



Colloidal CdTe Nano Crystals Synthesis and Characterization

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14. ABSTRACT Synthesis of CdTe nano crystals (NCs) in uniform sizes and in good quality was performed in our nano lab and further characterized by absorption spectra, photoluminescence (PL), and atomic force microscopy (AFM). In this growth procedure, CdTe nano crystal band gap is strongly dependent on the growth time and not on the injection temperature or organic ligand concentration. This is very attractive because the nano crystal size can be easily controlled by the growth time only and is very attractive for large scale synthesis. The color of the solution changes from greenish yellow to light orange, then to deep orange and finally grayish black to black over a period of one hour. This is a clear indication of the gradual growth of different size (and different band gap) of CdTe nano crystals as a function of the growth time. In other words, the size of the nano crystal and its band gap can be controlled by adjusting the growth time after injection of the tellurium. The prepared CdTe NCs were characterized by absorption spectra, photoluminescence (PL), AFM and X-ray diffraction. Measured absorption maxima are at 521, 560, 600, and 603 nm corresponding to band gaps of 2.38, 2.21, and 2.07 eV respectively for growth times of 15, 30, 45, and 60 minutes. From the absorption data, nano crystal growth size saturates out after 45 minutes. AFM scanning of these materials indicate that the size of these particles is between 4 to 10 nm in diameter for the growth time of 45 minutes. This report presents growth and characterization data on CdTe nano crystals for various growth times.					
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1. Introduction

II-VI type of nano Crystal are extensively studied for their optoelectronic, photochemical, and nonlinear optical properties (1, 2, 3). Semiconductor nano crystals, like CdTe, show size dependent optical properties and are very important in basic nano science research, colloidal science, biomedical labeling, light emitting diodes, solar cells, and lasers (4-6). In general, semiconductor nano crystals show novel optical and electronic properties when they have size comparable to, or smaller than, the dimensions of the exciton within their corresponding bulk material. This allows us to create unique properties for the nano crystal by engineering the size and composition and the chemical functionality of their surrounding medium. The techniques and capability of this manipulation of the size is an important way to create desired nano crystals (7, 8). By using size-selective precipitation techniques, cadmium chalcogenide NCs have been successfully obtained (9). The most common semiconductor materials grown by precipitation technique are CdTe, CdSe, CdS, and ZnS of which CdTe has special technological importance because it is the only known II-VI material that can form conventional p-n junctions (10). There are many reports on the synthesis of semiconductor nano crystals with very good monodispersity (11-13). Synthesis involving injection method give NCs with good quality. Usually injection is carried out at a certain temperature. Nano crystal preparation can also be done with non injection synthesis without nucleation initiators (14). The formation of high-quality nano crystal is often favored.

2. Experimental

Colloidal CdTe nano crystals were synthesized using the method of Cao (14) and Lifshitz (15). The synthesis was carried out as follows. A highly purified tellurium (Te) solution was prepared in tri octylphosphine (TOP) and octadecene (ODE). In an experiment 0.128 gm of Te and 0.2112 gm of TOP was added to ODE so that total was 2 mL. The cadmium (Cd) precursor solution was prepared by mixing cadmium oxide (CdO) and an oleic acid (OA) and ODE mixture. In the experiment 0.0256 gm of CdO and 200 μ L of OA and 10 mL of ODE were used. CdO was dissolved in OA/ODE mixture when heated under Ar flow at 240 °C. A grey precipitate was formed when further heated to 270 °C which was characterized as Cd particles and considered as the first stage of the reaction. The second part of the reaction included an instantaneous injection of the Te precursor which was previously prepared to the Cd solution at 270 °C solution. Immediate reaction takes place and CdTe nano crystals formed. Immediately after the injection, the color of the solution started changing from greenish yellow to light orange and then to deep orange and finally grayish black over a period of one hour. Aliquots of the CdTe nano crystals were withdrawn 15, 30, 45, and 60 minutes after injection and dispersed in toluene. The

dispersed mixture was centrifuged at 3000 rpm for 5 minutes. The supernatant liquid – CdTe nano crystals dispersed in toluene was separated and characterized for absorption, photoluminescence, substrate surface and particle size determination using AFM.

3. Results and Discussion

CdTe nano crystal solutions in toluene for reaction times of 15, 30, 45, and 60 min shown in figure 1, were used to obtain the absorption spectra using a Perkin Elmer UV-visible Lambda 19 spectrometer. All luminescence measurements were acquired by using a Renishaw *inVia* Reflex confocal Raman microscope (Hoffman Estates, Illinois) equipped with three independent excitation sources (514, 633, and 785 nm). The 514 nm was focused onto the sample at the microscope stage through either a 50 (N.A. 0.75) or 100 (N.A. 0.90) objective. Before all measurements, the instrument was wavelength calibrated by using an internal Si standard. Each spectrum was collected and stored. AFM scanning of the nano crystals on silicon was done with Digital Instruments (DI) tapping mode technique.

The color of the nano crystal growth solution as a function of time after the initial injection is presented in figure 1. The picture shows the four different solutions obtained after various injection times as indicated. One can clearly see the change in color indicative of the difference in the size of particles from left to right. In our case, the size difference was the primary concern.

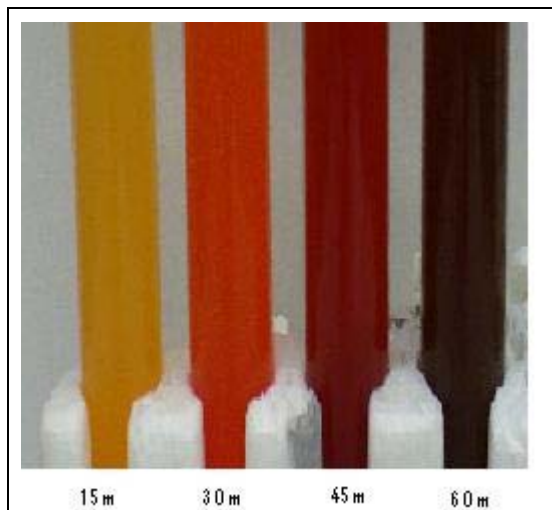


Figure 1. CdTe nano crystal growth solution as a function of growth time of 15 min, 30 min, 45 min, and 60 min.

Immediately after injection, the color of the solution started changing from greenish yellow to light orange then to deep orange and finally grayish black to black over a period of one hour. This is a clear indication of the gradual growth of different size (and different band gap) CdTe nano crystals as a function of the growth time. In other words, the size of the nano crystal and its band gap can be controlled, by adjusting the growth time after injection of the tellurium. The grayish black and black solutions are not included in the picture. As the time changed, the particle size changed and correspondingly the band gap also changed. The size change continued for an hour where it reached the saturation point.

Figure 2 shows the absorption spectra of the nano crystals grown at various times. As can be seen, there is a shift of absorption peak as well as the band gap as the time of growth changes. Clearly the sixty minute growth sample indicates the saturation in terms of the peak position as well as the band gap. The absorption maxima are at 521, 560, 600, and 603 nm respectively corresponding to band gaps of 2.38, 2.21, and 2.07. It appears that nano crystal growth size saturates out between 45 and 60 minutes indicating no further shift in the peak height nor band gap change.

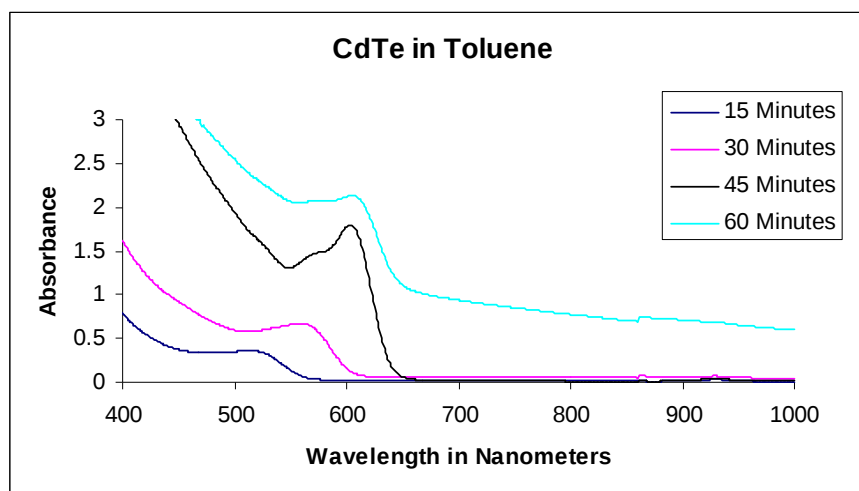


Figure 2. Absorption spectrum of CdTe nano crystals grown at different times.

The luminescence spectrum of the CdTe nano crystals synthesized 30 minutes and 45 minutes after injection of the tellurium precursor are presented in figure 3.

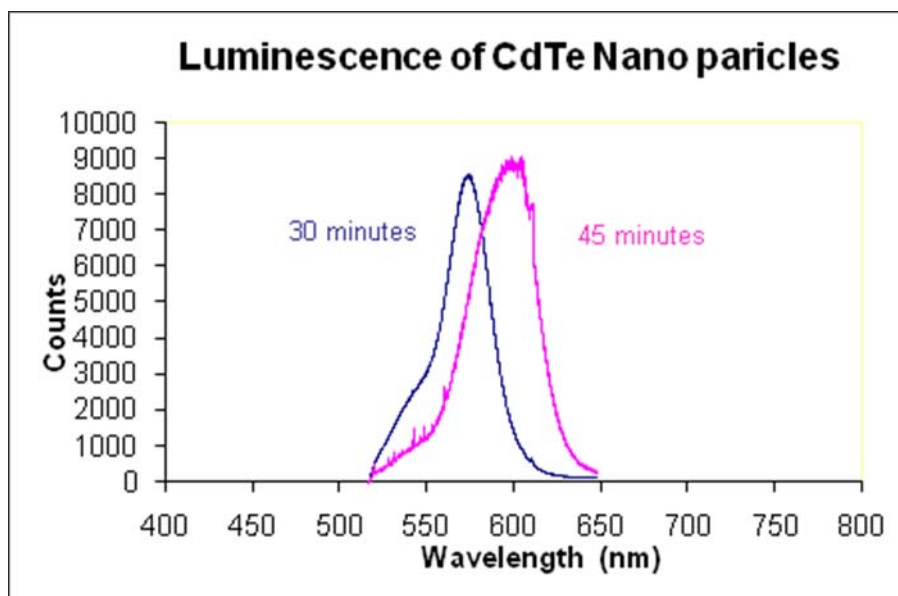


Figure 3. Luminescence spectrum of CdTe nano crystals after 30 and 45 minutes

In the case of the luminescence, the FWHM increases from 27 nm for the 30 minute growth sample and to 32 nm for the 45 minute growth sample. Red shifting of luminescence with respect to temperature change has been reported before for the temperature dependent growth of CdTe nano particles (16). In this procedure, as shown by the results, high quality CdTe nano crystal growth was based upon time and not on the injection temperature or the organic ligand concentration; also shown is the red shift of the luminescence. Since this is similar to the previous results, the time dependent growth also becomes an attractive way of growth for the large-scale synthesis of nano crystals.

Surface morphology of CdTe nano crystals was determined by atomic force microscopy. Sample preparation with drop casting always resulted in piling up of the nano crystals and did not result in uniform thin film. This is usually the case with drop casting and to avoid piling up and to obtain uniform film spin casting method needed to be adopted. We tried extensively to produce close packed continuous nano crystalline thin film. Spin casting was tried using several dilutions of nano crystals in chloroform with different rotation speeds and time. In many cases we ended up with islands of mono layer of nano crystalline film with spots of 3-D aggregates over the entire substrate surface. This type of deposition occurs always when nano crystalline film is deposited on solid substrate surfaces like silicon (17). But for our AFM study both drop casted and spun samples were used. CdTe nano crystalline film was formed on Si[211] substrate either by spin casting or drop casting. In a special case, the nano crystals grown at 45 minutes were initially drop casted on 211 silicon substrate and studied by Atomic Force Microscopy (AFM) and the AFM pictures are presented in figure 4. As can be seen, the AFM image the particle

height is 4.2 nm and the particles are distributed unevenly. The following is the bearing chart which characterizes the relative roughness of the surface in terms of high and low areas.

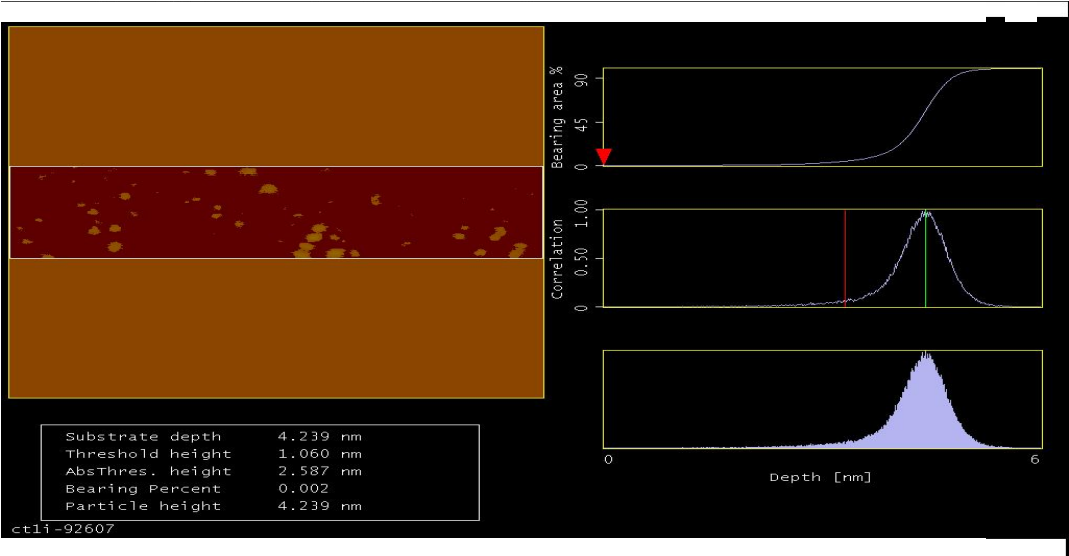


Figure 4. AFM picture of CdTe nano crystals drop cast on 211 Silicon .

Figure 5 gives the localized depth data within a specified area and it shows that a particular dot was chosen for the analysis and the chosen box indicates that the size of the nano particle is about 4.7 nm.

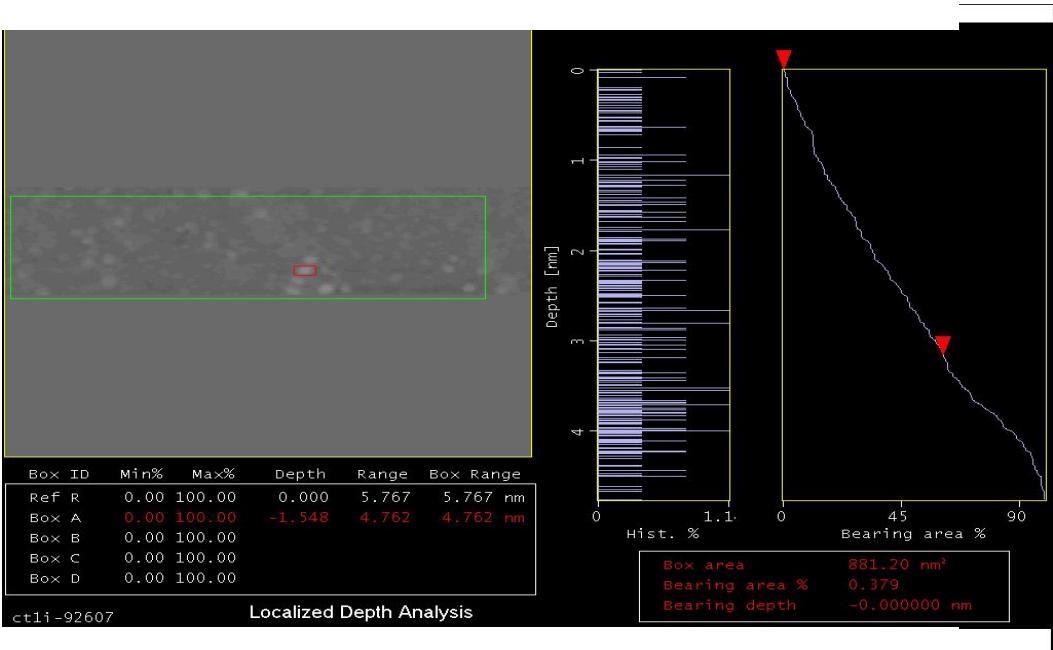


Figure 5. Localized depth picture of CdTe nano crystals drop casted on 211 Silicon.

Figure 6 shows the 3D version of the roughness plot of the nano crystals. One can see that the particles are randomly scattered and in general of uniform size. Figure 7 gives the top view image with the reference lines drawn across the region to be measured. The height profile is generated from averaged data in the referenced region. The midlevel horizontal line to the top gives a height of 80 nm and clearly the height of these particles are below 10 nm.

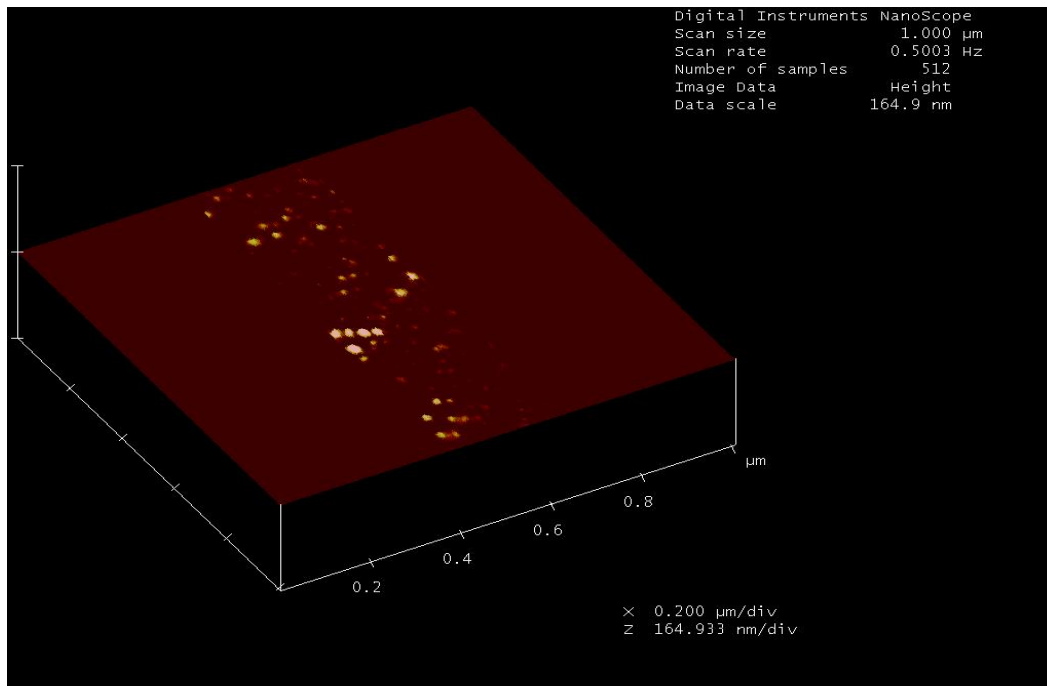


Figure 6. 3d CdTe nano crystals by AFM.

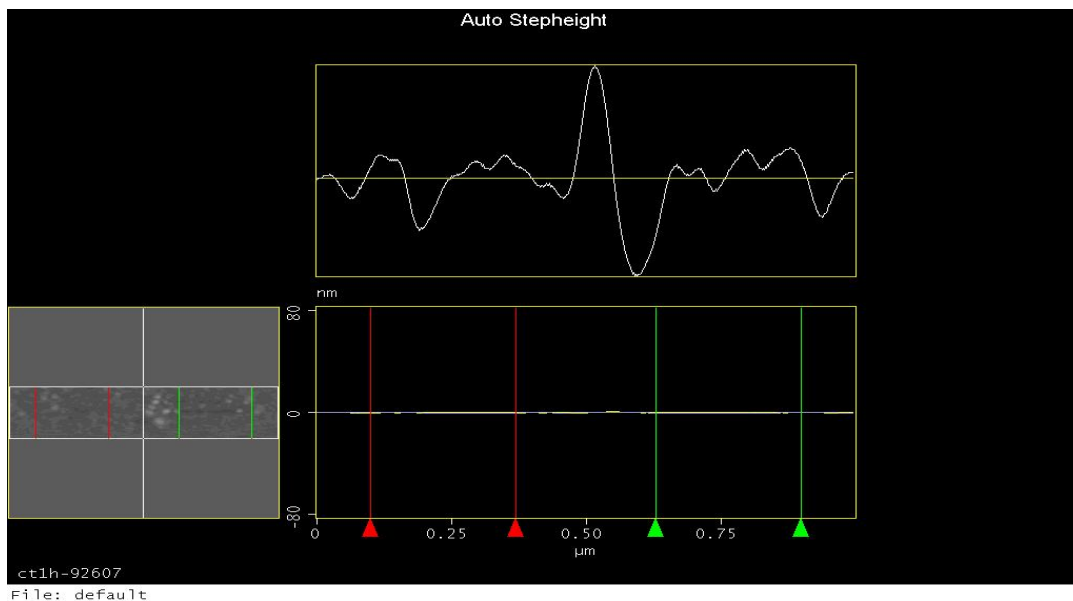


Figure 7. Step height measurement of nano particles.

4. Conclusions

In this work we have modified the synthesis procedure of CdTe nano crystals from temperature, or ligand concentration based growth to time dependent growth. In this synthesis procedure, CdTe nano crystal band gap is strongly dependent on the growth time and not on the injection temperature or organic ligand concentration. We think that this procedure is very attractive because that the size of nano crystal can be easily controlled by the growth time only and hence useful for large scale synthesis. A growth based upon time will more likely provide uniform nano particles compared to a growth based on temperature, since uniform temperature is difficult to obtain in a reaction flask. The color of the solution changed from greenish yellow to light orange then to deep orange and finally grayish black to black over a period of one hour. This was a clear indication of the gradual growth of different size (and different band gap) of CdTe nano crystals as a function of the growth time. In other words, the size of the nano crystal and its band gap could be controlled by adjusting the growth time after injection of the tellurium. Results of absorption spectra, photoluminescence (PL), and AFM were presented. Measured absorption maxima were found to be at 521, 560, 600, and 603 nm corresponding to band gaps of 2.38, 2.21, and 2.07 eV respectively for growth times of 15, 30, 45 and 60 minutes. From the absorption data one can see that nano crystal growth size saturates out after 45 minutes. AFM scanning of these materials indicate that the size of these particles are about 3-10 nm in radius for growth time of 45 minutes.

5. References

1. Bawandi, M.; Steigerwald, M.; Brus, I. *Annu. Rev. Phys. Chem.* **1990**, *41*, 477.
2. Alivisatos, P. *Science* **271** **1996**, 933.
3. Markovich, G.; Collier, C.; Henrichs, S.; Remacle, F.; Levine, R.; Heath, J. *Acc. Chemm. Res.* **1999**, *32*, 415.
4. Medintz, I. L.; Uyeda, H. T.; Goldman, E. R.; Martoussi, H. *Nature Mater.* **2005**, *4*, 435.
5. Peng, A.; Peng, X. G. *J. Am.Chem. Soc.* **2002**, *124*, 3343.
6. Peng, X. G.; Manna, L.; Yang, W. D.; Wickam, J.; Scher, E.; Kadanvich, A.; Alvisatos, A. P. *Nature* **2000**, *404*, 59.
7. Coe, S.; Woo, W.; Bawendi, M.; Bulovic, V. *Nature* **2000**, *404*, 59.
8. Lieber, C. *Solid State Commmun* **1998**, *107*, 607.
9. Murray, C.; Norris, D.; Bawendi, M. *J. Am. Chem. Soc.* **1993**, *115*, 8706.
10. McCaldin, J. *J. Vac. Sci. Technol* **1990**, *A*, *8*, 1188.
11. Cumberland, S. L.; Hanif, K. M.; Javier, A.; Khitrov, G. A.; Strouse, G. F.; Woessner, S. M.; Yun, C. *Chem. Mater* **2002**, *14*, 1576.
12. Pradhan, N.; Efrima, S. *J. Am.Chem. Soc.* **2003**, *125*, 2050.
13. Talapin, D. V.; Haubold, S.; Rogach, A. L.; Kornowski, A.; Hasse, M.; Weller, H. *J. Phys. Chem,B.* **2001**, *105*, 2260.
14. Yang, Y. A.; Wu, H.; Williams, K. R.; Chao, Y. C. *Angew. Chem. Int. Ed* **2005**, *44*, 6712.
15. Kolney-Olesiak, J.; Kloper, V.; Osovsky, R.; Sashchiuk, A.; Lifshitz, E. *Surf. Sci* **2007**, *601*, 2667.
16. Walker, G. W.; Sunder, V. C.; Rudzinski, C. M.; Wun, A. W.; Baeendi, M. G.; Nocera, D. G. *App. Phys. Lett.* **2003**, *83*, 3555.
17. Mott, L.; Billoudet, F.; Lacaze, E.; Douin, J.; Pileni, M. P. *J. Phys. Chem, B* **1997**, *101*, 138.

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