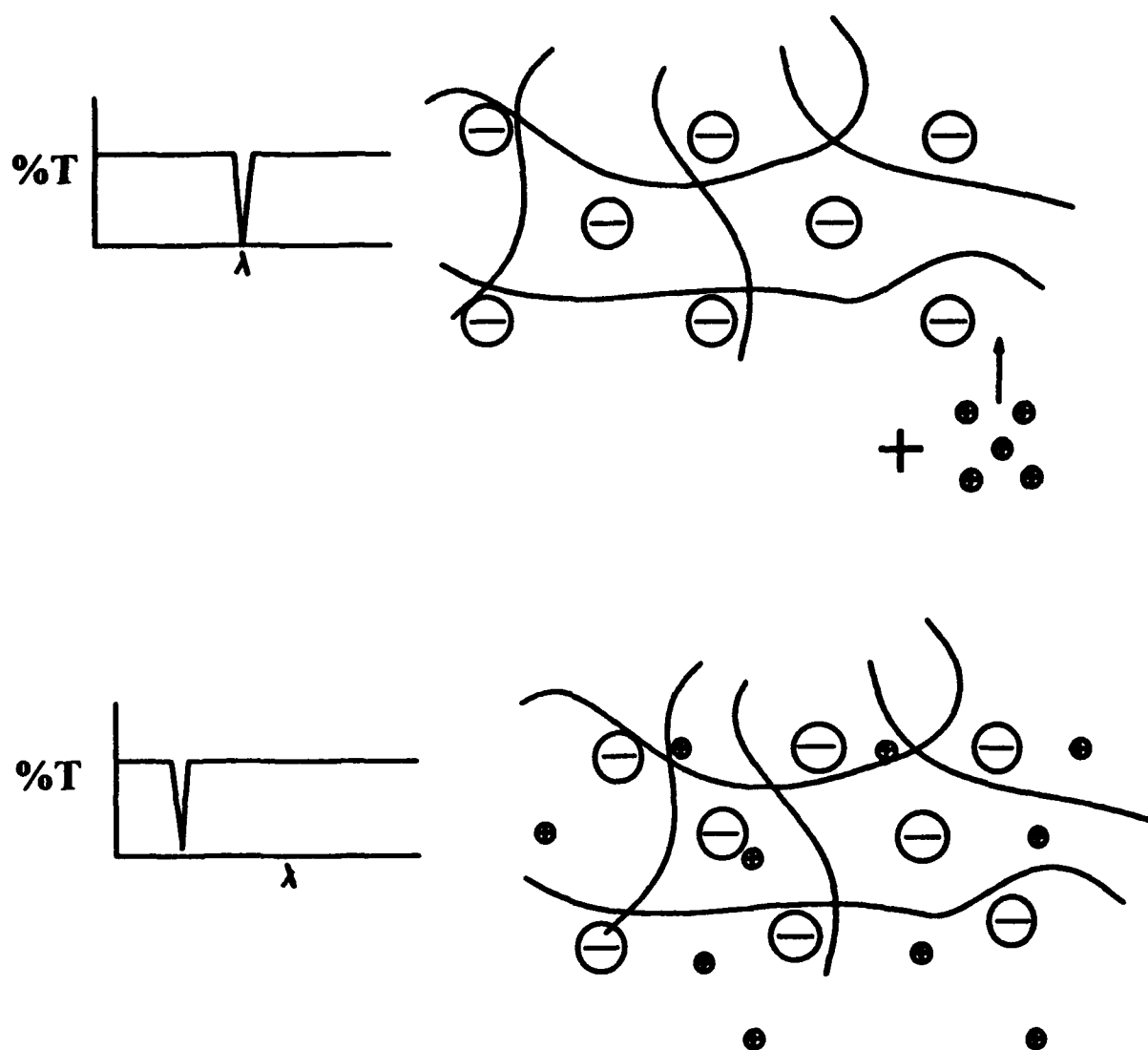


Figure 8. Schematic of the new material showing the free positive spheres in the polymerized negative sphere system.

Figure 9. The effect of positive spheres on the negative sphere lattice.



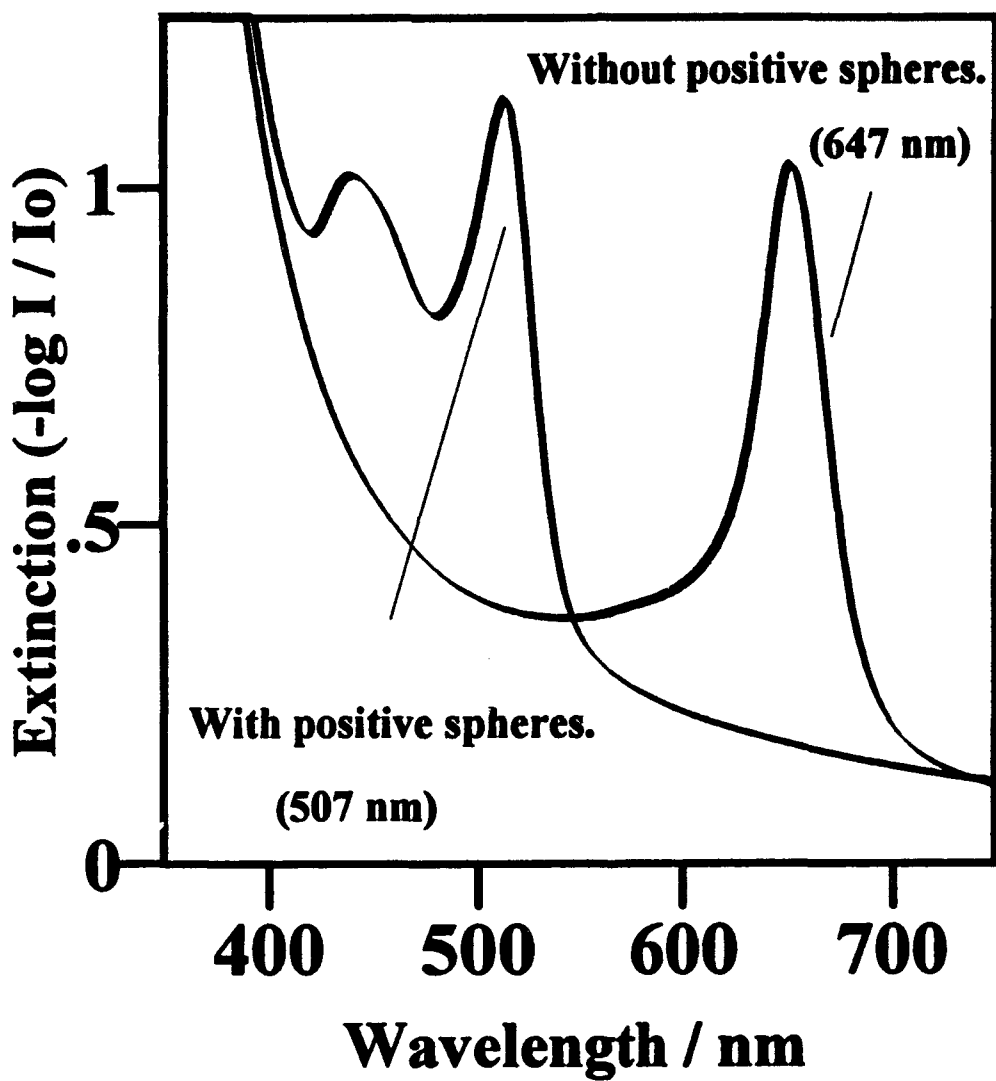
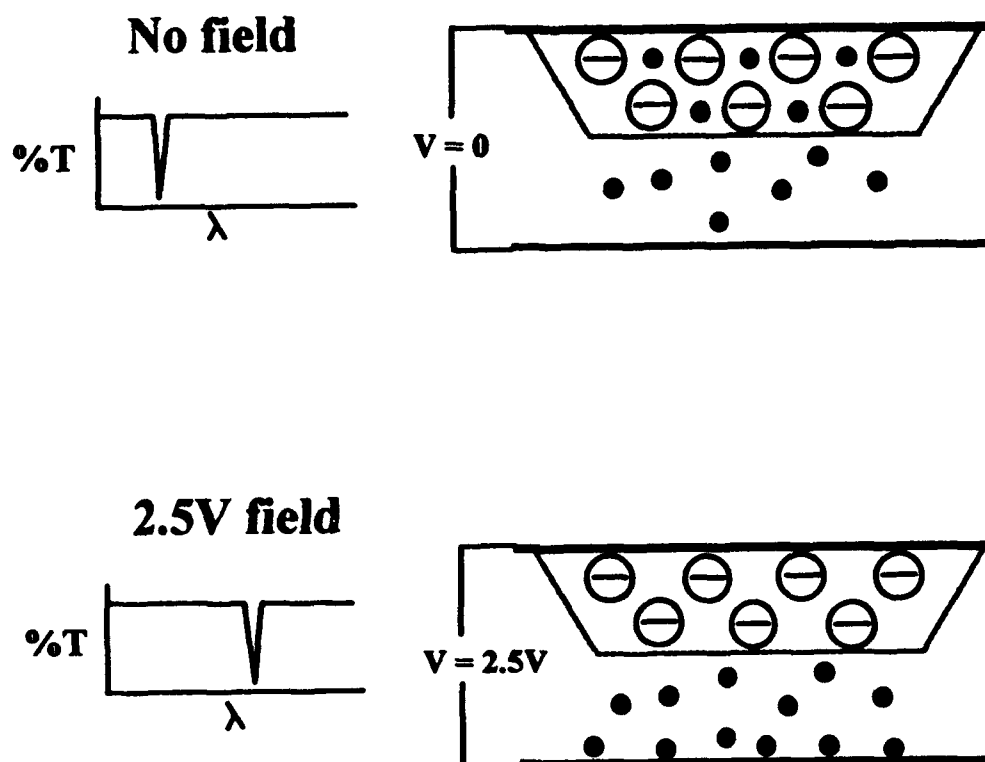


Figure 10. Shift in Bragg diffraction of polymerized CCA due to the presence of free 30 nm positive spheres.

Figure 11. The effect of an electric field on the positive / negative sphere system.



**phase transition of the system induced by
electric field**

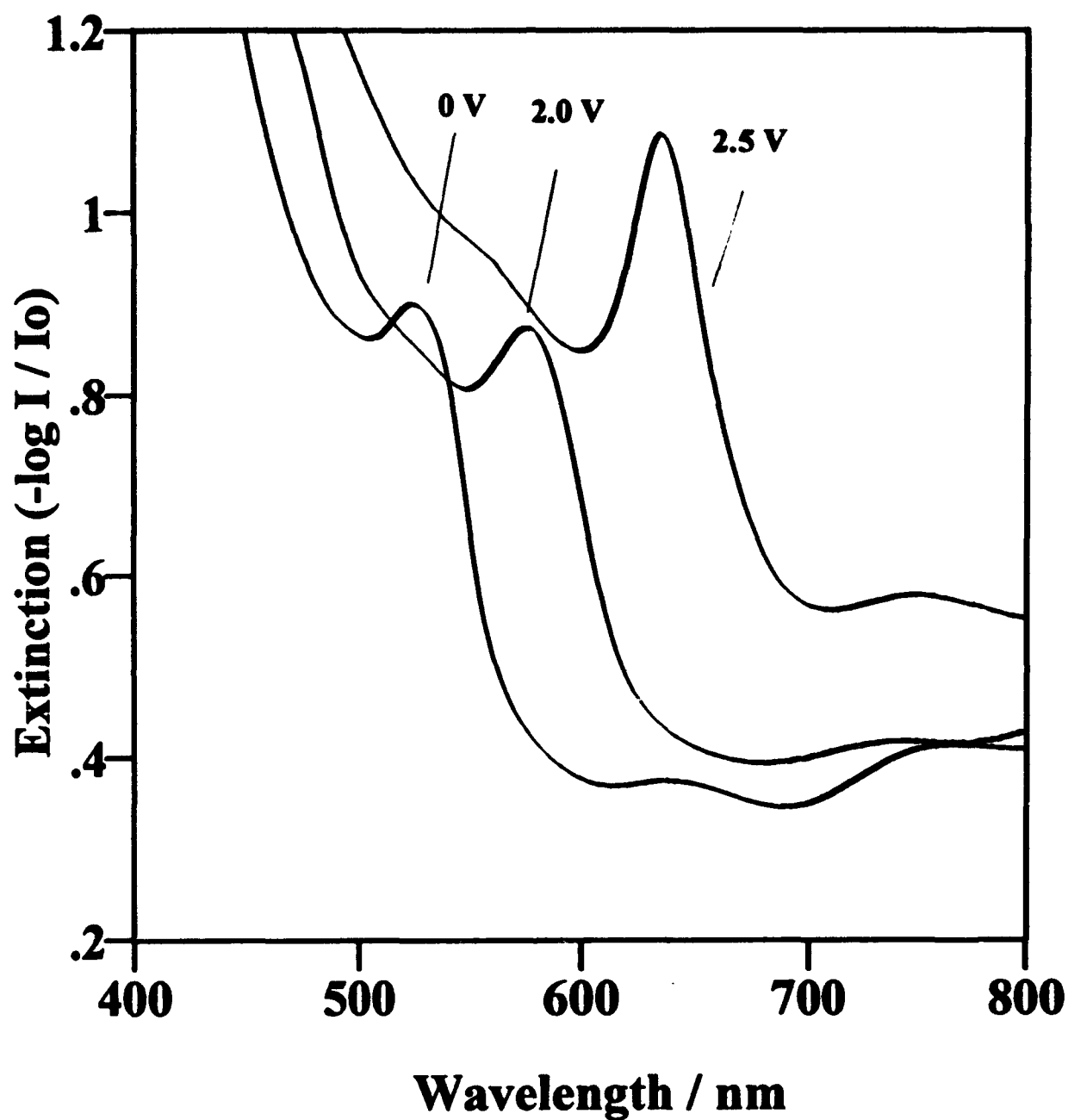
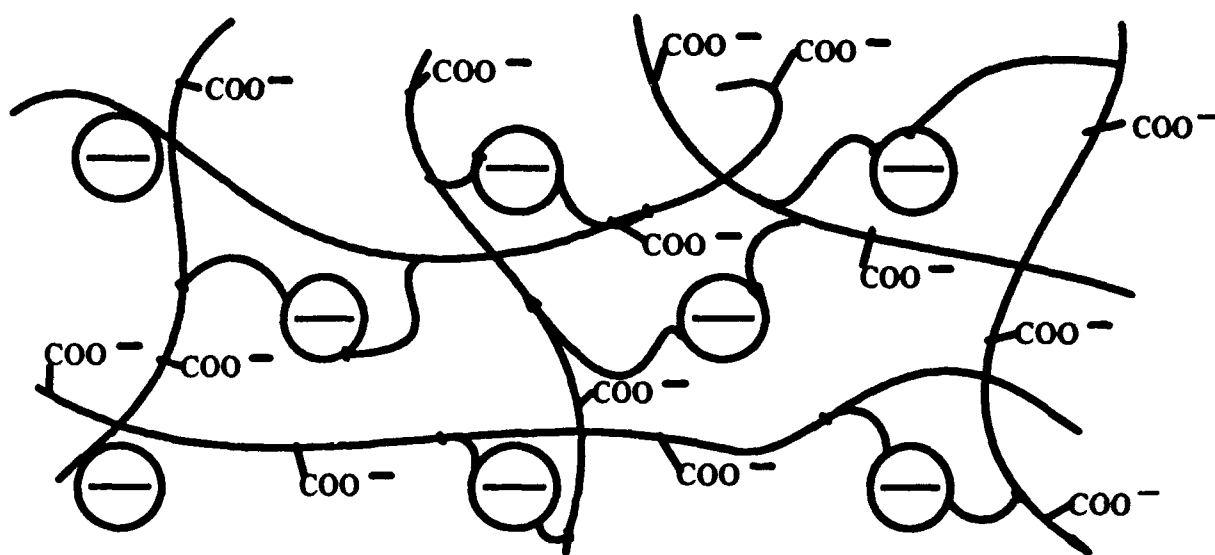


Figure 12. Effects of electric field on a polymerized CCA in contact with positive 30 nm spheres.

Figure 13. Novel material consisting of a BCC lattice of negatively charged spheres in a charged acrylamide hydrogel network.



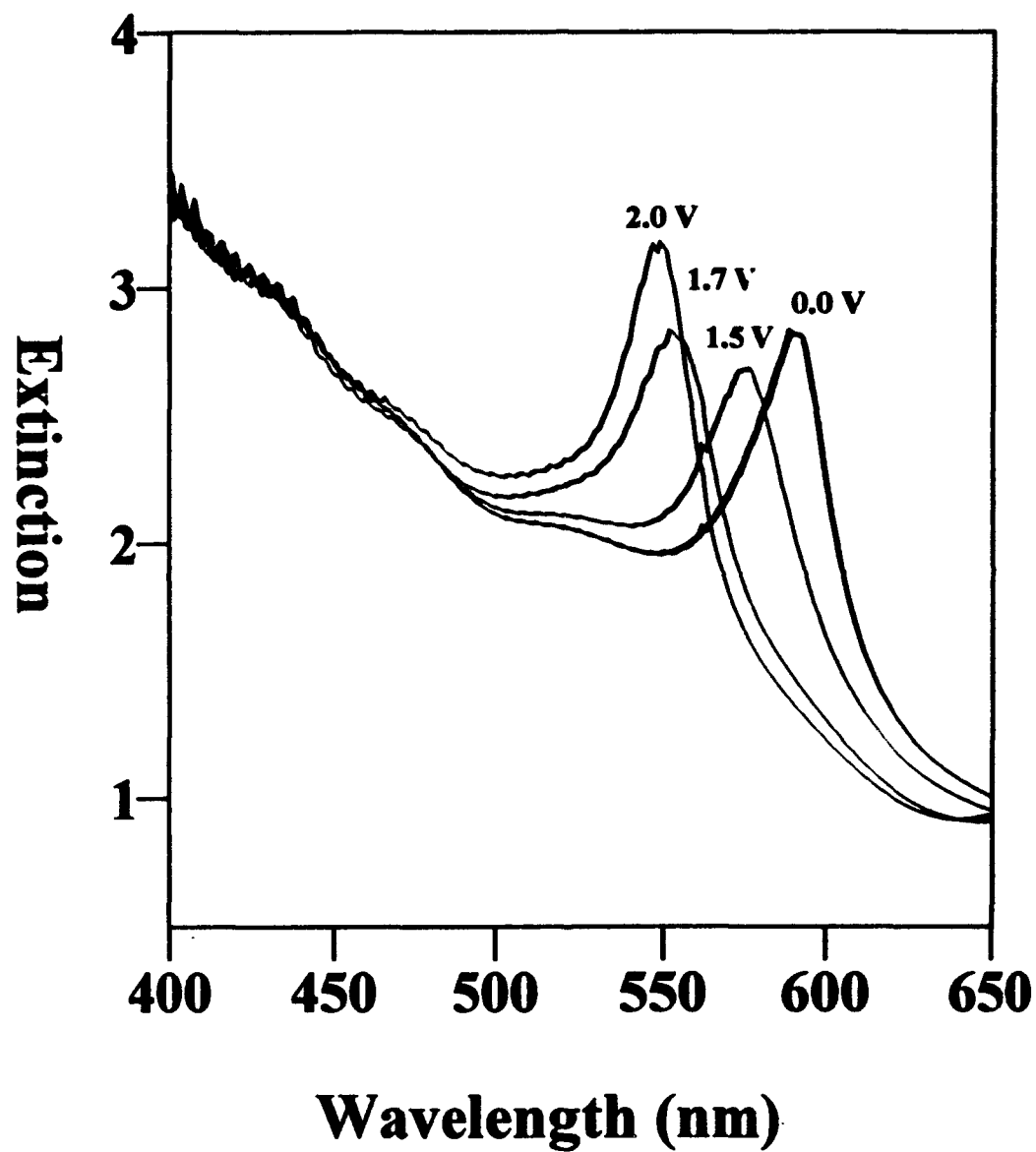


Fig. 14. Change in diffraction peak of hydrolyzed PCCA from applied voltage.

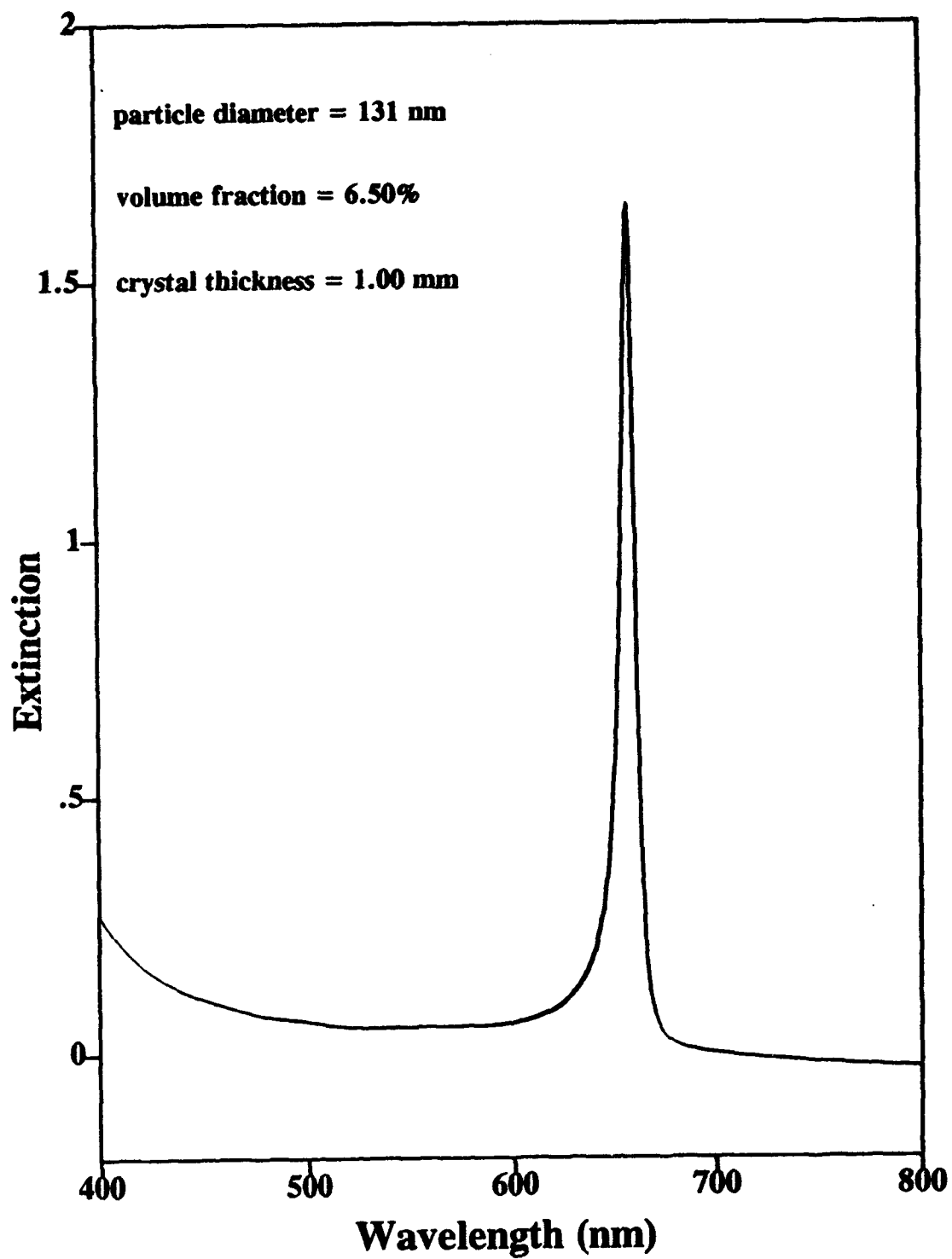


Figure 15

Particle Diameter Changes due to Thermal Phase Transitions

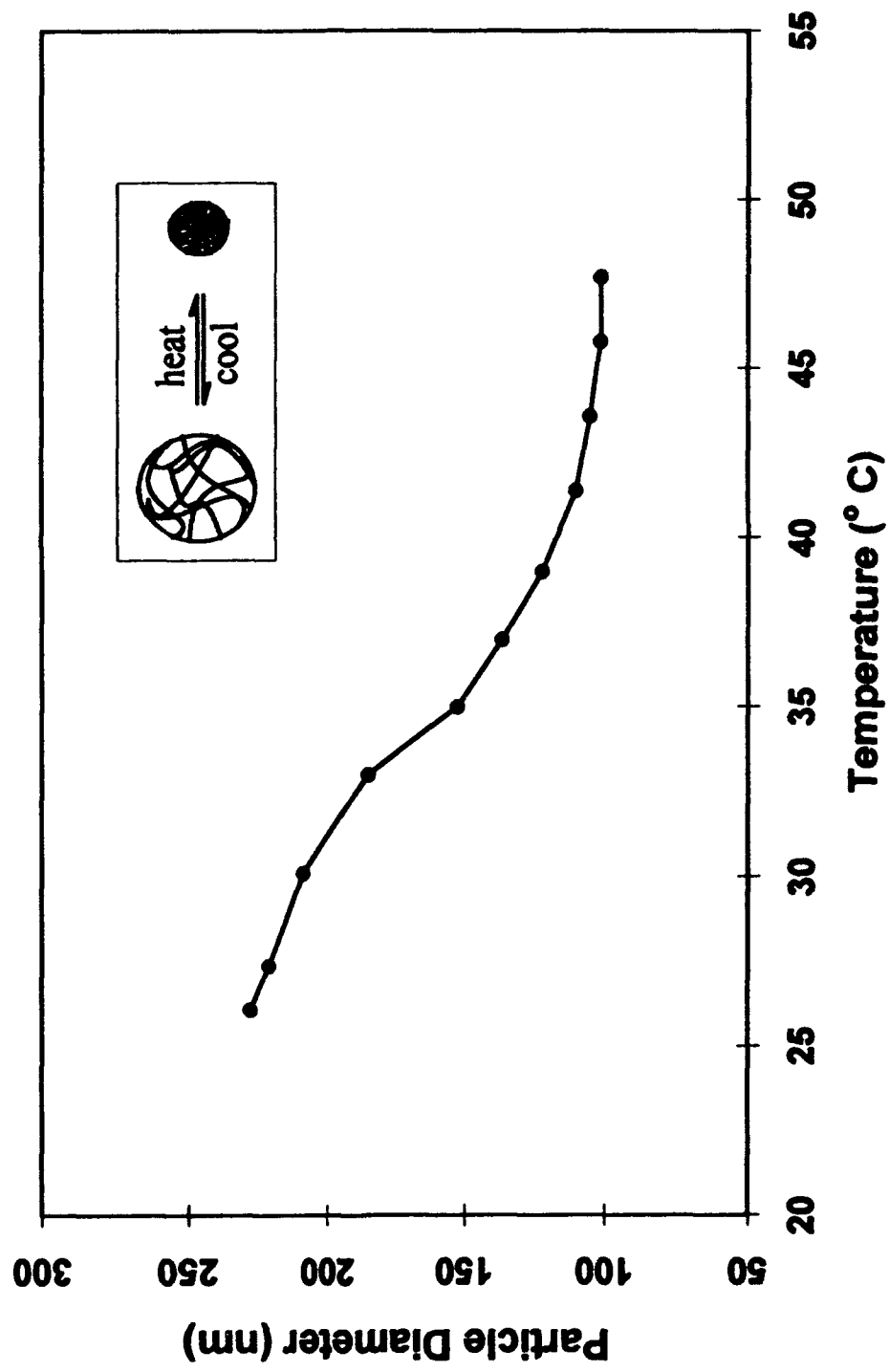


Figure 16

Temperature Dependent Change in Diffracted Intensity of CCA of PNIAAM Microspheres

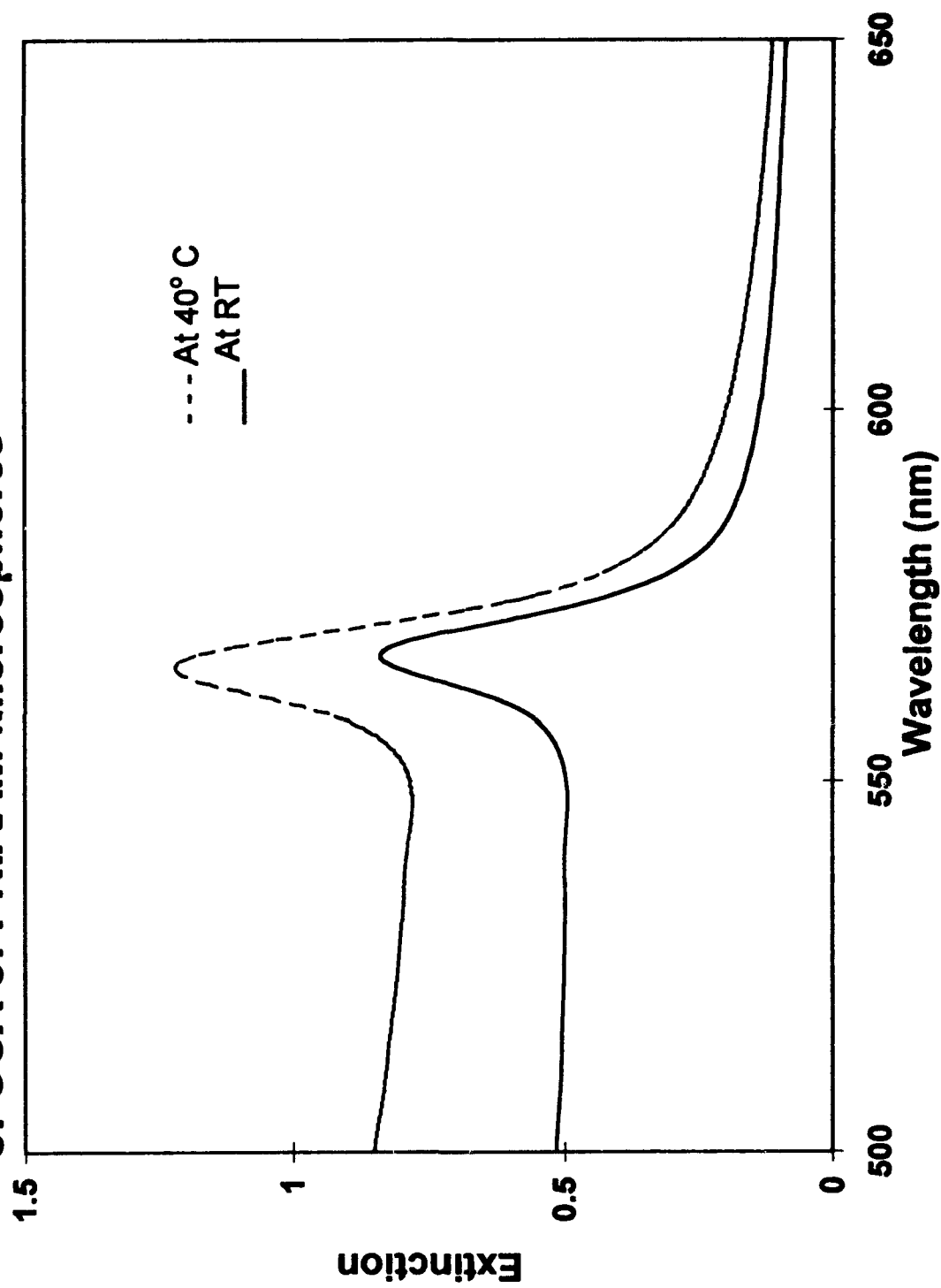


Figure 17

Zone Refining of CCA of PNIPAAM Microspheres

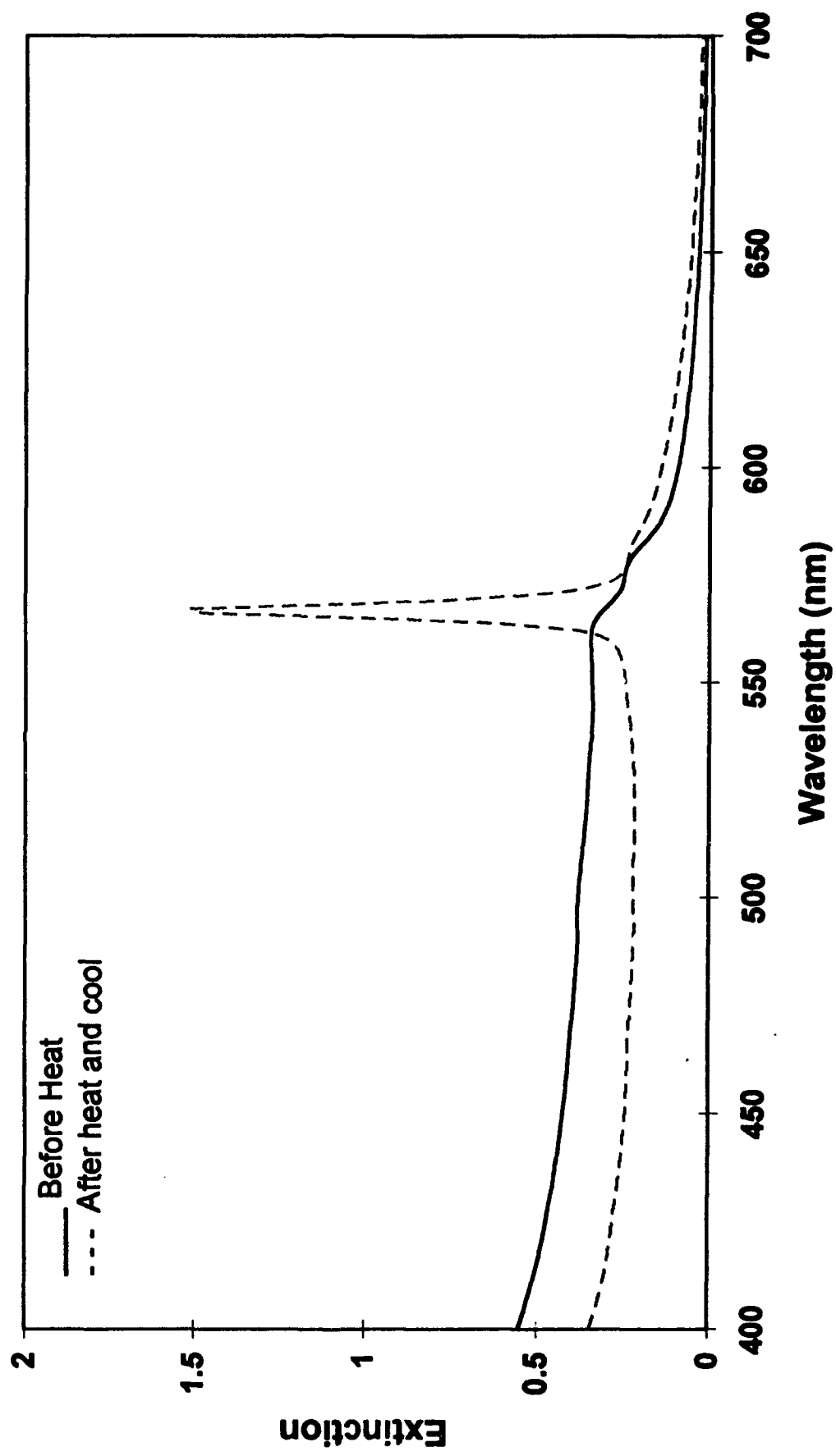
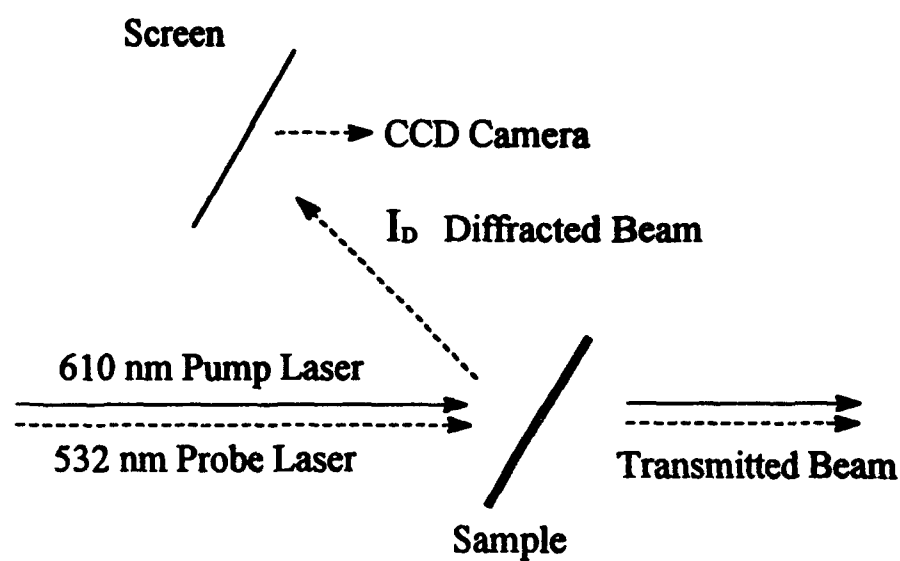
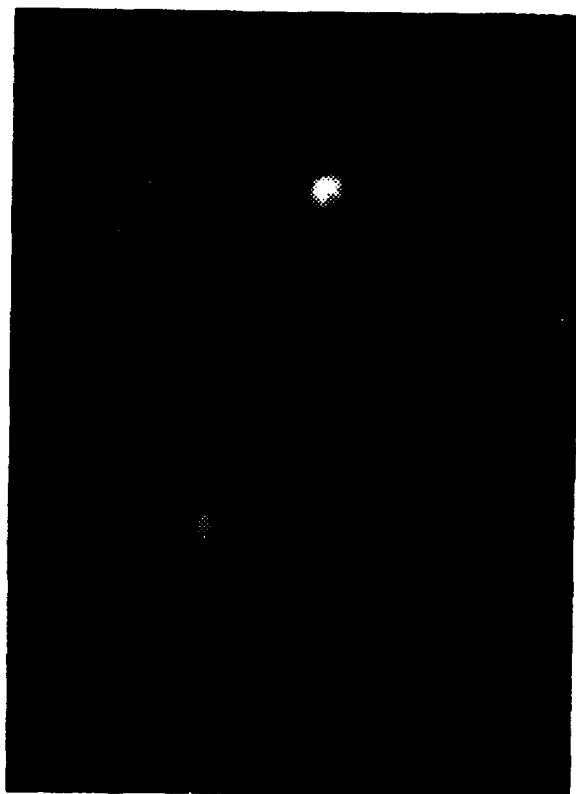


Figure 18

Figure 19: Pump-Probe Experiment Setup



Probe Beam Only

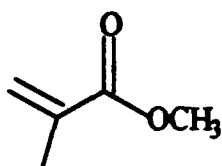


Probe + Pump Beam

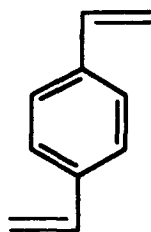


The Bottom Spots are Reference Spots

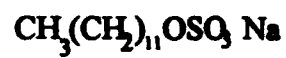
Figure 20: Structures of the Reagents



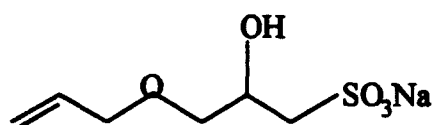
MMA



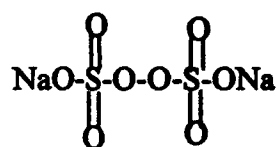
DVB



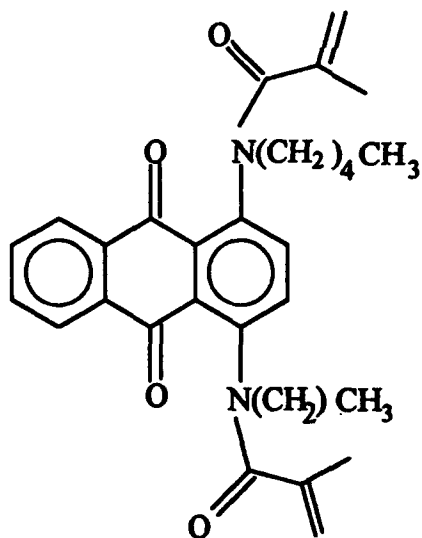
SDS



COPS-1

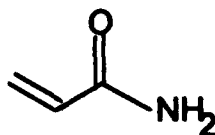


Sodium Persulfate

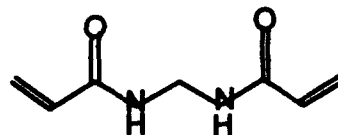


Acylated Oil Blue N

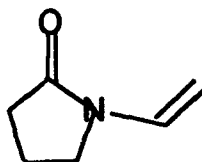
Figure 21 Monomers in Hydrogels



Acrylamide (AMD)



Methylene-bis-acrylamide(MBA)



N-vinylpyrrolidone(NVP)

Recipe:

PMMA Colloids:	8-15%
AMD : MBA	: 7:1
AMD%	: ~6%

Figure 22: Formation of PMMA Colloidal Crystals

60--200 nm PMMA colloids are prepared by emulsion polymerization. The following transmission spectra demonstrate that large colloidal crystals formed in water or in polyacrylamide hydrogel from 146 nm PMMA colloids in a 0.4 mm cell.

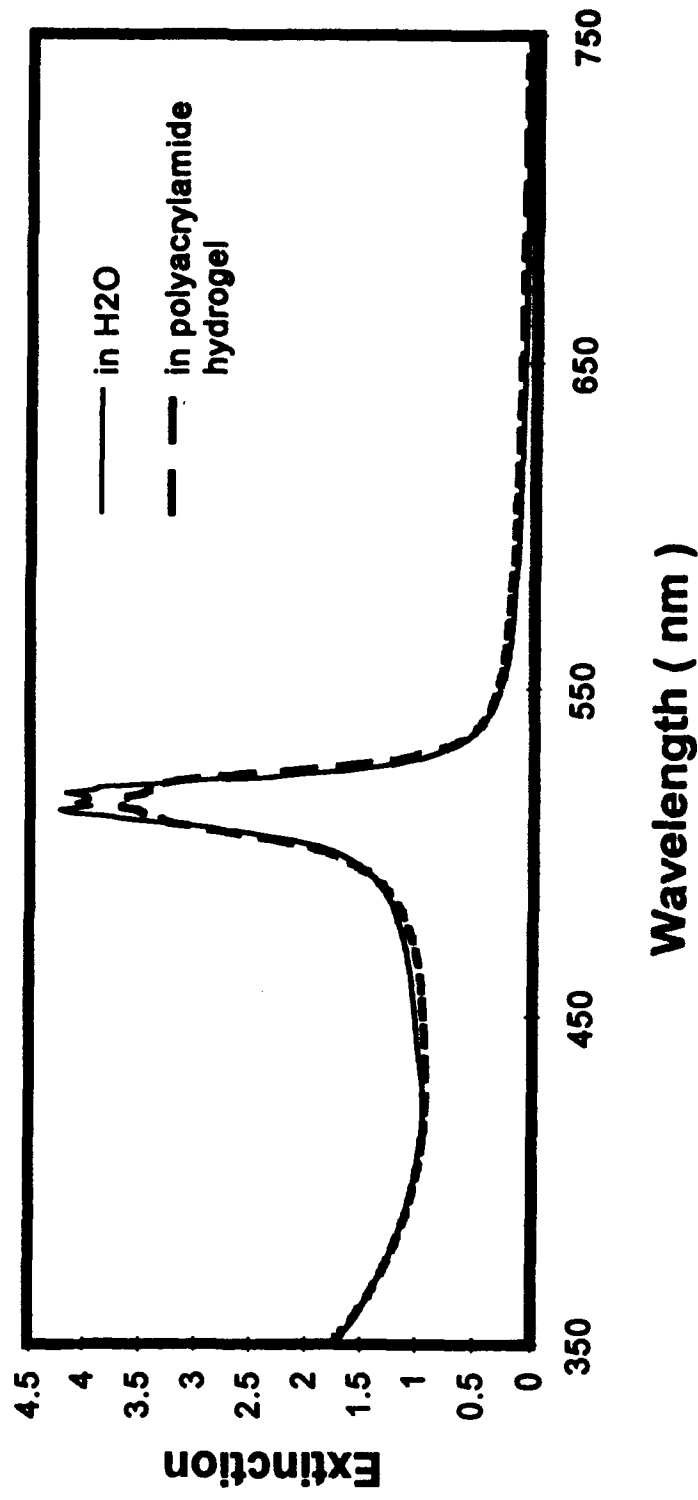


Figure 23: Covalently bonded dyed PMMA spheres in an almost index-matched medium

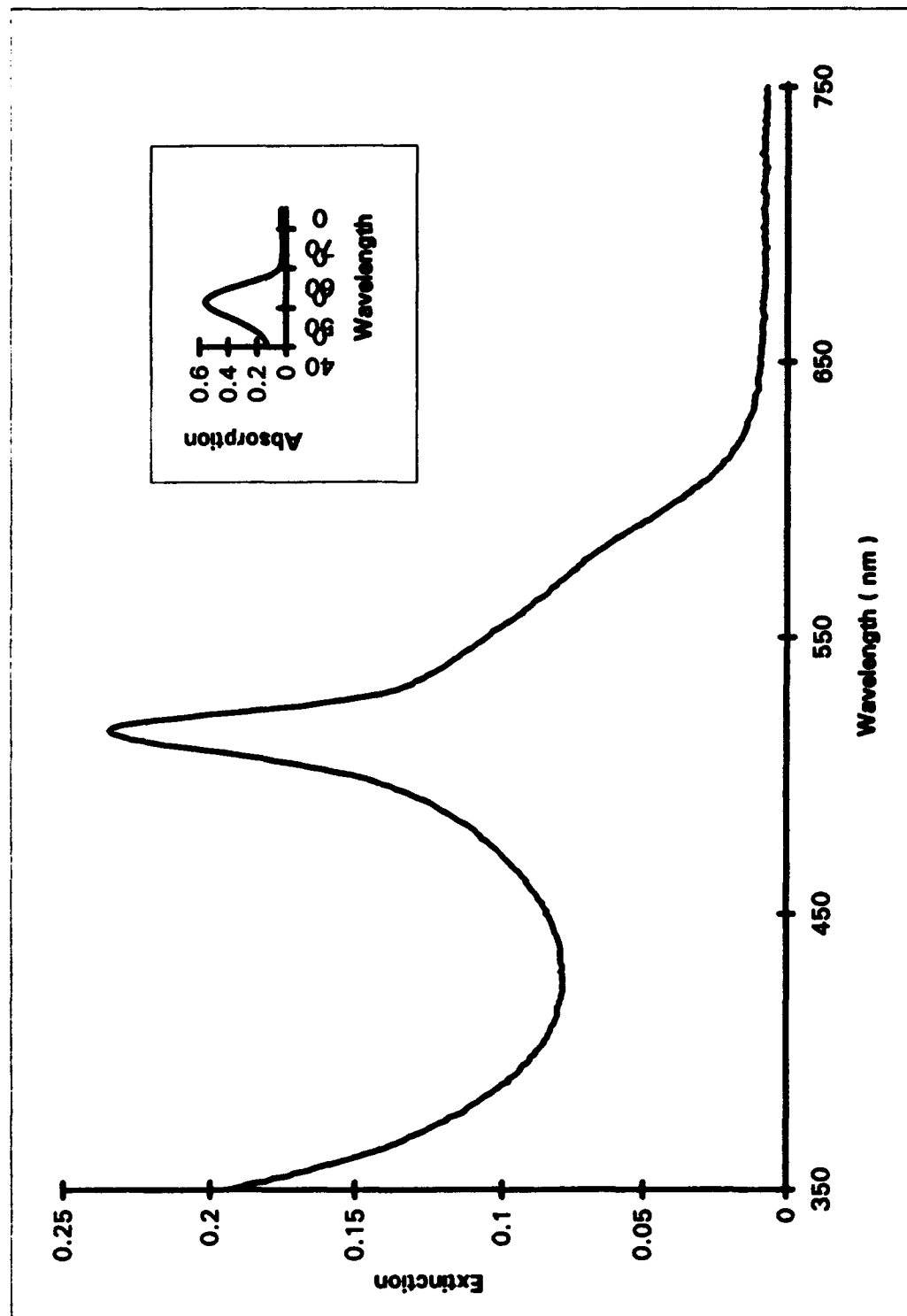
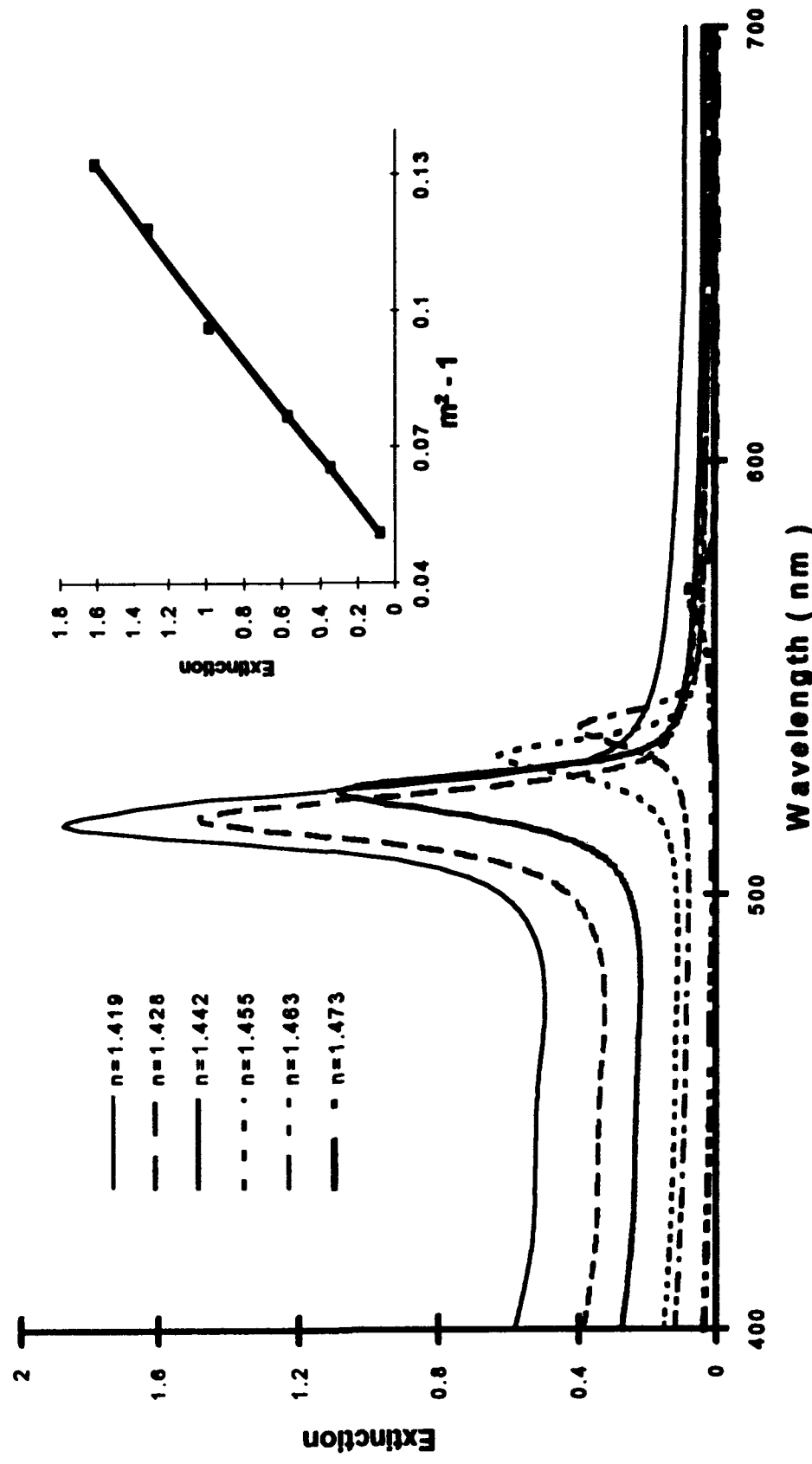


Figure 24: Refractive Index Matching of PMMA CCA Hydrogel with the Medium



• m is the refractive index ratio of PMMA to the medium, a mixture of DMSO and water. The insert is the plot of extinction versus $m^2 - 1$.

PREPARATION AND PROCESSING OF MONODISPERSE COLLOIDAL SILICA-CADMIUM SULFIDE NANOCOMPOSITES

SONG-YUAN CHANG, LEI LIU AND SANFORD A. ASHER

Department of Chemistry, University of Pittsburgh, Pittsburgh, PA 15260

ABSTRACT

A novel synthetic methodology has been developed for preparing monodisperse colloidal silica-cadmium sulfide nanocomposite spheres in the 50 - 300 nm size regime. This methodology uses water-in-oil microemulsions as the reaction medium. Monosize silica colloids are first produced by the controlled hydrolysis of tetraethyl orthosilicate in the micro water droplets of the microemulsion. Cadmium sulfide quantum dots are incorporated into the silica colloids during synthesis by the introductions of Cd^{2+} and S^{2-} microemulsions. Various morphologies of the nanocomposite are fabricated by controlling the heterogeneous coagulation of CdS and SiO_2 . Unique high surface area silica particles can be prepared when nitric acid etches out the CdS and leaves behind topologically defined voids. The CdS nanocomposites are new materials useful for non-linear optics, while the high surface area silica particles should have novel applications in areas such as catalysis.

INTRODUCTION

Development of methods to synthesize monodisperse particles is important for the advancement of numerous areas of science and technology¹. The development of new methods which give well defined but complex morphologies will present new opportunities in materials science. In this paper we describe a novel methodology to prepare monodisperse composite particles in the 50 nm to ~300 nm size range. Our major interest is to use these spherical particles in colloidal self-assembly processes for preparing crystalline colloidal arrays²⁻⁸ useful for novel optical devices. These nanoscale periodic materials are useful for fabricating optical devices because the spherical particles array themselves at the lattice sites of body centered cubic or face centered cubic arrays; these arrays efficiently diffract light in the visible and near IR spectral regions.

We are developing optically nonlinear

crystalline colloidal arrays (CCA) where the colloidal spheres are prepared from nonlinear materials.⁸ High incident light intensities alter the sphere refractive indices such that the array diffraction properties change. The nonlinear CCA would act as an optical limiter or switch. This application requires a material with a high nonlinear coefficient. CdS quantum dots may have among the largest optical nonlinearities known. Thus, we have developed synthetic methods to prepare CdS quantum dot inclusions in much larger monodisperse colloidal spheres.

This article describes the fabrication of a new nanocomposite composed of CdS quantum dots (ca 25 Å) uniformly dispersed in monodisperse silica spheres (40-150 nm). Furthermore, this method can be applied to fabricate nanocomposites where the CdS forms a core within each sphere, or where the CdS forms patches on the surface, or where it forms multidecker shells of silica, CdS, silica, etc.

MATERIALS AND PROCEDURES

The detailed procedures for preparing the CdS-silica nanocomposites are reported elsewhere.⁹ Cadmium nitrate (certified grade, Fisher), ammonium sulfide (certified grade, Fisher), and nitric acid (70.4%, Mallinckrodt) were used as received. The non-ionic surfactants Igepal CO-520 (GAF chemicals) and Triton N-101 (Rohm & Haas) were used to formulate water-in-oil microemulsions containing water, cyclohexane (Mallinckrodt) and hexanol (Aldrich). Typically, a reaction utilized a 250 ml microemulsion containing 0.127-0.184 M of NH_3 , 0.086-0.537 M of Igepal CO-520 or Triton N-101, and 0.053-0.179 M of tetraethyl orthosilicate (TEOS, Fluka) with the remainder of the reaction mixture consisting of cyclohexane and hexanol.

Nanocomposite colloids of silica-CdS were synthesized using either Igepal or Triton microemulsions containing Cd^{2+} and S^{2-} ions. The CdS inclusions were implanted through the precipitation of CdS during the simultaneous condensation of silica. This CdS implant results in yellow nanocomposites. However, the yellow CdS inclusions can be dissolved to recover white silica alone when washed with concentrated nitric acid.

Transmission electron microscopes (JOEL 2000FX and Zeiss 902) and a x-ray diffractometer (X'pert, Philip) were used to determine the morphology/size and structure of the particles. Surface areas were measured by using the BET nitrogen absorption method (Automatic Surface Area Analyzer 4200, Beta Scientific Corp.).

RESULTS AND DISCUSSION

Silica Particles Synthesis

Previous work¹⁰ has shown that monodisperse SiO_2 spheres can be grown in the size range of 40 to 70 nm by controlled

hydrolysis and condensation of TEOS within Igepal reverse micelles. The particle size and size distribution are sensitive to the microemulsion formulation, i.e. the ratio of water to surfactant concentration, w , and the ratio of water to alkoxide concentration, h . The polydispersity depends strongly on the alcohol concentration because of the sensitivity of the microemulsion phase diagram to the alcohol content. Increasing the alcohol concentration generally increases the polydispersity. This therefore limits the maximum concentration of TEOS which can be used for good monodispersity since the TEOS hydrolysis and condensation releases ethanol. Nevertheless, we find that higher concentrations of TEOS can be utilized in microemulsions containing Triton N-101 because this microemulsion is less sensitive to alcohol content. In this case the presence of the co-surfactant hexanol improves the particle size distribution.

The reaction kinetics were examined by monitoring the particle size evolution using TEM. Figure 1 shows the effects of w and h on particle growth in Igepal CO-520 microemulsions. For a constant ratio of water to TEOS of $h=4.8$, a decrease in the total water content (smaller w) results in a faster growth rate and larger spheres. This is exactly the opposite of what would occur in the Stober process. A decrease in water concentration is also reported to yield more polydisperse silica spheres.¹⁰ In contrast, we observe little dependence. Our synthesis with $h=4.8$ and $w=5$ gave 46 nm spheres with a size relative standard deviation of 5.2%, while for $h=4.8$ and $w=1$ the 55.8 nm spheres had a size relative standard deviation of 4.0%.

For a constant w , an increase in h decreases the growth rate and the particle size. The synthesis in a microemulsion with $w=1$, $h=4.8$ yields 55.8 nm spheres, while a synthesis with $w=1$, $h=10$ yields 50.4 nm spheres. This is contrast to that in Stober process, where an increased h increases the

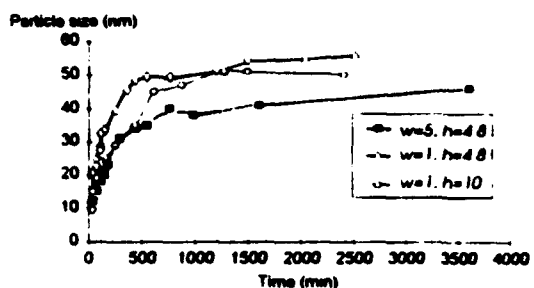


Figure 1. Growth kinetics of silica colloid in Igepal CO-520 microemulsion.

hydrolysis rate and increases the particle size.¹² We examined the dependence of the microemulsion reaction on ammonia concentration, and found little dependence. This also is much different than in the Stober process, where the NH_3 concentration determines the hydrolysis rate and the particle size.

Silica-CdS Sphere Composites

CdS quantum dot inclusions in the monodisperse silica spheres were obtained by injecting microemulsions containing Cd^{2+} and S^{2-} ions into the growing silica sphere microemulsions. This process involves the controlled co-precipitation of SiO_2 and CdS. By altering the order and timing of the injections, various tailored morphologies for the composite particles can be obtained. Figure 2 schematically demonstrates the types of morphologies we have prepared. These types including homogeneously distributed CdS spheres (raisin bread), large patches of CdS, cores of CdS, shells of CdS, CdS sandwiches and exterior bound CdS quantum dots (freckles). A typical micrograph for the raisin bread type is given in Fig. 3 where it is easy to visualize the ultrafine CdS dots dispersed in silica particles.

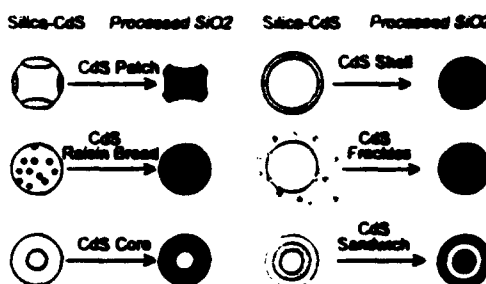


Figure 2. Schematic diagram of various SiO_2 -CdS nanocomposites before and after acid etching.

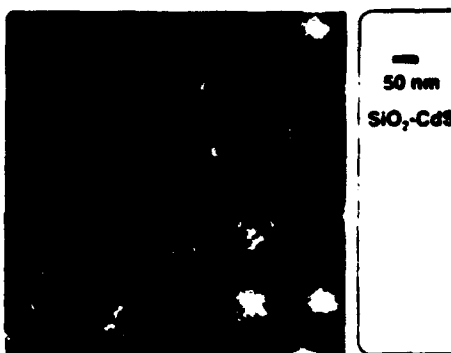


Figure 3. Typical SiO_2 colloids with CdS homogeneously dispersed within.

Chemical Composition and Structure

Elemental composition of the CdS- SiO_2 sphere composites were determined by using SEM/EDS. A typical spectrum of EDS is given in the upper right of Fig. 4 where the separate peaks from the Si, Cd and S were used to determine the relative atomic concentrations. X-ray powder diffraction measurements, also shown in Fig. 4, of the silica spheres give a broad peak that indicates that the SiO_2 is not crystalline, but is instead amorphous. The silica-CdS sphere composites show sharper peaks for the CdS

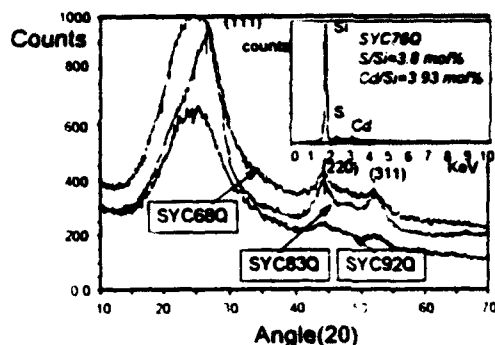


Figure 4 SEM/EDS and x-ray powder diffraction spectra for SiO_2 -CdS nanocomposite colloids.

inclusions. The positions of these diffraction peaks indicate that the CdS inclusions are in a cubic phase of a Hawleyite structure.¹³

The CdS diffraction peaks are relatively broad due to the small size of the inclusions. Using the Scherrer diffraction formula we obtain 25 Å for the diameter of the CdS inclusions.

Quantum Confinement

CdS quantum dots show blue shifts of their band edge due to quantum confinement effects associated with the small size of the particles. Figure 5 shows the UV-visible absorption spectra of the pure silica spheres and the silica-CdS nanocomposite spheres. No absorption of the silica spheres is evident until ca 330 nm, although some increase in the background is evident from the increased light scattering which occurs at shorter wavelengths. For the silica-CdS composites a band edge occurs at ca 430 nm from the CdS inclusions. From the experimental correlation of band edge and quantum dot size¹², we estimate that the inclusion size is ca 24 Å, which is close to that estimated from both the TEM photographs and the x-ray diffraction peak width measurements.

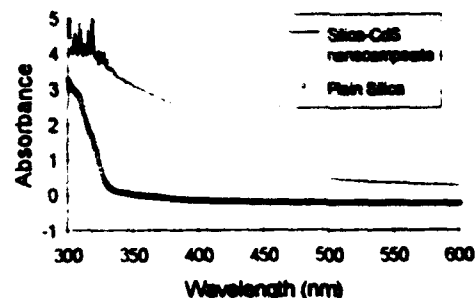


Figure 5. UV-visible absorption spectra for SiO_2 -CdS and plain SiO_2 colloidal suspensions.

Processing of SiO_2 -CdS Nanocomposite Particles

As indicated schematically in Fig. 2, CdS inclusions can be incorporated in monodisperse silica spheres in a variety of morphologies. The CdS inclusions can be prepared as large patches on the surface, or as uniform quantum dot inclusions within the spheres (raisin bread), or as the cores of the silica particles, or as annular shells within a silica-CdS sandwich arrangement, or as small quantum dots on the surface (freckles).

Pure silica does not react with strong acids except for HF. In contrast, CdS is very soluble in strong acids. Acids readily dissolve the CdS inclusions to leave a white silica residue. For example, Fig. 6 shows a CdS-silica nanocomposite with CdS patches on the surface after acid etching; Craters appear on the surface.

The TEM micrograph (Fig. 7) taken after acid etching of 50 nm raisin bread CdS-silica nanocomposite spheres shows numerous dimples on the surface and suggestions of internal voids. Figure 8 shows a TEM micrograph of acid etched ca 30 nm silica colloids which originally contained 4 - 8 nm CdS cores. The dark

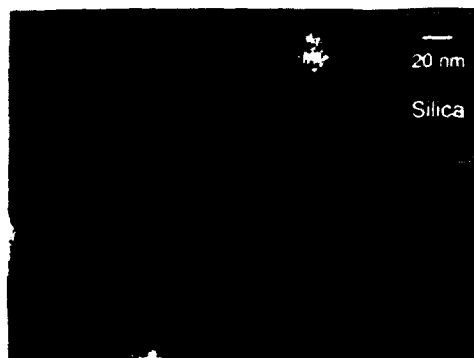


Figure 6. SiO_2 -CdS nanocomposite colloids with CdS patches after acid etching.



Figure 7. SiO_2 -CdS raisin bread nanocomposite colloids with CdS after acid etching.

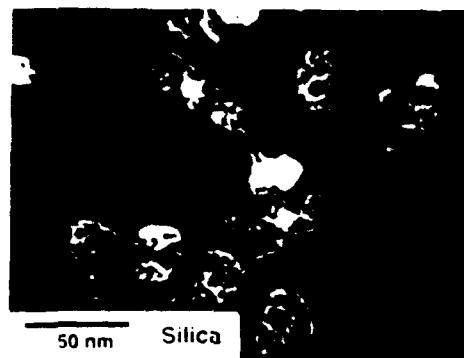


Figure 8. SiO_2 -CdS nanocomposite with CdS cores after acid etching.

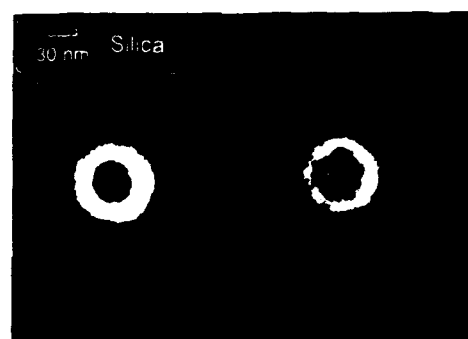


Figure 9. SiO_2 -CdS composite colloids with large CdS core after acid etching.

central spots result from small hollow spherical voids. We also can create larger spherical cavities as shown in Fig. 9. These hollow particles are ca 90 nm in outer diameter with ca 30 nm in inner diameter holes. Silica colloids can be constructed with diameters as large as 300 nm with hollow cores of any size desired.

The creation of these voids causes an increase of sphere surface area. BET nitrogen absorption measurements were employed to characterize this increase. Table I shows the surface areas of three samples before and after acid etching. The surface

Table I. Measured BET surface areas for silica-CdS composite spheres before and after acid etching.

sample	particle size (nm)	surface area (m^2/g)	
		measured, before etching	measured after etching
68Q	62	104	152
121Q	80	61	232
122Q	84	76	208

area increases are between 1.5- to 4-fold. Thus, this methodology can be used to create high surface area porous materials.

CONCLUSIONS

Silica colloid synthesis in water-in-oil microemulsions can be combined with coprecipitation of other materials to form complex nanocomposites with complex morphologies. We demonstrate the production of homogeneously dispersed CdS quantum dot-silica sphere composites, as well as other composites where the CdS inclusions are larger and are situated either at the particle centers or on the surfaces. These quantum dot composites are designed to be useful as new highly nonlinear optical materials. Our intention is to incorporate them into crystalline colloidal arrays for optical switching.

These nanocomposites can be further modified by the application of additional processing. We demonstrate the fabrication of new class of high surface area topologies in silica particles made by the etching removal of the CdS inclusions. These porous materials will be useful as matrices for catalysis support applications.

ACKNOWLEDGMENTS

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Self-Assembly Motif for Creating Submicron Periodic Materials. Polymerized Crystalline Colloidal Arrays

Sanford A. Asher,* John Holtz, Lei Liu, and Zhijun Wu

Department of Chemistry
University of Pittsburgh
Pittsburgh, Pennsylvania 15260

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We report the development of a method for creating new submicron periodic materials. These materials will have numerous applications in various areas of technology. This periodic material is composed of a body-centered cubic (BCC), face-centered cubic (FCC), or random hexagonal stacked array of spherical particles in which the periodicity is locked into a hydrogel polyacrylamide network.¹ The lattice constant of this array can be varied between ca. 10 nm and >1 μ m. The particles are generally monodisperse polymer or inorganic spheres with diameters smaller than the lattice constant of the array. The volume percent of particles can be made as large as ca. 75% or smaller than 1%.

The periodic array forms through the electrostatic self-assembly of charged colloidal particles. It is well-known that submicron periodic ordered structures called crystalline colloidal arrays (CCA) will self-assemble from monodisperse colloidal spheres containing surface functional groups that ionize in solution.²⁻⁵ If these spheres are dispersed in a polar medium such as water, the surface groups ionize to form spherical macroions which are surrounded by a diffuse counterion cloud. If the solution medium is pure and contains few other ionic species, the repulsive interaction between spherical macroions can be significant over macroscopic distances greater than 1 μ m.⁶⁻⁸ For high particle concentrations (>10¹³/cm³) significant interparticle repulsion occurs at the average interparticle spacing; the minimum energy configuration for the assembly of spherical macroions is a BCC or FCC crystal structure.

Monodomain CCA arrays can be made very large; these well-ordered crystalline arrays efficiently Bragg diffract light.² Our group has developed techniques to grow large, thin single crystals of these arrays for use as Bragg diffraction devices.^{2,9} For example, Figure 1 shows diffraction from a CCA composed of 150-nm

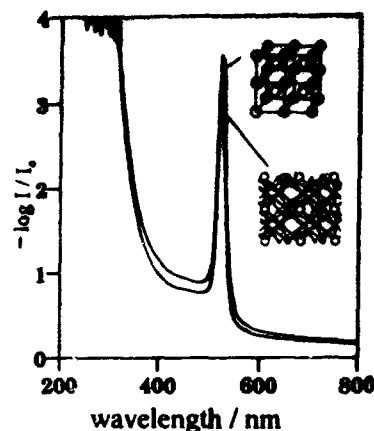


Figure 1. Extinction spectra of a liquid crystalline colloidal array (CCA) and a polymerized crystalline colloidal array (PCCA). The CCA and PCCA were composed of 150-nm polystyrene spheres with surface sulfonate groups in a liquid medium containing 50% *N*-vinylpyrrolidone, 17% acrylamide, 4.5% *N,N'*-methylenebis(acrylamide), and 1% benzoin methyl ether. The similarity of the diffraction peaks of the CCA and the PCCA indicates that little disturbance of the array occurred upon polymerization. The refractive index of the system is ca. 1.44.

polystyrene spheres with a particle concentration of 9.4×10^{13} spheres/cm³, which corresponds to a volume fraction of 8.3%. These spheres were made by emulsion polymerization of styrene with divinylbenzene as a cross-linker and the sodium salt of 1-(allyloxy)-2-hydroxypropanesulfonate (COPS-1) as an ionic monomer. Each sphere contains 7600 ionizing sulfonate groups. The Bragg diffraction at 525 nm occurs in the dynamical diffraction regime and almost follows the classical Bragg's law:⁹

$$\lambda_0 = 2nd \sin \theta$$

where λ_0 is the wavelength of light in vacuum, n is the refractive index of the system, d is the plane spacing, and θ is the Bragg glancing angle.

These liquid-phase CCA are stable, but will transiently disorder under shock. The CCA will also disorder upon introduction of ionic impurities which screen the interparticle repulsive interactions. Thus, their long-term stability depends upon the cleanliness of their environment and their containers.

We have developed an approach to permanently lock in the CCA array ordering in a solid matrix. We introduce into the CCA highly purified nonionic polymerizable monomers that can form a hydrogel network around the CCA spheres. For example, we form a solid CCA matrix by introducing highly purified acrylamide, *N,N'*-methylenebis(acrylamide), and *N*-vinylpyrrolidone into the CCA solution, and we use UV light to excite benzoin methyl ether to initiate the polymerization.

This liquid polymerized CCA (PCCA) forms a solid hydrogel which locks in the CCA periodic order; the CCA will remain stable in the presence of these polymerizable species provided that the monomers do not contain ionic impurities. The CCA polymerization results in only modest changes in the CCA ordering as evidenced by the modest alterations of the diffraction peak (Figure 1). The hydrogel film is very stable; addition of solutes does not perturb the array ordering since the lattice order no longer depends upon electrostatic interactions between spheres.

The PCCA hydrogel film formed is elastic and contains 30 vol % water. Stretching the gel causes the diffraction peak wavelength to decrease in response to a decrease in the layer spacing;¹⁰ the layer spacing along the film normal decreases as the film is stretched (Figure 2).

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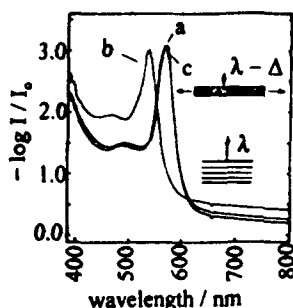


Figure 2. (a) Extinction spectra of a polymerized crystalline colloidal array (PCCA) composed of 170-nm colloidal particles polymerized in a hydrogel composed of 50% *N*-vinylpyrrolidone, 6% acrylamide, and 1% *N,N'*-methylenebis(acrylamide). The PCCA shows a diffraction maximum at 573 nm. (b) Extinction spectrum of the PCCA during a uniaxial strain in the plane of the film; the diffraction maximum shifts down to 538 nm due to the decrease in the interplanar distances. (c) Extinction spectrum of the PCCA after the stress was relieved. The PCCA again shows a diffraction maximum at 573 nm.

The water medium in the film can be replaced by other materials without changing the CCA ordering. For example, in our work¹¹ on developing optical limiters we have used benzyl alcohol to refractive index match a PCCA made from poly(methyl methacrylate) spheres and hydrogel network above. Although the periodic order is maintained, the refractive index matched system does not Bragg diffract light. However, any perturbation which alters the relative refractive index between the spheres and the medium causes the array to diffract light; the device becomes an optical limiter.

The liquid medium of the PCCA can also be replaced by a polymerizable monomer or inorganic glass precursor. Polymerization or condensation of this system results in a rigid film

which contains the submicron periodic structure. The shape remains identical to that of the original PCCA film.

The work here demonstrates a motif for preparing solid submicron periodic systems out of a variety of materials. The only requirement is that the spherical particles must be monodisperse and possess numerous surface ionizing groups. Monodisperse spheres can be prepared from both organic and inorganic materials. Emulsion polymerization can be used to synthesize monodisperse polymer spheres from polystyrene, poly(methylmethacrylate), fluorinated polymer materials, etc.¹² Monodisperse inorganic materials can be synthesized using techniques such as the Stöber process¹³ and microemulsion synthesis.¹⁴ Electrostatic self-assembly creates a CCA periodic array with a wide variety of possible lattice constants from colloidal particles with a wide variety of particle diameters.

These systems will have numerous applications in technology. For example, they will be useful as optical filters^{2a} and optical limiters^{11a,b} and variable mechanically controlled wavelength rejection filters.¹⁰

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Supplementary Material Available: Experimental details for polymerizing the array (1 page). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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Preparation and Properties of Tailored Morphology, Monodisperse Colloidal Silica-Cadmium Sulfide Nanocomposites

Song-yuan Chang, Lei Liu, and Sanford A. Asher*

Contribution from the Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania 15260

Received February 4, 1994*

Abstract: We have developed a new synthetic methodology for preparing ca. 40–300-nm monodisperse silica-cadmium sulfide nanocomposite spheres. This methodology uses water-in-oil microemulsions in which monodisperse silica colloids are produced by the controlled hydrolysis of tetraethyl orthosilicate (TEOS) in water nanodroplets. The resulting pure silica spheres can be grown to between 40 and 80 nm in diameter and can be used as seed particles for production of larger silica colloids upon further reactions with TEOS in the microemulsion. Cadmium sulfide quantum dots are incorporated into the silica colloids during the silica sphere synthesis by the simultaneous coprecipitation of cadmium nitrate and ammonium sulfide in the water nanodroplets. The CdS can be introduced as a homogeneous dispersion of CdS quantum dots (ca. 25 Å diameter), as large inclusions, as surface caps, as the central core of a silica particle, or as shells of CdS interleaved between silica shells. These different nanoscale complex morphologies in silica are created by controlling the coprecipitation of CdS. Techniques including TEM, SEM/EDS, X-ray diffraction, and light scattering were used to characterize the elemental analysis as well as particle morphology. In addition, we have prepared doublet and triplet spheres which are connected by welds of CdS. This silica-CdS nanocomposite is a new material with potential utility for nonlinear optics. Further processing makes this material useful for a new class of high surface area catalytic supporting materials.

Introduction

Synthetic chemistry is a mature science which has developed a host of successful strategies for fabricating complex molecular structures. For example, methodologies have been developed to make clusters of atoms and molecules such as, buckminsterfullerene¹ and CdS quantum dots.^{2–6} The present frontier of chemical synthesis involves development both of strategies to create even larger assemblies, with molecular weights greater than 10⁹ g/mol, and of assemblies composed of complex composites of macromolecular size.

In this regard, numerous groups have developed synthetic methods to form monodisperse particles of organic polymers^{7,8} or of inorganic materials.⁹ Generally these particles are spherical and have molecular weights greater than 10⁹ g/mol. In special cases these particles can be nonspherical and may have unique materials science applications.

One objective of this work discussed here is to use these monodisperse particles for new ceramic materials or for use as catalyst supports. One major interest, however, is to use these spherical particles in colloidal self-assembly processes for preparing crystalline colloidal arrays.^{10–16} These nanoscale periodic

materials are useful for fabricating optical devices because the spherical particles array themselves at the lattice sites of body-centered cubic or face-centered cubic arrays, which efficiently diffract light in the visible or near-IR spectral regions.

It would be desirable to prepare nonlinear crystalline colloidal arrays where the colloidal spheres were prepared from nonlinear materials which changed their refractive indexes such that the diffraction properties of the array changed at high incident light intensities. The material could act as an optical limiter or switch. In this regard, the refractive indices of the spherical colloidal particles would change as the incident light intensity increased. Our choice for the nonlinear material has centered on CdS quantum dots.

CdS quantum dots have among the largest optical nonlinearities known. In this report we describe the fabrication of new nanocomposites composed of CdS quantum dots (ca. 25 Å) uniformly dispersed in monodisperse silica spheres in the size range of 40–150 nm. In addition, our preparation can be used to fabricate nanocomposites where the CdS forms patches within the spheres and on the surfaces of the spheres, as well as forming a CdS core in the silica spheres. In addition, we can form multidecker shells of silica, CdS, silica, etc.

In an accompanying paper¹⁷ we demonstrate that we can selectively etch out the CdS inclusions to form silica spheres with complex cavities and porosities. These porous systems will be useful for novel supporting materials for catalytic applications.

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Our approach for this new synthesis utilizes water-in-oil microemulsions where the silica spheres are synthesized by the hydrolysis of tetraethoxysilane (TEOS), followed by its condensation in the water nanodroplets. This microemulsion method of formation of silica spheres was recently reported by Osseo-Asare and Arriagada.¹⁸ We have combined this method of synthesis of silica spheres with the controlled precipitation of CdS particulates in water nanodroplets in these water-in-oil microemulsions. This work follows previous demonstrations by others that monodisperse CdS quantum dots can also be synthesized in water-in-oil microemulsions.²⁻⁴ We have combined these approaches to, for the first time, prepare monodisperse CdS quantum dot inclusions in monodisperse silica sphere colloids.

Our microemulsion approach, which yields more uniform spheres than the classic Stöber process¹⁹ for the smaller size range (30–150 nm), gives comparable uniformities for larger spheres (150–300 nm). We believe we have developed a simple general approach for creating nanocomposites with complex morphologies which can be used for a variety of materials, such as CdSe, etc., in silica spheres or for synthesizing spherical colloids made of other materials, such as alumina, etc. We also have developed an approach to synthesize doublets and triplets of spheres where the CdS acts as a weld between spheres.

Experimental Section

Water-in-oil microemulsions were prepared from nonionic surfactants using procedures similar to those of Osseo-Asare and Arriagada.¹⁸ We used two nonionic surfactants, poly(oxyethylene) nonylphenyl ether with an average of five oxyethylene groups per molecule (Igepal CO520) from GAF Chemical and obtained from Aldrich Chemical and Triton N-101 from Rohm and Haas (obtained from Fluka). Both surfactants were used without further purification. The tetraethyl orthosilicate (TEOS, 99%, Fluka) was distilled before use. The other chemicals, such as cyclohexane (Fisher Scientific), hexyl alcohol (Aldrich), ammonium hydroxide (29%, Mallinckrodt), cadmium nitrate (certified, Fisher Scientific), ammonium sulfide (22%, Fisher Scientific), and deionized water (obtained using a Nanopure water purifier, Barnstead Co.), were used as received.

The microemulsion reaction matrix was prepared using either Igepal CO-520 or Triton N-101. Although different detailed recipes were used for each preparation, a typical recipe would involve 270 mL of a microemulsion prepared at ambient temperature in a 500-mL four-neck reaction flask stirred by a Teflon paddle connected to a high torque stirring motor. The microemulsion reactant concentrations were 5.20 M cyclohexane, 0.72 M H₂O, 0.18 M hexanol, 0.12 M Triton N-101, and 0.094 M NH₄OH. The Igepal CO-520 microemulsions contained a similar surfactant concentration but contained no hexanol. Ten milliliters of pure TEOS liquid was injected within 10 min into the stirred microemulsion matrix by using a syringe pump. As the reaction proceeded over a period of 24 h, the TEOS slowly hydrolyzed, and Si(OH)₄ precipitated and condensed within the water nanodroplets to eventually form monodisperse SiO₂ spheres.

The SiO₂-CdS quantum dot sphere composites were made by injecting separate microemulsions containing Cd²⁺ and S²⁻. To produce 10% (by mole) CdS quantum dot inclusions, we injected approximately 54 mL of two microemulsions containing either Cd(NO₃)₂ or (NH₄)₂S. These microemulsions contained the following final reactant concentrations: 26.85 M cyclohexane, 1.65 M H₂O, 0.41 M hexanol, 0.275 M Triton N-101, and 4.48 × 10⁻³ M Cd(NO₃)₂ or (NH₄)₂S. These microemulsions were prepared by addition of the aqueous salt solutions to the microemulsion.

The order and timing of injection of the TEOS and the Cd(NO₃)₂ and (NH₄)₂S microemulsions determine the CdS morphology within the SiO₂ spheres. For example, to make uniformly dispersed CdS quantum dots in the SiO₂ spheres, we first injected the TEOS solution within 10 min and 1 h later began injecting the Cd(NO₃)₂ and (NH₄)₂S microemulsions. We simultaneously injected these two solutions over a period of 24 h. It is important to note that the TEOS reaction rate is much slower in the microemulsions than that in the Stöber process.

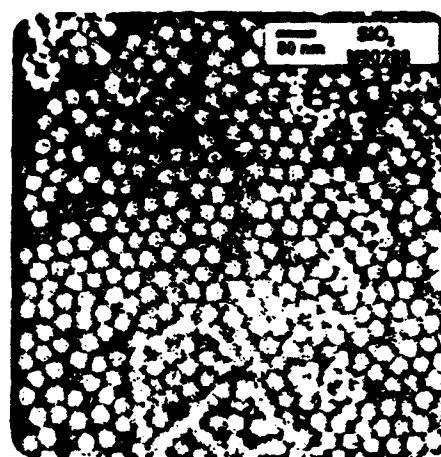


Figure 1. TEM micrograph of monodisperse silica spheres synthesized in an Igepal CO-520 microemulsion with $w = 5$, $h = 4.8$, 0.0537 M TEOS, and 0.1269 M NH₃ (size relative standard deviation is 4.2%).

The particle morphology was examined by transmission electron microscopy (TEM) (JEOL 2000FX/LINK AN10000 and Zeiss 902). The micrographs were analyzed by using a digital imaging system (BioScan, Inc., WA). Energy dispersive scanning electron microscopy X-ray analysis (JEOL 35CF) was employed for semiquantitative element determinations. The samples were prepared for SEM/EDS by drying a dispersion of the reaction products on a carbon stage and transferring this stage to the microscope. The colloids were washed, solvent exchanged, and dialyzed before Zeta potential determinations made by using a Malvern Zetasizer 4 electrophoretic light scattering instrument. Particle surface areas were measured by using the BET nitrogen absorption method (Automatic Surface Area Analyzer 4200, Beu Scientific Corp.). The crystal structures were determined by X-ray powder diffraction measurements of freeze-dried nanocomposite particles (Philips X'PERT). Absorption measurements to investigate CdS quantum confinement effects were performed by directly examining the liquid reaction products by using a UV-visible/near-IR spectrometer (Perkin-Elmer, Lambda 9).

Results

Silica Sphere Growth. Previous studies by Arrigada and Osseo-Asare¹⁸ demonstrated that monodisperse, small SiO₂ spheres can be grown in the size range of 40–70 nm by controlled hydrolysis and condensation of TEOS within reverse micelles. We have scaled up this synthesis by 50-fold for preparative purposes and developed new synthetic methods for creating complex nanocomposites. Figure 1 shows a TEM micrograph of 41.3-nm SiO₂ spheres prepared by using a microemulsion with Igepal CO-520 surfactant. The reaction utilized a concentration 0.0537 M TEOS and 0.1269 M NH₃ with a water-to-surfactant concentration ratio, w , of 5 ($w = [\text{water}]/[\text{surfactant}]$) and a water-to-TEOS concentration ratio, h , of 4.8 ($h = [\text{water}]/[\text{TEOS}]$). The silica sphere diameter and the diameter distribution are sensitive to reactant concentrations; the w value is most important for determining size. Increasing the alcohol concentration gradually increases the polydispersity because of the sensitivity of the microemulsion phase diagram to the alcohol content. This limits the maximum concentration of TEOS which can be used since TEOS hydrolysis releases ethanol. For example, we find that the relative standard deviation in particle size increases from 5% to 14% as we increase the TEOS concentration from 0.09 to 0.179 M.

Higher concentrations of TEOS can be utilized in microemulsions containing Triton N-101 because this microemulsion is less sensitive to alcohol content. In this case, the presence of hexanol as a cosurfactant improves the uniformity. For example, we synthesized silica particles with an average diameter of 76 nm with a relative standard deviation of 4.8% by using a triton N-101 microemulsion containing 0.179 M TEOS and 0.15 M NH₃ with $w = 6$, $h = 6$, and $cs = 4$ ($cs = [\text{water}]/[\text{hexanol}]$).

Arragada and Osseo-Asare have shown for Igepal microemulsions that increasing w decreases the particle size and results in

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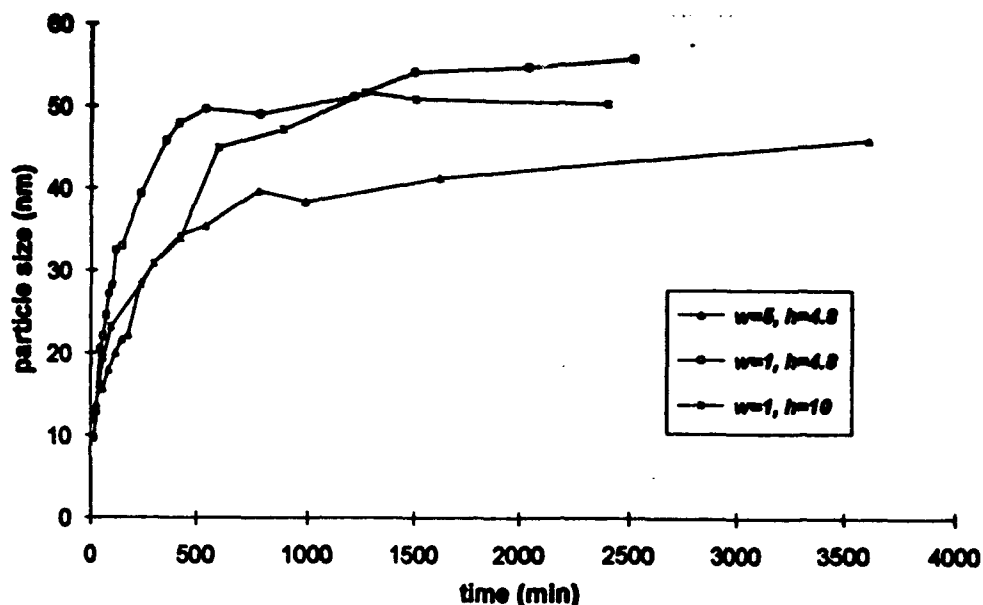


Figure 2. Particle size evolution for silica spheres synthesized in Igepal CO-520 microemulsions with different values of w and h .

better uniformity. However, we observe that Triton N-101 microemulsions permit higher w values, which allow us to double the particle diameter while maintaining an excellent uniformity. Although Triton N-101 and Igepal CO-520 have similar chemical structures, they have different molecular weights. Our results indicate that Triton N-101 microemulsions can be used to synthesize larger monodisperse silica spheres.

We examined the reaction kinetics by monitoring the time dependence of the particle size by using TEM. Figure 2 shows the effects of w and h on particle growth in Igepal CO-520 microemulsions. For a constant ratio of water to TEOS of $h = 4.8$, a decrease in the total water content (smaller w) results in a faster growth rate and larger spheres. This is exactly the opposite of what would occur in the Stöber process. A decrease in water concentration is also reported to yield more polydisperse silica spheres.¹⁸ In contrast, we observe little dependence. Our synthesis with $h = 4.8$ and $w = 5$ gave 46-nm spheres with a size relative standard deviation of 5.2%, while for $h = 4.8$ and $w = 1$, the 56-nm spheres had a size relative standard deviation of 4.0%.

For a constant w , increasing h decreases the growth rate and the particle size. The synthesis with $w = 1$, $h = 4.8$ yields 56-nm spheres, while a synthesis with $w = 1$, $h = 10$ yields 50-nm spheres. This contrasts to the Stöber process, where an increased h increases the hydrolysis rate and increases the particle size.²⁰ We find little dependence of the reaction on ammonia concentration. This differs from the Stöber process, where the NH_3 concentration determines the hydrolysis rate and the particle size.

Nucleation and Growth of Large Particles. To obtain larger silica spheres, we continued the growth of small monodisperse spheres by adding additional TEOS after the original growth phase. This technique is similar to that demonstrated by Unger's group for the Stöber process.²² We probably can grow mono-

Table 1. Results of Second Growth of Silica Colloids in Triton N-101 Microemulsions

sample	initial size (nm)	no. of particles	additional TEOS (mol)	expected size (nm)	determined size (nm)
SYC101RG	77 ± 5	1.2×10^{15}	2.2×10^{-3}	134	129 ± 6
SYC107RG1	77 ± 4	1.2×10^{15}	1.8×10^{-3}	110	103 ± 5
SYC107RG2	76 ± 4	1.2×10^{15}	1.8×10^{-3}	110	112 ± 7
SYC107RG4	76 ± 4	1.2×10^{15}	6.7×10^{-3}	150	147 ± 6

disperse silica spheres as large as 300 nm by this process. This process also allows us to accurately synthesize any desired particle diameter in the range of 40–300 nm since the final diameter is determined solely by the initial size of the seed silica sphere and by the additional TEOS added, which totally condenses upon the seeds without formation of any new silica spheres. This is evident from Table 1, which compares the size expected to that determined for the larger silica spheres grown from the smaller silica nuclei.

Silica-CdS Sphere Composites. CdS quantum dots incorporated in the monodisperse silica spheres were obtained by injecting microemulsions containing Cd^{2+} and S^{2-} ions into the growing silica spheres. This process involves the controlled coprecipitation of SiO_2 and CdS. As shown in Figure 3, different morphologies could be prepared by altering the order and timing of the injection. These morphologies include homogeneously distributed CdS quantum dots; large patches of CdS; cores of CdS; shells of CdS; CdS sandwiches; and exterior bound CdS quantum dots.

Homogeneously distributed CdS dots were prepared by pulsed injection of the Cd^{2+} and S^{2-} microemulsions, with a pulsation rate proportional to the increasing volume of silica spheres. Figure 4 shows a TEM micrograph of silica spheres containing uniformly dispersed ca. 25-Å CdS quantum dots (vide infra) at a final CdS concentration of 3 mol %. These ca. 100-nm composite silica-CdS spheres were synthesized by using 50 mL of a Triton N101 microemulsion with $w = 6$, $h = 6$, and $sc = 4$ to grow silica sphere nuclei of 76 nm. After formation of these nuclei, 4 mL of pure TEOS was quickly injected, and two streams containing Cd^{2+} and S^{2-} microemulsions were injected in a pulsed mode over a period of 24 h. Initially the Cd^{2+} and S^{2-} microemulsions were injected in 10-s pulses to each deliver 5×10^{-4} mol of Cd^{2+} and S^{2-} ions. A 40-s interval followed each 10-s injection. Over a period of 24 h, we gradually increased the injection time to deliver an increasing amount of Cd^{2+} and S^{2-} ions during each cycle to ultimately result in a final concentration of 3 mol % CdS inclusions in the silica spheres.

Figure 5 shows a TEM micrograph of silica spheres with

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CdS distribution in SiO ₂	Morphology of composite particles
CdS Homogeneous	
CdS Surface Patch	
CdS Core	
CdS Shell	
CdS Sandwich	
CdS Surface Inclusions	

Figure 3. Schematic illustrating the fabricated morphologies of silica-CdS composites.

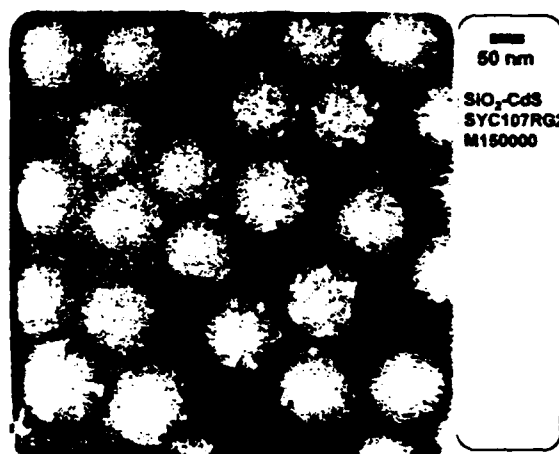


Figure 4. TEM micrograph of homogeneous distribution of CdS dots in silica-CdS nanocomposite spheres.

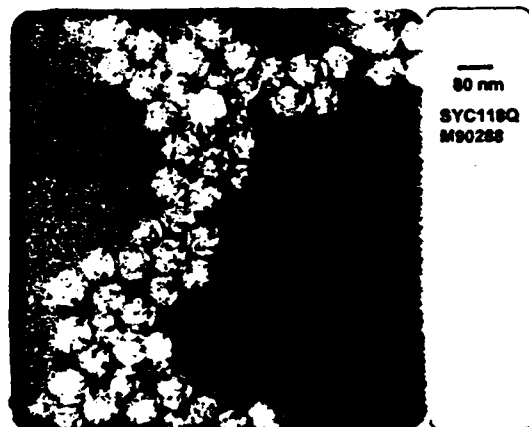


Figure 5. TEM micrograph of silica-CdS nanocomposite spheres with CdS patches within and on the sphere surface.

cadmium sulfide patches on the surface and within the interior. These nanocomposite spheres were prepared by injecting a larger amount of the Cd and S microemulsions at each injection while utilizing fewer injections.

The CdS core silica particles (Figure 6) were prepared by first synthesizing 6-nm CdS cores in the microemulsion with $w = 3$, $h = 4.8$ and subsequently growing silica spheres around the cores

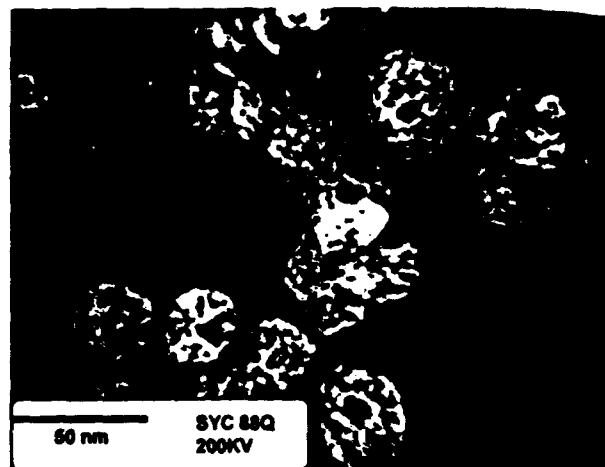


Figure 6. TEM micrograph of ca. 39-nm silica particles with ca. 6-nm CdS cores. The photograph shows these silica particles after acid dissolution of the CdS cores. This results in ca. 6-nm voids at the sphere centers.

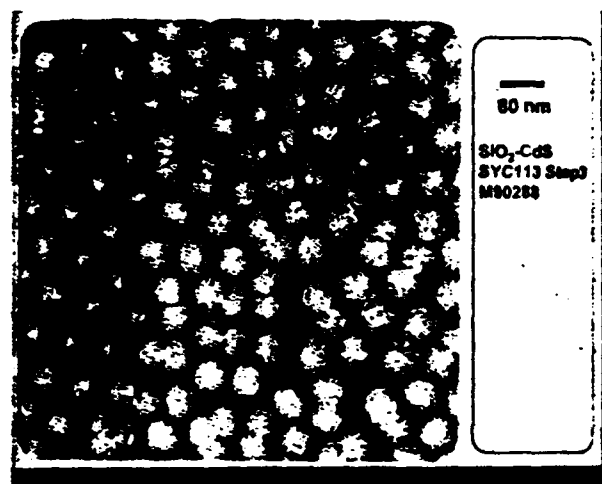


Figure 7. TEM micrograph of doublet and triplet silica spheres welded by CdS inclusions.

to a final 39-nm diameter. To synthesize the CdS cores, two Igepal microemulsions containing the Cd and S ions were slowly injected into an identical Igepal microemulsion. The total amount of Cd and S added depended upon the desired size of the CdS core. We injected a total of 2.2 mmol of Cd and S over a period of 2 h. We then added 5 mL of TEOS within 10 min. The reaction was completed over a period of 20 h.

Spherical shells of CdS were grown around the silica spheres by first synthesizing the silica cores, followed by addition of Cd and S microemulsions, followed by another step of silica growth. These sandwiches can be visualized only by etching away the CdS layers, as shown in the accompanying paper.¹⁷ If desired, additional layers of CdS and TEOS can be added. In principle, numerous layered shells could be prepared using this method to allow multidecker silica-CdS sandwiches.

Silica spheres synthesized with CdS quantum dot surface inclusions were prepared by using thioacetamide, which reacts more slowly with cadmium nitrate in the water nanodroplets. For example, we prepared 54-nm silica spheres with CdS particle surface inclusions of sizes ranging between 4 and 7 nm by using alcohol-free Igepal microemulsions with 5 mM thioacetamide with $w = 3$, $h = 4.8$. The Cd(NO₃)₂ microemulsion was injected in a pulsed mode over a period of 24 h.

Sphere doublets and triplets, where two or three silica spheres are joined by CdS quantum dot welds (Figure 7), were grown by a three-step growth process. The initial synthesis fabricated a 45-nm CdS-coated silica sphere with large CdS caps on the surface.

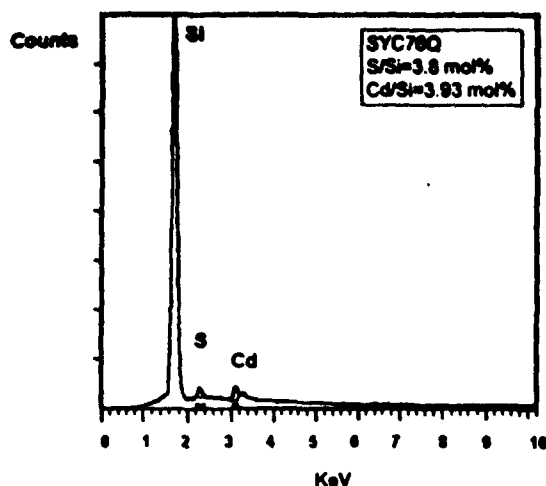


Figure 8. SEM/EDS elemental analysis of silica-CdS nanocomposite.

Table 2. Results of SEM/EDS Analysis on Silica-CdS Nanocomposites

sample	determined		expected	
	S/Si, mol %	Cd/Si, mol %	S/Si, mol %	Cd/Si, mol %
SYC76Q	3.8 ± 0.2	3.9 ± 0.1	8	8
SYC82Q	8.5 ± 0.1	11.5 ± 0.1	10	10
SYC92Q	8.8 ± 0.5	8.5 ± 0.2	7.9	7.9

These core particles were synthesized over a period of 20 h in an Igepal CO-520 microemulsion with $w = 3$, $h = 4.8$. The initial reaction microemulsion contained 0.14 M Igepal. Cd(NO₃)₂ and (NH₄)₂S-containing microemulsions were added after an initial reaction period of 6 h after the TEOS injection, in order to localize the CdS patches on the surface. The Cd and S microemulsions were added by pulsed injection over a period of 14 h. The final CdS concentration was 5 mol % of that of the silica.

In the second step, additional Igepal (0.025 mol), TEOS (0.18 mol) and NH₄OH solution (0.52 mol) were added to 100 mL of the above solution in order to increase the sphere size to 75 nm. The $h = 4.8$ value was maintained to be identical to that above. This reaction microemulsion was rapidly stirred for an additional 12 h. TEM micrographs show formation of doublets and triplets at the end of step 2.

In the third step, additional Igepal (0.042 mol), TEOS (0.022 mol), and NH₄OH solution (0.17 mol) were added, and the reaction continued with rapid stirring for an additional 50 h. The final microemulsion had $w = 4$. These reactions resulted in a complex colloid containing mainly 90-nm diameter silica spheres. However, many of the spheres formed doublets and some triplets in which the spheres were attached by CdS welds, as observed in Figure 7.

The formation of these welded spheres during the synthesis probably occurred due to collisions between spheres with CdS patches during step 2. Since the patches are sparse, most collisions were elastic, and the spheres repelled one another due to their surface charge and due to constraints imposed by the microemulsion water droplet size. Collisions where the CdS patches fortuitously touched caused adhesion. Further condensation of silica irreversibly fixed the doublets and triplets.

Chemical Composition and Structure. We determined the elemental composition of the CdS-SiO₂ sphere composites by using SEM/EDS. Figure 8 shows a typical spectrum, where the separate peaks from the Si, Cd, and S were used to determine the relative atomic concentrations. Table 2 tabulates the results for three homogeneously distributed silica-CdS sphere composites. Good agreement is generally found between the calculated and expected CdS concentrations. However, some preparations did not incorporate all of the CdS added, as indicated for sample

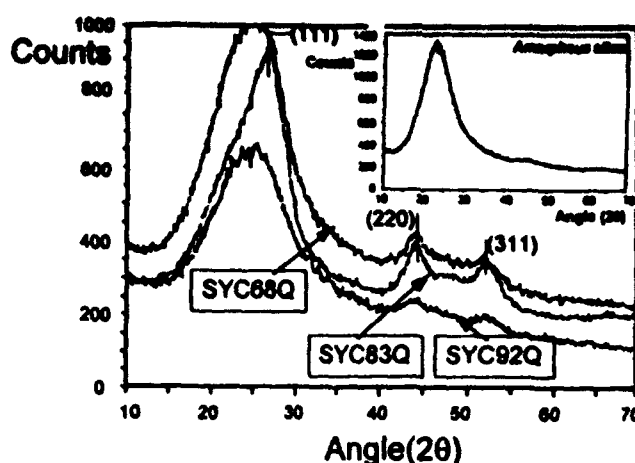


Figure 9. Typical X-ray powder diffraction spectrum of silica spheres and silica-CdS nanocomposite spheres.

Table 3. BET Specific Surface Area Measurements of Selected Silica and Silica-CdS Nanocomposites

sample ID	particle diameter (nm)	specific surface area (m ² /g)
Plain SiO ₂		
SYC60	62	105
SYC66	74	117
SYC98	60	78
SYC89	61	82
SiO ₂ -CdS Nanocomposite		
SYC68Q	62	104
SYC83Q	46	112
SYC99Q	71	113
SYC92Q	62	183

SYC76Q, where less than half of the 8 mol % originally added was incorporated.

The broad X-ray diffraction of the silica spheres indicates that the SiO₂ is amorphous (Figure 9). The silica-CdS sphere composites show sharper peaks for the CdS inclusions (Figure 9b), which indicates that the CdS inclusions are in a cubic phase^{21,22} of a Hawleyite structure.²³

The CdS diffraction peaks are relatively broad due to the small size of the inclusions (*ca.* 25 Å from the TEM micrographs). We use the Scherrer diffraction formula relating diffraction angular width, β , to the domain size, D , to get an independent measure of the CdS inclusion size:

$$D = k\lambda/\beta \cos \theta$$

where $k = 1$ for the CdS cubic structure, λ is the X-ray wavelength (1.541 Å), and θ is the diffraction angle. We calculate a 25-Å CdS diameter.

Particle Properties. The surface charge of the silica-CdS nanocomposites differs from that of the pure silica particles. The isoelectric point of our silica-CdS sphere composites is pH 2.5, while that of the silica spheres is 3.8.

Table 3 lists the BET surface area measurements of our particles. The particles show surface areas approximately 2 times larger than those calculated to result from their spherical outer surface areas, assuming a particle density of 1.9 g/mol.²⁶ There are typically large variations in the surface areas of Stöber synthesized silica spheres since the porosity depends strongly on the preparation conditions.^{24,25} Although some variation exists between our preparations, the porosities of the silica-CdS nanocomposite spheres are similar to those of the pure silica spheres.

Quantum Confinement. CdS quantum dots show blue shifts of their band edges due to quantum confinement effects associated with the small size of the particles which limit the volume occupied by the electron and the electron hole pair formed. Figure 10

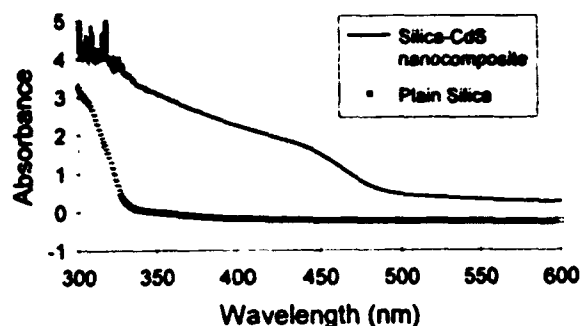


Figure 10. UV-visible absorption spectrum for pure silica and silica-CdS nanocomposite spheres.

shows the UV-visible absorption spectrum of pure silica spheres and the silica-CdS nanocomposite spheres. No absorption of the silica spheres is evident until ca. 330 nm, although some increase in scattering is evident at shorter wavelengths. For the silica-CdS composites, the CdS band edge occurs at ca. 430 nm; the existing experimental correlation of band edge and quantum dot size²⁷ can be used to estimate an inclusion size of ca. 24 Å, which is close to that estimated from both the TEM photographs and the X-ray diffraction peak width measurements.

Conclusions

We have demonstrated new methods to grow silica-CdS sphere nanocomposites which allow us to produce colloidal particles with a variety of morphologies. We can easily modify the recipe to synthesize silica particles of various sizes. This process for forming monodisperse silica spheres between 30 and 150 nm is superior

to the Stöber process because the uniformity is better and larger spheres can be grown by continuing the growth of previously grown small monodisperse silica spheres.

This synthesis in a water-in-oil microemulsion can be combined with the precipitation of other materials to form complex nanocomposites with complex morphologies. We demonstrate the production of homogeneously dispersed CdS quantum dot-silica sphere composites, as well as other composites where the CdS inclusions are larger and are situated either at the particle center or on the surface. In addition, the CdS particulates can be used to weld together the silica spheres to form dimers and trimers. The quantum dot composites are designed to be useful as new highly nonlinear optical materials. Our intention is to incorporate them into crystalline colloidal arrays for optical switching.

These nanocomposites can be further modified by the application of additional processing. The accompanying paper demonstrates the fabrication of a new class of high surface area topologies in silica particles made by the etching removal of the CdS inclusions. These porous materials will be useful as matrices for catalysis support applications.

Acknowledgment. The authors would like to express their thanks to Professor Jean Blachere for his help on SEM/EDS and X-ray measurements and Mr. Thomas Harper and Mr. Cole van Ormer for their help in the TEM measurements. The authors gratefully acknowledge support for this work from the Materials Science Center of the University of Pittsburgh, which is supported by the Air Force Office of Scientific Research through Grant No. AFOSR-91-0441, and from an Air Force Office of Scientific Research grant, No. F49620-93-1-0008, to S.A.A.

Creation of Templated Complex Topological Morphologies in Colloidal Silica

Song-yuan Chang, Lei Liu, and Sanford A. Asher*

Contribution from the Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania 15260

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Abstract: We have developed a new method to create complex monodisperse silicon dioxide particles which contain voids with unique morphologies. These particles are prepared from monodisperse silica spheres (ca. 100 nm) which contain CdS inclusions organized as large patches on the silica sphere surfaces, as small quantum dots within the spheres, as interior spherical shells, or as the central cores of the silica spheres. We create voids with the identical morphology as the CdS inclusions by etching out the CdS inclusions with strong acid. The silica sphere-CdS composite particles are prepared within a microemulsion reaction medium as described in the accompanying paper (Chang, S.-Y.; et al. *J. Am. Chem. Soc.*, preceding paper in this issue). The etched silica particles have craters on their surface, 2.4-nm diameter spherical voids dispersed within the silica spheres, hollow cores, or hollow shells separating silica shells from silica cores. In addition, we have formed unique ellipsoidal cavities within doublets of silica spheres. These doublets were formed through the attachment of silica spheres by CdS patches on the silica surfaces. A silica shell was subsequently grown around the sphere doublets. Etching away the CdS results in ellipsoidal caverns connecting the two spheres of each doublet. These high surface area materials have geometrically tailorable voids and may prove useful as novel catalyst support media.

Introduction

One major frontier of chemical synthesis is the development of novel methodologies to create tailor-made complex morphologies within macromolecular complexes. The argument is that these complex morphologies can be used for creating sophisticated chemical processes where an assembly line of chemical reactions can be linked within connected regions of macromolecular entities. In the accompanying paper¹ in this issue, we describe the microemulsion synthesis of ca. 40–300-nm monodisperse silica-CdS colloids, where the CdS inclusions were incorporated within porous silica spheres. These inclusions were synthesized as quantum dots uniformly dispersed in the silica spheres, as large surface caps, as surface quantum dots, as cores of CdS surrounded by silica shells, or as a set of concentric spherical shells of silica, CdS, silica, etc., i.e., multidecker sandwiches.

We describe here a method to further process these nanocomposite spheres in order to form complex voids within the silica colloids. This processing forms voids identical in shape and volume to the original CdS inclusions by quantitatively etching out the CdS inclusions. For the homogeneously dispersed quantum dots, this results in numerous small (ca. 2.5 nm) spherical voids, while the CdS core-silica sphere composites yield silica spheres with spherical voids at their centers. More complex annular voids are formed from the silica-CdS shells, while craters are formed from the silica spheres with surface CdS patches.

Numerous other research groups are also developing approaches to create complex nanostructure morphologies in various materials. For example, a number of groups have prepared hollow inorganic powders by dehydration and decomposition of aerosol particles or through the removal of solvent from the interior of particles. However, these approaches do not permit careful control of the void sizes and shapes.^{2–4} Matijevic's group has prepared hollow particles by the thermal decomposition of the polymer cores of

particles prepared such that a polymer core was overcoated by a shell of thermally stable inorganic material.⁵

Our approach described here¹ allows us to create these voids at room temperature; in addition, our silica particles contain voids within pure silica cavities. These cavities can be further modified using the standard chemical approaches for silica surfaces. We expect that the approach outlined here is of general utility and can easily be extended to other materials such as titania and alumina. We expect that these porous materials with well-defined voids will find utility in areas of technology such as catalysis.

Materials and Procedures

The detailed procedures for preparing the CdS-silica nanocomposites are given in the accompanying paper.¹ Typically, a reaction utilized a 250-mL microemulsion containing 0.127–0.184 M NH_3 , 0.086–0.537 M Igepal CO-520 or Triton N-101, and 0.053–0.179 M tetraethyl orthosilicate (TEOS, Fluka), with the remainder of the reaction mixture consisting of cyclohexane and hexanol.

Nanocomposite colloids of silica-CdS were synthesized using either Igepal or Triton microemulsions containing Cd^{2+} and S^{2-} ions. The CdS inclusions were implanted through the precipitation of CdS during the simultaneous condensation of silica due to the simultaneous injection of TEOS. The resulting yellow nanocomposites were solvent exchanged into water and washed several times with concentrated nitric acid until the yellow CdS inclusions were completely dissolved and the turbid solution became white. The final product was a pure colloidal silica suspension. Surface areas were measured by using the BET nitrogen absorption method (Automatic Surface Area Analyzer 4200, Beta Scientific Corp.).

Results and Discussion

As indicated in the preceding paper,¹ CdS inclusions can be incorporated in monodisperse silica spheres in a variety of morphologies. These morphologies are determined by the timing and the precipitation rate of the CdS during the growth of the silica spheres in the microemulsion reaction medium. As indicated schematically in Figure 1, the CdS inclusions can be prepared as large patches on the surface, as uniform quantum dot inclusions within the spheres, as the cores of the silica particles, as annular

* Author to whom correspond should be addressed.

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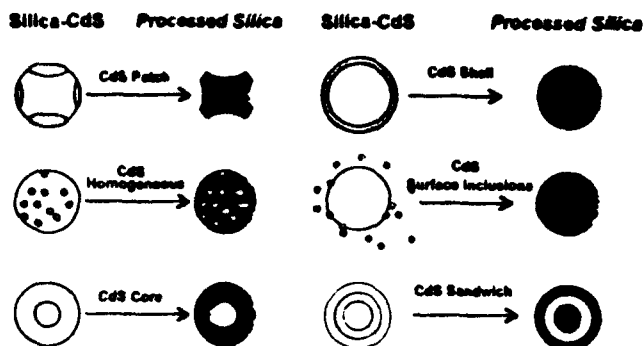


Figure 1. Schematic diagram illustrating the various silica-cadmium sulfide nanocomposites that can be synthesized and the resulting particle formed after the acid etching removal of the CdS inclusions.

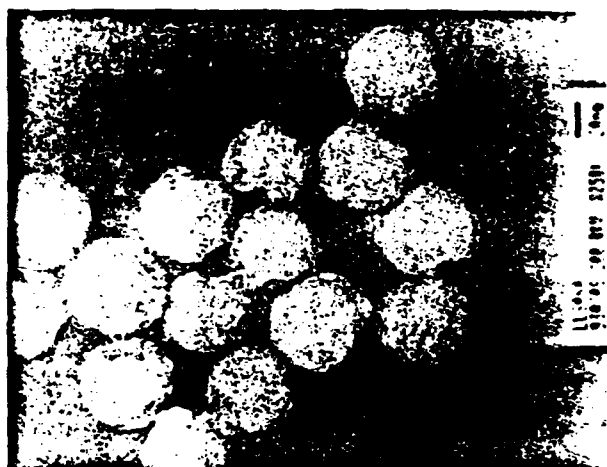
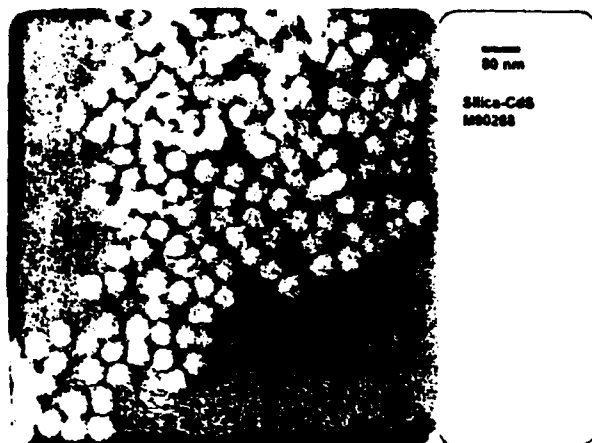


Figure 2. (a) TEM micrographs of nanocomposite particles with cadmium sulfide surface patches before nitric acid etching. (b) TEM micrographs after etching. The bare silica particles show craters on the surface where the cadmium sulfide patches were removed.

shells within a silica-CdS sandwich arrangement, or as small quantum dots on the surface.

Pure silica does not react with strong acids except for HF. In contrast, CdS is very soluble in strong acids, which readily dissolve the CdS inclusions. Figures 2a and b show a CdS-silica nanocomposite with CdS patches on the surface before and after acid etching; acid etching forms craters on the surface.

Figure 3 shows a TEM micrograph of ca. 50-nm CdS-silica nanocomposite spheres with homogeneously dispersed CdS quantum dots after acid etching. The figure demonstrates numerous dimples on the surface. It is difficult to clearly visualize the interior small 2.5-nm voids by TEM. However, the fact that the sample is no longer yellow indicates that the interior CdS inclusions have been removed. Further, the BET surface area



Figure 3. TEM micrographs of nanocomposite particles with cadmium sulfide quantum dots homogeneously distributed after etching. The bare silica particles show dimples where the cadmium sulfide quantum dots were removed on the surface. The interior voids cannot be clearly visualized.

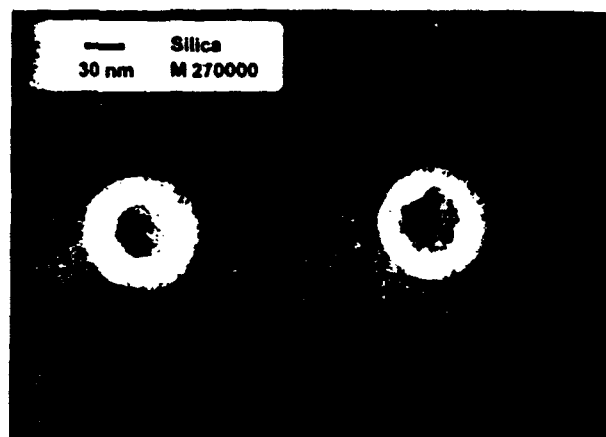


Figure 4. TEM micrograph of spheres where large ca. 30-nm CdS cores were removed by acid etching to leave large spherical voids.

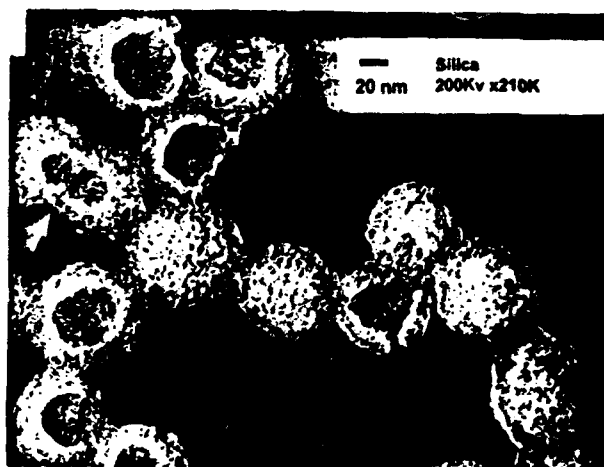


Figure 5. TEM micrograph of silica sphere doublets after acid etching. These doublets were formed during the synthesis of silica spheres with CdS patches.¹ The doublets are attached at CdS welds, and the doublets are overcoated with silica shells. Acid etching of the doublets resulted in ellipsoidal caverns joining the sphere doublets.

measurements discussed below demonstrate that the particles contain numerous ca. 2.5-nm diameter spherical cavities.

Acid etching of ca. 30-nm silica colloids which originally contained 4–8-nm CdS cores results in central voids. Our accompanying paper shows a TEM photograph of this preparation after acid etching. The dark central spots result from the small hollow spherical voids. We also can create larger spherical

Table 1. Calculated and Measured BET Surface Areas for Silica-CdS Composite Spheres before and after Acid Etching

sample	particle morphology	particle size (nm)	surface area (m ² /g)			
			measured		calculated	
			before etching	after etching	before etching ^a	after etching ^a
SYC121Q	shell, plus doublets and triplets	80	61	232	39	169
SYC122Q	shell, plus doublet and triplets	84	76	208	37	179
SYC68Q	homogeneous holes	62	104	152	51	102

^a Ignoring aggregates and assuming density of 1.9 g cm⁻³.

cavities. Figure 4 shows hollow ca. 90-nm particles with ca. 30-nm diameter holes. We can easily construct silica colloids with diameters as large as 300 nm with hollow cores of any size desired.

Figure 5 shows acid-etched doublets of silica spheres. These doublets were formed through the attachment of silica particles by welds of CdS surface patches. Subsequently a silica shell was formed around the sphere doublets. Acid etching results in ellipsoidal cavities where the CdS welds between the spheres were removed to form ellipsoidal caverns joining the spheres.

We directly measured the increase in the sample surface area by BET nitrogen absorption measurements after acid etching. Table 1 shows the measured surface areas and that calculated using simple models for samples SYC121Q and SYC122Q, where the CdS was formed as annular rings within the silica spheres, and sample SYC68Q, where CdS quantum dots were homogeneously distributed in the silica spheres. The samples with the CdS annular shells had large concentrations of doublet and triplet spheres.

If the spheres are nonporous, we can calculate that the surface area, A (m², gm), of the silica sphere-CdS composites is simply the surface area of the spherical particles:

$$A = 6000W/d\rho$$

where W is the weight of the sample (1.0 g), d is the sphere diameter (nm), and ρ is the density (g/cm³) of the silica-CdS sphere composites.

We see that prior to etching the area measured is approximately 2-fold greater than that calculated. The larger surface area of the sample probably results from pores within the silica spheres; silica colloids made by the Stober process are often highly porous,^{1,6} with porosities as large as 11–15%. However, varying the preparation conditions can dramatically decrease the porosity.^{7,8} The silica-CdS composite spheres prepared here appear to be much less porous than the highly porous Stober silica spheres. The surface areas associated with the pores can be very large, depending on the pore diameters. For example, 10% porous 80-nm silica spheres with 0.4-nm diameter pores are calculated to show surface areas greater than 600 m²/g. Our silica-CdS

composite samples show silica sphere internal surface areas 10-fold smaller. However, our silica-CdS composite spheres are at least somewhat porous, since the entire particle volume is readily accessible to chemical reagents such as nitric acid, which dissolves the CdS.

After etching, the surface area increases 3–4-fold for samples SYC121Q and SYC122Q and by 50% for sample SYC68Q. For samples SYC121Q and SYC122Q, we modeled the increase in surface area to be that associated with the surface area of the void shell that originally contained CdS. For sample SYC68Q, the surface area increase calculated was that which resulted from the 2.4-nm spherical voids formed by removal of the CdS quantum dots in the spheres:

$$A_c = 6000WR/\rho_c d_c$$

where A_c is the surface area which results from the voids created by removal of the CdS quantum dots, R is the weight ratio of CdS to silica ($R = 0.105$ for sample SYC68Q), ρ_c is the density of CdS, and d_c is the diameter of the voids (2.4 nm).

The measured increases in surface area are very close to those calculated from the simple models. This result supports the idea that we have tailored voids in the silica spheres which are geometrically well defined in size and shape and in their location within the silica spheres.

Conclusions

We have demonstrated a new method to form silica particles with voids of a variety of morphologies. The relative amounts, sizes, and positions can be easily and accurately controlled. These monodisperse silica spheres are porous, and additional chemistry can be used to further modify the cavity surfaces. These materials will be useful for catalyst support applications and for novel other applications where it is important to carry out chemical reactions in separate small chambers.

Acknowledgment. We gratefully acknowledge Mr. Thomas Harper and Mr. Cole van Ormer for their help in the TEM measurements. We gratefully acknowledge financial support from the Air Force Office of Scientific Research through Grant No. F49620-93-1-0008 and from the University of Pittsburgh Materials Research Center through the Air Force Office of Scientific Research Grant No. AFOSR-91-0441.

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United States Patent [19]

Asher et al.

US005281370A

[11] Patent Number: 5,281,370

[45] Date of Patent: Jan. 25, 1994

[54] **METHOD OF MAKING SOLID CRYSTALLINE NARROW BAND RADIATION FILTER**

[75] Inventors: Sanford A. Asher; Sesh Jagannathan, both of Pittsburgh, Pa.

[73] Assignee: University of Pittsburgh of the Commonwealth System of Higher Education, Pittsburgh, Pa.

[21] Appl. No.: 571,251

[22] Filed: Aug. 22, 1990

[51] Int. Cl.³ B29D 11/00; B06B 1/02

[52] U.S. Cl. 264/1.1; 264/22; 264/24; 264/108

[58] Field of Search 264/1.1, 1.3, 1.7, 24, 264/22, 108; 350/311, 362

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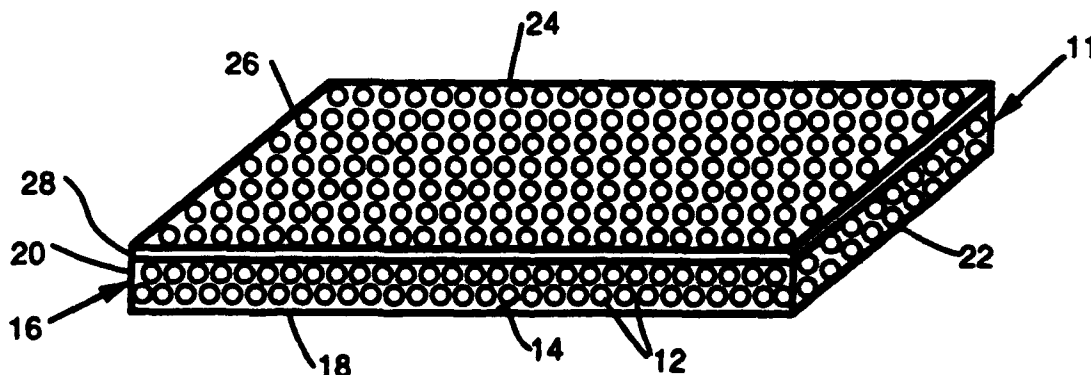
Primary Examiner—Jan H. Silbaugh
Assistant Examiner—Christopher A. Fiorilla
Attorney, Agent, or Firm—Arnold B. Silverman

[57]

ABSTRACT

A method of making a solid filter material which filters a predetermined wavelength band from a broader spectrum of radiation includes creating a colloidal structure composed of particles dispersed within a medium, and introducing a solvent thereto. Thereafter, the solvent is evaporated and the remaining structure solidifies into a solid crystalline array. Another embodiment of the method includes electrophoretically attracting the particles in a medium to form an ordered array. The particles can also be fused together by polymerization using one of several methods which are provided. Additionally, one aspect of the invention involves coating the particles with an electrostatically-charged material to facilitate inter-particle interactions.

18 Claims, 2 Drawing Sheets



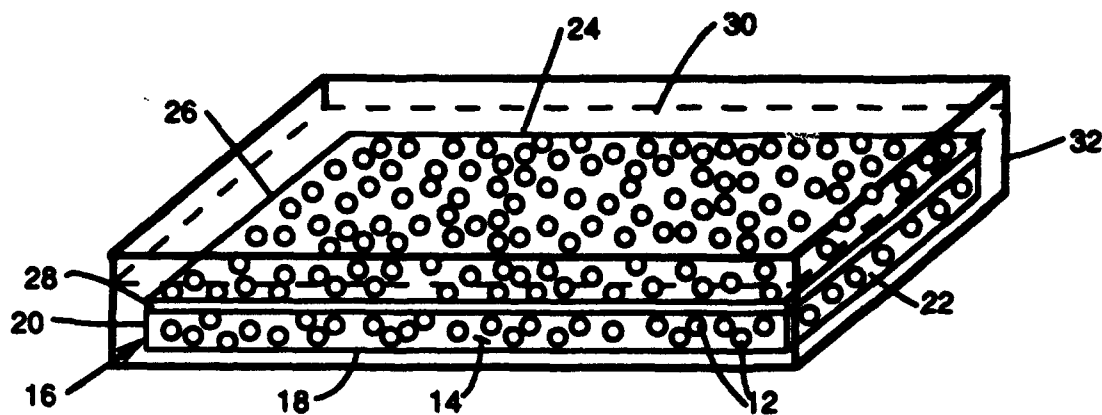


FIG. 1

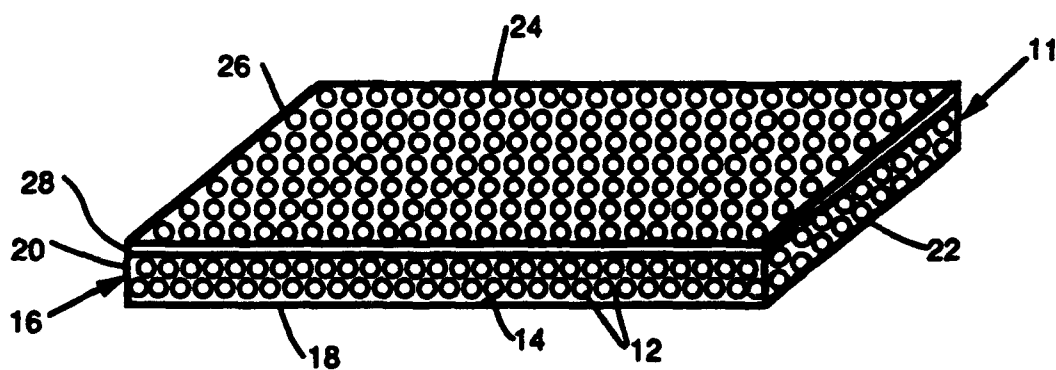


FIG. 2

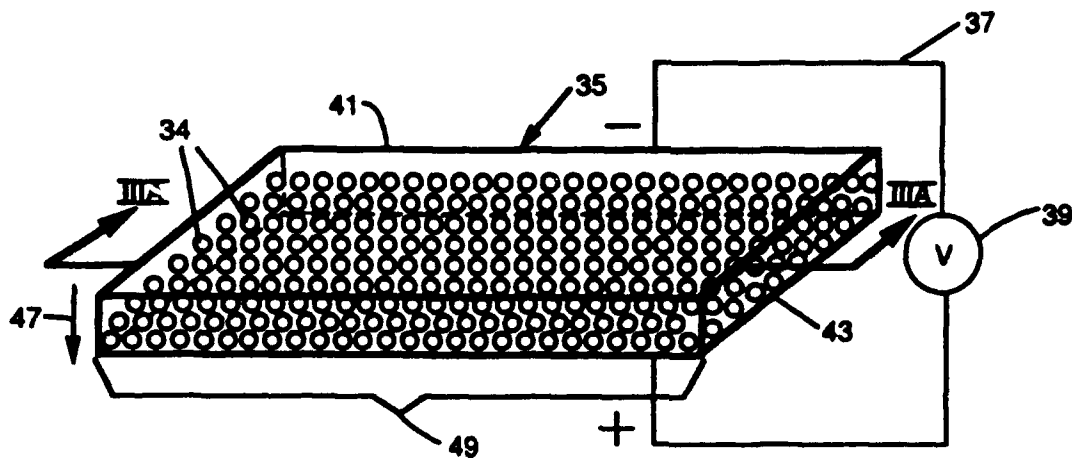


FIG. 3

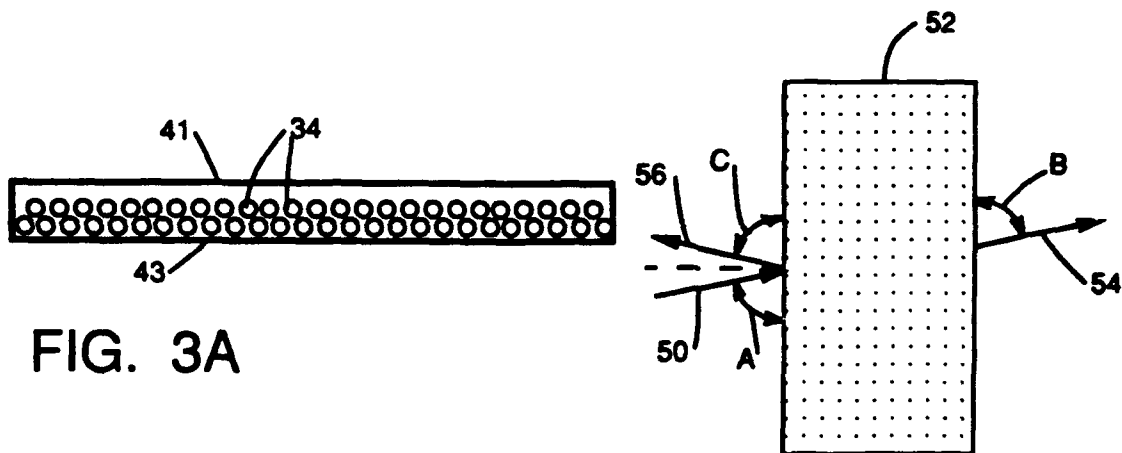


FIG. 3A

FIG. 4

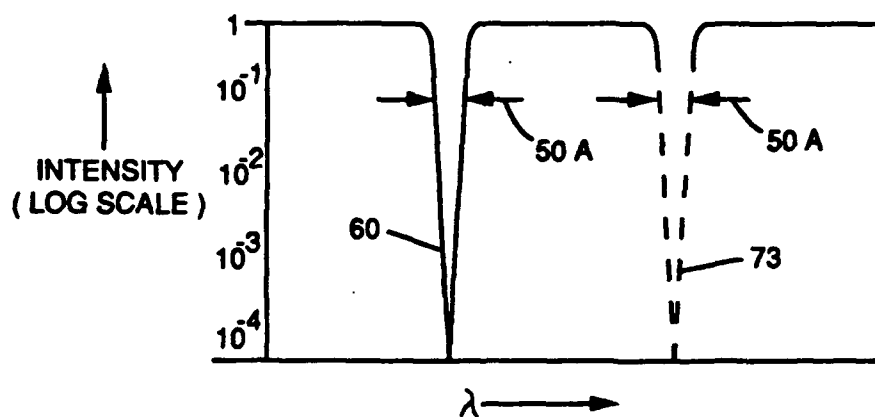


FIG. 5

METHOD OF MAKING SOLID CRYSTALLINE NARROW BAND RADIATION FILTER

This invention was made with government support under Contract F3315-88-C-5432 awarded by the Department of the Air Force. The government has certain rights in the invention.

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates generally to a method of creating filters which may be used to select and/or reject predetermined frequencies of electromagnetic radiation. The invention relates more particularly to a method of making solid crystalline materials in which colloidal electrically charged particles form an ordered dispersion and are solidified into a hardened material which has certain predetermined filtering characteristics.

2. Description of the Prior Art

It has been recognized that colloidal dispersions of polymer particles in various solvents can form crystalline structures having lattice spacings comparable to the wavelength of ultraviolet, visible and infrared radiation. Bragg diffraction techniques have been used to examine these polymer colloidal crystals with a view towards identifying their interparticle spacing, lattice parameters and phase transitions. My U.S. Pat. No. 4,627,689 discloses a crystalline narrow band radiation filter which is made by forming a highly ordered Crystalline colloidal structure within cell. My U.S. Pat. No. 4,632,517 also discloses a narrow wavelength band filtering device created by forming a highly ordered crystalline colloidal structure within a cell.

More recently, it has been known that these crystalline structures can be very useful and that such structures have many practical applications for filter devices. In many instances it is necessary or desirable to filter out narrow bands of selected wavelengths from a broader spectrum of incident radiation while permitting the transmission of adjacent wavelengths. High spectral-purity commercial monochromators which are available for this purpose generally use a plurality of gratings and prisms. However, such devices are extremely complex, bulky and expensive.

As mentioned hereinbefore, U.S. Pat. No. 4,627,689 discloses a crystalline colloidal narrow band radiation filter which is made by forming a highly ordered crystalline colloidal structure within a cell. The crystalline colloidal structure is formed by dispersing electrically charged particles, for example, polystyrene particles within an appropriate solvent.

U.S. Pat. No. 4,632,517 discloses another crystalline colloidal narrow band radiation filter involving polystyrene particles. The device of this patent forms the basis for a mechanically simple and highly efficient monochromator. It has application in improved systems for investigating Raman or emission spectra of selected sample materials. U.S. Pat. No. 4,632,517 does allude to a type of solid structure in that it suggests that a lattice spacing gradient may be formed and as part of this process a "freezing" of certain conditions could be achieved using polymerization techniques. However, this suggestion did not disclose the unique aspects of the method of the present invention for forming filtering devices which are entirely solid and self-supporting.

U.S. Pat. Nos. 4,627,689 and 4,632,517, are expressly incorporated herein by reference.

Other filtering devices have also been known. See, for example, U.S. Pat. No. 4,803,688 which discloses ordered colloidal suspension optical devices. This patent relates to the addition of a water based polymer to a colloidal structure.

Although an allusion was made to solid devices in above-mentioned prior art, the above patents involve crystalline colloidal structures which are not solids and are not self-supporting. Because of their high peak absorbance value, state-of-the-art colloidal crystalline array filters may be widely used for eye protection and sensor protection. However, a more rugged filter would obviously have wider application. Thus, there has been a need for a solid filter. Solids provide better mechanical stability and machinability. Non-solids, on the other hand, are subject to become disordered upon vibration. In addition, liquid media can undergo phase transitions quite easily by freezing or boiling and this may often be undesirable.

For these reasons a solid structure is more desirable in many applications. For example, solid filtering devices are often necessary for filtering out certain bands of radiation in aviation and space travel, as they provide mechanical rigidity and this allows for a greater range of design features. It has heretofore been an extremely difficult polymer chemistry problem to create a solid filter.

Therefore, there remains a need for a solid crystalline filtering device.

SUMMARY OF THE INVENTION

These and other needs are satisfied by the present invention which provides a simple and relatively inexpensive method of creating a solid narrow band radiation filter and related filter devices. The narrow band radiation filter selectively and effectively filters a narrow band of wavelengths from a broader spectrum of incident radiation while transmitting adjacent wavelengths to a high degree. For example, a filter can be produced in accordance with the present invention which filters out greater than about 99 to 99.999% of a wavelength band of about 50 to 150 Å while transmitting more than about 70 to 90% of the intensity of remaining wavelengths.

A method of making the filter is also disclosed in which a crystalline structure is created which is composed of particles dispersed in a liquid medium. As used herein, "particles" includes any shape suitable for the desired filtering need, but preferably the particles for the present invention will be spheres. In accordance with one aspect of the invention, a solvent is introduced into the crystal structure that fuses the particles together. Thereafter, the solvent is evaporated to condense the particles into a three-dimensional array having a highly periodic lattice spacing. The lattice spacing is created such that it can diffract a predetermined wavelength band.

As noted hereinbefore, the particles are fused together and a geometric ordering occurs. The lattice structure exists largely due to electrical repulsive forces between the particles which each have a charge of the same polarity. Several different methods of fusing the particles together are disclosed which are set forth in further detail hereinafter.

One aspect of the method of securing the particles in the desired relative position together involves polymer-

ization of the medium surrounding the particles to fix the particles in the desired relative spaced relationship to each other. A particular method of such polymerization includes adding acrylamide or bisacrylamide and preferably a nonionic UV photoinitiator to a colloidal solution contained between two quartz plates. Ultraviolet light is then utilized to initiate the polymerization.

In accordance with another embodiment of the method a polymer solution is introduced into the region around the polystyrene spheres. This polymer rigidizes the medium and fixes the sphere positions. The polymer may be an organic or inorganic material.

An alternate method includes providing particles, which may be polystyrene, polymethyl methacrylate or silica spheres, for example, in colloidal form with a coating which provides a film of polymerizing residue on the surfaces of the particles. The ordered colloidal array is formed and is then solidified by polymerizing together the adjacent sphere surfaces.

Another method of the invention involves packing the particles utilizing an electric field to attract the particles and further enhance the ordering of the array. Subsequent to achieving this ordering, polymerizing may be effected with the assistance of the electric field which will electrochemically initiate polymerization of material, such as acrylamide and bisacrylamide, for example.

The device resulting from the methods of this invention can form the basis for a mechanically simple and highly efficient filter which is useful in many applications, such as, for example, sensor protection, eye protection, scientific instrumentation and medical instrumentation in laser surgery. Such filters can also eliminate the need for dichroic mirrors in Optic technology. Overall, the device can be used with any product in which the disclosed radiation filtering characteristics are desirable.

It is an object of the present invention to provide an inexpensive, simple method of creating a solid crystalline structure having predetermined filtering characteristics.

It is another object of the invention to provide a method of creating a solid filter which can effectively filter a predetermined narrow wavelength band from a broader spectrum of incident radiation.

These and other objects of the invention will be more fully understood from the following description of the invention, with reference to the illustrations appended hereto.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a schematic illustration of colloidal particles dispersed within a medium prior to ordering of the particles in accordance with one aspect of the present invention.

FIG. 2 is a schematic illustration of a solid crystalline array of polystyrene particles created in accordance with the method of the present invention.

FIG. 3 is a schematic illustration of the electrophoretic method of organizing and polymerizing the particles in a packed array.

FIG. 3A is a cross section of the array taken along line IIIA—IIIA of FIG. 3.

FIG. 4 is a schematic illustration of the angle at which radiation is diffracted using the filter of the present invention.

FIG. 5 is a representation of a spectrum indicating the narrow band wavelengths which can be filtered using

devices created in accordance with the present invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

With reference to FIG. 1, there is shown a schematic illustration of a group of particles 12 prior to ordering of the array which is discussed hereinafter. Particles 12 are interdispersed within a medium 14. As will be discussed more fully hereinafter, the filtering characteristics of the filtering device so created may be varied by controlling the spacing between the particles 12 or by altering the shape and size of the particles 12.

Although not limiting to the invention, in a preferred form, particles 12 are preferably composed of polystyrene, polymethylmethacrylate, silicon dioxide, aluminum oxide, polytetrafluoroethylene or other suitable materials which are generally uniform in size and electrical charge. The material chosen depends upon the optimum degree of ordering desired in the resulting lattice. The higher the ordering of the lattice structure, the narrower the wavelength band which may be filtered with the resulting filtering device. Other parameters also affect filtering characteristics such as particle size and shape.

Particles 12 used in the method of this invention preferably have a diameter between about 50 and 250 nanometers. These particles 12 may be synthesized using the technique disclosed hereinbelow. Alternatively they currently may be obtained commercially from Polysciences, Inc. of Warrington, Pa.

The particles 12 are generally stored in a dispersion including a detergent and relatively small amounts of an electrolyte. They are first cleaned of the electrolyte and surfactant impurities. This cleaning may be accomplished by dialysis against a bath of doubly distilled water containing a mixed bed ion exchange resin. After dialysis, the particles 12 may be stored in a bath of, preferably, 10% by weight suspension of ion exchange resin called Analytical Grade AG501X8 mixed bed resin obtainable from Bio-Rad of Richmond, Calif. The ion exchange resin should be cleaned prior to use through a suitable procedure such as that taught by Vanderhoff, et al. in the *Journal of Colloid Interface Science*, 1968, 28,336-337.

In the form illustrated in FIG. 1, the particles 12 are contained in a medium 14 which may be water, glycerol, ethylene glycol, methanol, ethanol, dimethyl sulfoxide, phenyl methyl sulfoxide, dioxane, dimethylformamide, polyethylene glycol, or glycerine, or any material possessing similar properties. The particles 12 within medium 14 in the form shown are placed in a generally rectangular chamber 16 which is sealed by cover 28. Chamber 16 is, preferably, composed of quartz, LEXAN or LEXAN-coated glass. Chamber 16 has bottom portion 18, and upstanding sidewalls 20, 22, 24 and 26. The suspension composed of particles 12 and medium 14 is diluted with deionized, doubly distilled water to provide a partial volume fraction in the range of about 0.5 to 75 percent. Chamber 16 is then sealed with air-tight cover 28. Sealed chamber 16 is then placed in room temperature water 30 in outer container 32 for a period of time adequate to allow the array to crystallize. This environment should also be perturbation-free. Geometric ordering of the crystalline structure then occurs.

FIG. 2 shows chamber 16 after removal from outer container 32. The particles 12 are packed in an ordered array 11 within chamber 16.

Turning now to further details of the method of the present invention, various aspects of the method of forming a solid crystalline structure are discussed.

In accordance with one aspect of the invention, any suitable solvent such as benzene, toluene and chloroform is added to preferably a polymer latex solution and this is added to medium 14 (FIG. 1) to fuse the particles 12 together and create an ordered array 11 as shown in FIG. 2. Preferably, polystyrene or polymethyl methacrylate spheres of about 50 to 250 nm diameter may be used. However, any suitable particle with a polymer outer shell may be used within the method of the present invention. The solvent, when added, serves to solubilize and swell the outer shells of particles 12.

Thereafter, the solvent medium 14 is removed. A suitable method of removal of the solvent medium 14 is preferably by a gentle evaporation wherein chamber 16 is at a temperature between about 20° and 30° C. until the desired evaporation takes place.

During solvent evaporation, the particles 12 condense into an ordered three-dimensional array 11 and the surfaces of the particles 12 are fused to one another. The resulting solid array 11 can then be removed from chamber 16. This array 11 constitutes a film which is self-supporting. The film diffracts and filters radiation of specific predetermined wavelengths. The wavelengths at which such a film is effective depend upon the resulting lattice structure, however, the wavelength bands may be on the order of about 2000 to 15,000 Å. In other words, the film can be effective from the ultraviolet region through the visible spectral region and then into and through the infrared region.

EXAMPLE 1

A crystalline colloidal structure was created by a method discussed hereinbelow. This method may be used to create a filtering device which Bragg diffracts a relatively narrow wavelength band with a high rejection ratio. Spheres 12 having a diameter of between about 200 and 250 nanometers and a density of between about 1 and 1.1 were used. The spheres 12 were added to a medium 14 of water containing about 0.1 percent toluene. Spheres 12 were added to a total volume density of about 10^{13} to 10^{14} particles per cubic centimeter.

This suspension was sealed in a chamber 16 (FIG. 1) made of quartz, having internal chamber dimensions of about 5 cm×5 cm×0.5 mm. The solvent was then evaporated by placing the chamber at room temperature for about twenty hours. A solid crystalline structure was formed therein, as evidenced by a change from a cloudy appearance to an iridescent appearance.

The solid crystalline structure created from array 11 was then removed from chamber 16. The structure so formed was determined to Bragg diffract above about 99 to 99.999% of light at a maximum of about 4800 to 5200 angstroms wide wavelength band centered at about 5000 angstroms while passing about 60 to 80% of the light at adjacent wavelengths.

The filtering device so produced as a narrow band filter would be quite useful for many applications, such as goggles for filtering laser light from a pilot's eyes or for a windshield on an airplane or space vehicle. Alternatively, the material may be used in rejecting a narrow wavelength band for scientific instrumentation or in the field of optics.

In accordance with another aspect of the invention a method for preparing a solid filter by polymerization of the medium around the spheres involves addition of at least one of acrylamide and bisacrylamide and an ultraviolet photoinitiator to a colloidal solution such as that described hereinbefore. The solution is preferably contained between two quartz plates. The solution is then exposed to ultraviolet radiation which effects the desired polymerization.

In accordance with yet another aspect of the invention, a fabrication method for production of monodisperse silica spheres to be used to construct a filtering device in accordance with the method of the present invention will be disclosed. Silica particles having sulfonate groups on their surfaces were used. A preferred sulfonate material is 2-(4 chlorosulfonyl phenyl) ethyl trimethoxy silane. The resultant sulfonate groups on the surface of particles are strong acid groups which dissociate to provide negative charges on the surface of the particles, which in this case are preferably spherical. It should be understood, however, that positively charged particles in lieu of negative particles may also be utilized within the scope of the present invention.

Furthermore, in accordance with this aspect of the invention, particles self-assemble into a three-dimensional array which will diffract light. The medium in which particles are dispersed may be adjusted to vary the interparticle interactions. As the medium evaporates, the particles have a high density within the medium. The adjustments may be made by including in the medium compounds such as NaCl, other salts or more broadly (a) any ionic compound or (b) any nonionic compounds having different dielectric constants. Other compounds such as styrene or silicone oil, for example, leave a residue of a material around the particles. This residue will not evaporate when the remainder of medium evaporates and it will tend to seal the spaces between the particles. This method results in a three-dimensional array having a high particle volume fraction. The material solidifies to form a homogenous solid crystalline structure which diffracts radiation. While we have used acidic materials on the surface of the particles, it is also within the scope of the present invention to use basic materials for this purpose such as quaternary amines, for example. One of the primary considerations is that the particles be electrically charged and the residue material adheres to the surface thereof.

EXAMPLE 2

Silica spheres were produced by polymerizing tetraethyl orthosilicate in a water-ethanol-ammonium hydroxide mixture using the Stöber process. The spheres were then silanized with 2-(4 chlorosulfonyl phenyl) ethyl trimethoxy silane. The spheres were allowed to self-assemble into a three-dimensional array 11 (FIG. 2) in the manner hereinbefore discussed within a medium such as water. Thereafter, evaporation was then facilitated. The array was removed from chamber 16 and a homogenous solid crystalline structure was present. The structure so created was determined to Bragg diffract about 99 to 99.999% of the light at a maximum of about 4800 to 5200 angstroms wide wavelength band centered at about 5000 angstroms, while passing about 60 to 80% of the light at adjacent wavelengths.

In accordance with another aspect of the invention, a method is described with reference to FIG. 3. Polystyrene particles 34 are introduced into chamber 35 which is composed of preferably two SnO₂-coated quartz

plates, 41 and 43. Particles 34 are sandwiched between plates 41 and 43. The chamber 35 contains a medium selected from the group consisting of water, methanol and ethanol, and a monomer such as acrylamide, bisacrylamide, methyl methacrylate or hydroxy methyl methacrylate. Chamber 35 has a suitable electric field placed across it as schematically shown by wire 37 and voltage source 39. The electric field causes upper plate 41 to be negatively charged and lower plate 43 to be positively charged. The potential across the chamber 35 is preferably about 20 to 30 volts/cm. The field is preferably applied to chamber 35 for about 5 to 10 minutes. The particles 34, being negatively charged, are attracted in the direction 47 due to the electric field. They migrate towards lower plate 43 and are packed in an ordered array against lower plate 43 in the manner shown in FIGS. 3 and 3A. Particles 34 migrate due to negatively charged sulfonates on their surfaces. Of course, it should be understood that positively charged particles could be used which would then require an appropriate adjustment in the orientation of the electric field. The surface of the particles may be positively charged using quaternary amines on the surface of the particles in which case they would migrate towards the opposite electrode. After about 5 to 10 minutes, the particles 34 become packed in the array designated generally as 49 (FIG. 3). The monomer in the liquid medium polymerizes around the particles. The polymerization may be initiated either chemically or electrochemically. The structure thereafter is gelled and solidified as the medium evaporates. A more rigid solid can be obtained by allowing the liquid medium to evaporate and condense the ordered particles into a solid array. The resulting filter is capable of diffracting or filtering radiation in accordance with lattice spacing of the array 49.

EXAMPLE 3

An electrophoretic formation method as discussed hereinbefore was practiced employing polystyrene spheres. Spheres having a diameter of about 200 to 250 nanometers and a density of between about 1 and 1.1 were used. Spheres 34 (FIG. 3) were placed in a medium 36 of water containing about 0.1 percent toluene. The density of spheres 34 within medium 36 was between about 10^{12} and 10^{14} . The suspension was placed in chamber 35 made of tin oxide coated glass and having interior dimensions of about 50 millimeters $\times$ 50 millimeters $\times$ 0.5 millimeters.

An electric field of about 20 to 30 volts/cm was placed across chamber 35. The electric field caused the negatively-charged spheres 34 to migrate towards positive end 43. This was allowed to occur for between about 5 and 10 minutes. Thereafter, evaporation was facilitated by placing chamber 35 in an atmosphere of air kept at about room temperature, for about 16 to 20 hours. A filter film having a thickness of about 0.01 to 0.1 mm was produced which was determined to Bragg diffract above about 99 to 99.999% of light at a maximum of about 4800 to 5200 angstroms wide wavelength band centered at about 5000 angstroms while passing about 60 to 80% of the light at adjacent wavelengths.

It should be understood that the electrophoretic method disclosed herein is not the only method of packing the particles which are spheres in the exemplary embodiment. There are other methods known to those skilled in the art including gravitational settling and centrifugal settling.

With reference to FIGS. 4 and 5, the performance of the filtering device is illustrated. In FIG. 4, a beam 50 of electromagnetic radiation is incident upon a filtering device 52, made in accordance with the present invention, at an angle A. A transmitted beam 54 departs the filtering device 52 at a substantially equal angle B. A beam 56 of a narrow wavelength band is Bragg diffracted from the filtering device 52 at an angle C. In this manner, the beam 56 is effectively filtered from beam 50. The wavelength of beam 56 satisfies the Bragg diffraction equation:

$$n \lambda = 2d \sin A$$

wherein "d" represents the lattice spacing between each sphere 12 (FIG. 1) within the solid structure. "n" represents any integer which will preferably be about 1, "A" is angle A, and λ represents wavelength.

The curve 60 of FIG. 5 illustrates that the wavelength band which is Bragg diffracted by the filtering device 52 made in accordance with the present invention may be quite narrow. Referring still to FIG. 5, curve 73 depicts that the central wavelength of the narrow wavelength band filtered by filtering device 52 is dependent upon the incident angle as determined by the Bragg diffraction equation set forth hereinbefore. Accordingly, it will be appreciated that the filtering device is "tunable" to filter a range of different wavelength bands, by controlling and appropriately adjusting the orientation between the filtering device 52 and the incident electromagnetic radiation.

It will be appreciated therefore that the invention has provided a method for creating a solid filtering device which is capable of Bragg diffracting narrow bands of radiation. The disclosure includes several embodiments and aspects of the method of the invention which provides for versatility in preparing filtering devices for desired applications.

Whereas particular aspects of the method of the present invention and particular embodiments of the invention have been described hereinbefore for purposes of illustration, it will be appreciated by those skilled in the art that numerous variations of the details may be made without departing from the invention as described in the appended claims.

What is claimed is:

1. A method of making a solid filtering material for filtering a predetermined wavelength band from a broad spectrum of radiation, comprising the steps of creating a colloidal structure by providing particles with a polymeric outer shell dispersed in a crystalline array within a first liquid medium, introducing a second substance comprising a solvent into said colloidal structure to solubilize and swell the outer shells of said particles, and evaporating at least a substantial portion of said second substance and said first liquid medium from said structure to condense said particles into a solid three-dimensional, ordered array having a lattice spacing structure, which is substantially equal to said predetermined wavelength band, and to fuse surfaces of said particles to one another.

2. The method of claim 1 including providing as said particles ionized particles such that charges of said ionized particles create repulsion forces to enhance said spacing structure of said particles.

3. The method of claim 2 including

providing as said particles, particles selected from the group consisting of polystyrene, polymethylmethacrylate, silicon dioxide, aluminum oxide and polytetrafluoroethylene.

4. The method of claim 1 including

providing as said first liquid medium a substance selected from the group consisting of water, glycerol, ethylene glycol, methanol, ethanol, dimethyl sulfoxide, phenyl methyl sulfoxide, dioxane, dimethylformamide, polyethylene glycol and glycerine.

5. The method of claim 1 including

selecting said second substance from the group consisting of polymer latex and polymethylmethacrylate.

6. The method of claim 1 including

selecting said solvent from the group consisting of benzene, toluene and chloroform.

7. The method of claim 1 including

evaporating at least a substantial portion of said second substance and said first liquid medium at room temperature for a period of time adequate to allow said ordered array to crystallize.

8. The method of claim 1

therein said particles of said colloidal structure are spheres of a diameter of about 50 to 250 nm.

9. A method of making a solid filtering material for filtering a predetermined wavelength band from a broad spectrum of radiation comprising

creating a colloidal structure by providing ionized particles of the same polarity dispersed in a crystalline array established by the relative repulsion of said ionized particles within a medium,

adding a polymerization inducing substance to said medium, and

polymerizing said medium around said particles to form a solid, ordered array having a lattice spacing structure, said spacing structure being substantially equal to said predetermined wavelength band.

10. The method of claim 9 including

providing as said polymerization-inducing substance a mixture composed of at least one of acrylamide and bisacrylamide, and an ultraviolet nonionic photoinitiator, and

exposing said medium to ultraviolet radiation to induce said polymerizing of said medium.

11. A method of making a solid filtering material for filtering a predetermined wavelength band from a broad spectrum comprising the steps of

(a) coating surfaces of silica particles with a sulfonate-containing material on outer surfaces of said particles,

(b) adding said particles to a medium and allowing them to self-assemble into a three-dimensional array to create a colloidal structure, and

(c) evaporating at least a substantial portion of said medium out of said colloidal structure to solidify said structure to create a lattice structure having spacing substantially equal to said predetermined wavelength band.

12. The method of claim 11 including

providing as said sulfonate group on said outer shell of said particles 2- (4 chlorosulfonyl phenyl) ethyl trimethoxy silane.

13. The method of claim 11 including

adjusting said medium to vary interparticle interactions by including in said medium (a) ionic compounds or (b) compounds having different dielectric constants such that said particles have a predetermined density within the medium after a portion of the medium is removed.

14. The method of claim 13 including

leaving a residue around said particles to facilitate formation of said lattice spacing.

15. A method of creating a solid filtering material for filtering a predetermined wavelength band from a broad spectrum of radiation, comprising the steps of creating a colloidal structure composed of electrostatically-charged particles suspended within an electrically neutral medium comprising a monomer,

placing a bipolar electric field across said structure to facilitate travel of said particles toward one pole of said field and packing of said particles in an ordered array, and

polymerizing said monomer around said particles and allowing said structure to solidify into a lattice structure having spacing substantially equal to said predetermined wavelength band.

16. The method of claim 15 including

providing said colloidal structure contained between two SnO₂-coated quartz plates.

17. The method of claim 15 including

initiating said polymerization chemically.

18. The method of claim 15 including

initiating said polymerization electrochemically.

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