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Crystallographic Description for Nanoparticle Assemblies – Application to Cadmium Selenide Clusters.

A L Vasiliev¹, M Aindow¹, J Lee², F Papadimitrakopoulos² and F Jain³

1. Institute of Material Science, Department of Metallurgy and Materials Engineering, University of Connecticut, Storrs CT 06269-3136
2. Nanomaterials Optoelectronics Laboratory (NOEL), Polymer Program, Department of Chemistry, University of Connecticut, Storrs CT 06269-3136
3. Nanomaterials Optoelectronics Laboratory (NOEL), Department of Electrical and Systems Engineering, University of Connecticut, Storrs CT 06269-3136

ABSTRACT: The stacking sequence of several layers of self-assembled semiconducting CdSe nanoparticles has been investigated using transmission electron microscopy. FCC, HCP, saddle sites occupation and ring structures were found coexisting in the supercrystals formed by CdSe nanoparticles.

1. INTRODUCTION

The wide variety of applications of semiconducting, metal and isolating nanoparticles has motivated many studies of their structure and properties. Sample uniformity makes it possible to manipulate nanocrystals into glassy or ordered nanocrystal assemblies. Ordered metallic, insulating, or semiconducting nanoparticles represent an exiting new class of materials [1]. These self-assembled mono-modal size-selected nanoparticles frequently adopt close-packed three-dimensional arrangements. The resemblance of these arrangements to the face-centered cubic or hexagonal close-packed crystal structures exhibited by many elements has to led to the widespread adoption of these crystallographic terms to describe the assemblies. Self-assembling of passivated gold nanoparticles was described recently in [2]. Semiconductor nanostructures have attracted tremendous interest in the past few years because of their special physical properties and their potential for applications in micro- and optoelectronic devices [3]. Recently the possibility of the synthesis of CdSe nanocrystals highly regular in size and shape was shown [4]. The CdSe nanocrystals, which are coated with surfactant organic molecules can self-organize into highly ordered microstructures. The goal of the work was the study of self-assembling arrangements of CdSe nanocrystals.

2. EXPERIMENT

CdSe nanoparticles were produced by solution pyrolysis of organometallic precursors in trioctylphosphine. Details of the synthesis was described in [4]. The nanoparticles are organically coated. The CdSe clusters were dissolved in a toluene solution. The solution were deposited on a standard Cu grid covered with a thin

amorphous carbon film. Different amounts of solution were dropped to the grid to change the number of layers formed by the nanoparticles. The samples were studied in a Philips EM 420 TEM operated at 100kV.

3. RESULTS AND DISCUSSION

A TEM image of non-ordered, glassy CdSe nanoparticles two-dimensional assembly is shown in fig.1. The random distribution of the CdSe particles was caused by the quick drying of the solution on the carbon substrate and difference in the particle sizes.

An ordered CdSe assembly formed at a lower solvent evaporation rate with different numbers of layers is presented in fig. 2. Steps with one CdSe layer in height were associated with difference in contrast. The tentative number of layers derived from contrast variations are shown. Subsequent images were obtained from *this or similar stepped* areas where the number of layers was unambiguous, and from regions exhibiting chain and ring stacking.



Fig. 1. TEM image of non-ordered CdSe particles.

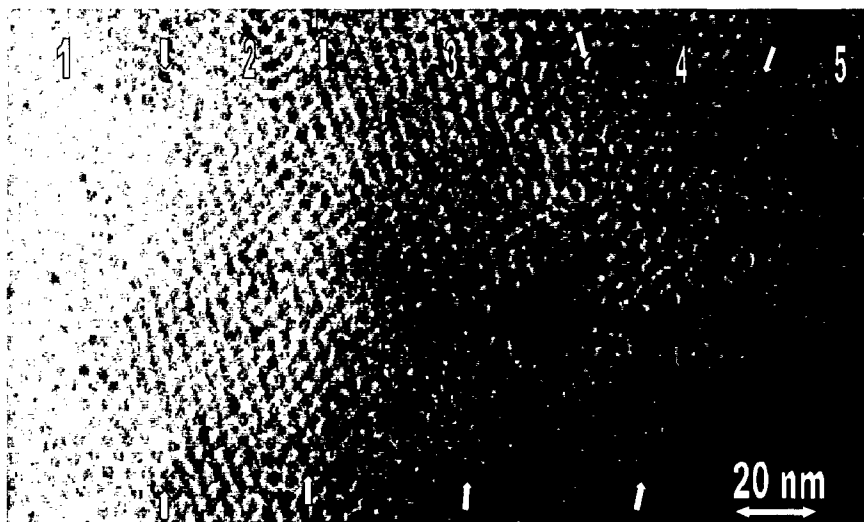


Fig. 2. TEM image of ordered CdSe nanoparticles with different number of layers (indicated by numbers). Arrows show the steps one CdSe nanoparticles layer in height.

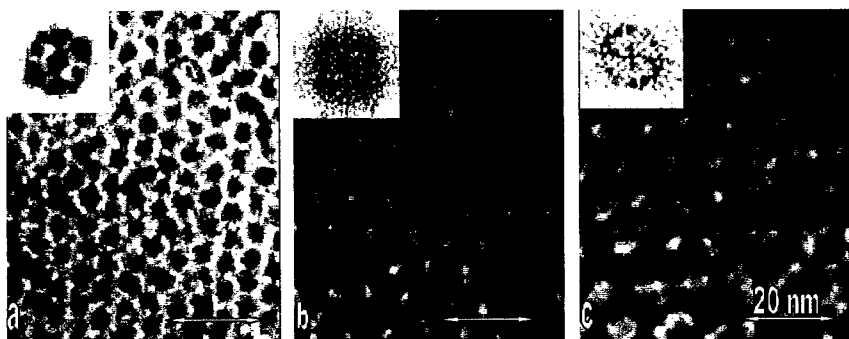


Fig.3. Single-(a), double-(b) and triple layers of CdSe nanoparticles. Correspondent FFT power spectra are in the inset.

The single layer of the CdSe nanoparticles (fig. 3a) shows hexagonal symmetry (note the FFT power spectrum). The nanoparticles in the second layer mostly occupied three-fold hollow sites (see fig. 3b). Correspondent FFT power spectrum from two layers more often demonstrated six-fold symmetry. However, in some areas the nanoparticles in the second layer occupied two-fold saddle sites (fig.4 a-c). The TEM images of such stacking demonstrate characteristic chains or lines. Similar arrangement were recently found experimentally by Wellner *et al.* [2] for gold nanoparticles. It was suggested that this type of ordering could be dependant on nanoparticle shape. The shape of the CdSe nanoparticles in our investigations was not perfectly spherical and that could cause

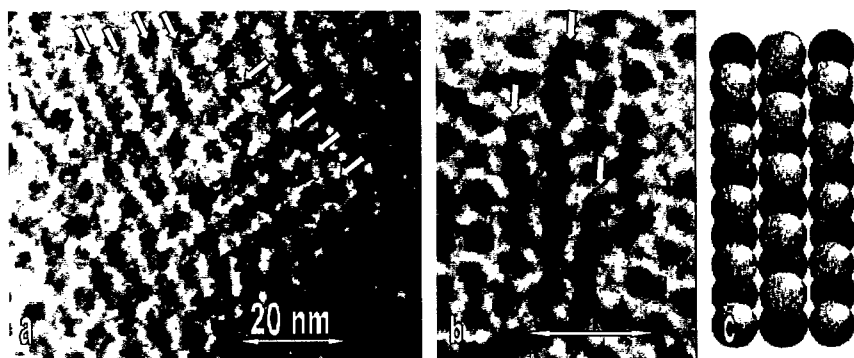


Fig. 4. Image of two layered part of the sample from fig.1 where second layer of CdSe nanoparticles occupied saddle sites (arrowed)-a). The enlarged image of the two-layer island with chains (arrowed) formed by particles in the saddle sites -b) and schematic representation of the twofold saddle sites occupation in the second layer -c).

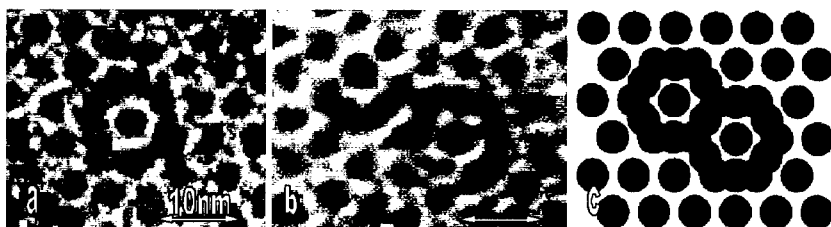


Fig.5. An image of ring structure –a). Two closely spaced parts of rings –c) and a schematic representation of ring structure –c).

the high density of chain-like structures in the sample. The chain-like structures were found as bi-layered islands (fig.4 b). We can not rule out the possibility of three and more layers formation of CdSe particles in the saddle sites in these areas. This corresponds to a disordered form of the $C11_b$ $MoSi_2$ structure [5]. There was one more stacking configuration of second layer. It looks like ring or semi-ring structure (fig.5 a-c). The ring arrangement of nanoparticles was recently shown in [6] when second layer was rotated and contracted leading to the energy minimization.

The contrast from the third layer was slightly different even in adjacent areas (fig. 2 and fig. 3c). The two-fold symmetry of the FFT power spectrum indicated the presence of hexagonal stacking or hcp structure (see fig. 3c, insert). However, close examination of other areas associated with the presence of a third layer pointed to the three-fold symmetry and fcc type of structure. The stacking of third and fourth layers near chain-like structures more often look like lines and may be due to further occupation of two-fold sites above the second layer which corresponds to a disorder form of the $C11_b$ $MoSi_2$ structure.

4. CONCLUSION

Three-dimensional arrangements of semiconducting CdSe nanoparticles can be fcc or hcp –type. Nanoparticle in the saddle sites or ring stacking of second layer can also coexist with these. Third and fourth layers deposited on the top of saddle site stacking can form the $C11_b$ $MoSi_2$ structure.

REFERENCES

1. A.P. Alivisatos, *J.Phys.Chem.* **100**, (31), 13226 (1996).
2. A. Wellner, P. Brown, M. Aindow, C.J.Kiely, and J.P. Wilcoxon, *Inst. Phys. Conf. Ser.* **161**, 561 (1999).
3. I.M. Goldby, L. Kuipers, B. von Assendorf, P.E. Palmer, *Appl. Phys. Lett.* **69**, 2819 (1996).
4. C.B. Murray, D.J. Norris, M.G. Bawendi, *J. Am. Chem. Soc.* **115**, (19), 8706 (1993).
5. M. Aindow, S.N. Williams, R.E. Palmer, J. Fink, C.J. Kiely, *Phil. Mag. Lett.* **79**, 569. (1999).
6. D. Zanchet, M.S. Moreno, D. Urgante, *Phys. Rev.Lett.* **82**, 5227. (1999).