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CdSe nanocrystals were synthesized in inverse micellar solution and then assembled on aluminum surface by bifunctional linker molecules. High resolution transmission electron microscope (HRTEM) photographs show that nanocrystals with uniform sizes were bound to aluminum and in some regions a structure of hexagonal close-packed was formed. Atomic force microscopy (AFM) and electron diffraction (ED) results confirmed the formation of this CdSe nanocrystal monolayer on aluminum substrate.

Keywords: self-assembly; nanocrystals; bifunctional linker molecules

INTRODUCTION

The techniques of colloidal chemistry open a new way to fabricate semiconductor nanocrystals, whose sizes can be varied systematically to study quantum size effects or to form new electronic or optical materials. Experimental works on the fabrication of ordered arrays of semiconductor nanocrystals have been started since ten years ago. The most exciting method for the formation of these man-made ordered structures is the self-assembly of semiconductor nanocrystals.[1],[2]

In this paper we report the synthesis of CdSe nanocrystals from Cd^{2+} and $SeSO_3^{2-}$ ionic reagents in inverse micellar solution and the self-assembly of those CdSe nanocrystals on aluminum surface by bifunctional linker molecules.

EXPERIMENTS

Synthesis of CdSe Nanocrystals in Micelles

CdSe nanoparticles in micelles were prepared according to following reaction:[3]

$$Cd^{2+} + 2\,OH^- + SeSO_3^{2-} \rightarrow CdSe + SO_4^{2-} + H_2O \qquad (1)$$

Two separate solutions were prepared by dissolving surfactant AOT (sodium dioctyl sulfosuccinate) in heptane.[4] Then deionized water was added to above two solutions. Stirring gave two homogeneous micellar solutions with W=2~5 ($[H_2O]/[AOT]$). Under quickly stirring a standard solution of Cd^{2+}

was added to one of above micellar solutions, while a $SeSO_3^{2-}$solution was added to another micellar solution. Then the Cd^{2+} micellar solution was transferred slowly to $SeSO_3^{2-}$micellar solution and this procedure resulted in a orange or red CdSe solution. The sizes of CdSe nanocrystals could be controlled by changing the Cd^{2+} concentration, $SeSO_3^{2-}$ concentration and the *W* value of the micellar solution. Figure 1 shows the ultraviolet-visible absorption spectra of CdSe nanocrystals in micellar solution prepared with different *W*. An obvious absorption peak (1S-1S transition) can be observed and the absorption edges lie from 510 nm to 610 nm which are blue shifted from 713 nm of bulk CdSe band gap. These results demonstrate the quantum size effect of carriers in the CdSe nanocrystals. The average sizes of CdSe nonacrystals are 2.1 nm, 3.0 nm and 4.2 nm, corresponding to spectrum a, b and c, determined from the TEM photographs.

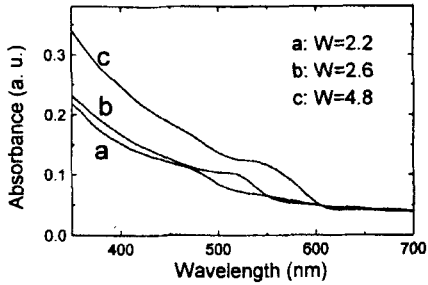

FIGURE 1 Ultraviolet-visible absorption spectra of CdSe nanocrystals in micellar solution prepared with different *W*.

Self-assembly of CdSe Nanocrystals on Aluminum Surface

We used mercaptoacetic acid ($HSCH_2CO_2H$), a linear bifunctional linker molecules, to assemble CdSe nanocrystals.[1] One end groups (-COOH) of mercaptoacetic acid molecules can attach to aluminum surface and the other end groups (-HS) can bond to Cd of CdSe nanocrystals, which were anchored to the surface of aluminum substrates. Aluminum layers were prepared by evaporating of aluminum on collodion-coated copper grid for TEM or Si wafers for AFM observation. By immersing aluminum substrates in a ethanol solution of mercaptoacetic acid for 12 hours, an initial monolayer of thiol acids was formed on aluminum surface. The aluminum substrates with free thiol groups were then transferred to micellar solution of CdSe nanocrystals and left for 12 hours. Those CdSe nanocrystals self-assembled on aluminum surface were stable for several weeks after they were rinsed two times by heptane and subsequently dried.

RESULTS AND DISCUSSION

Figure 2 is a HRTEM photograph for CdSe nanocrystals self-assembled on aluminum surface. We can see clearly the fine lattice images of CdSe

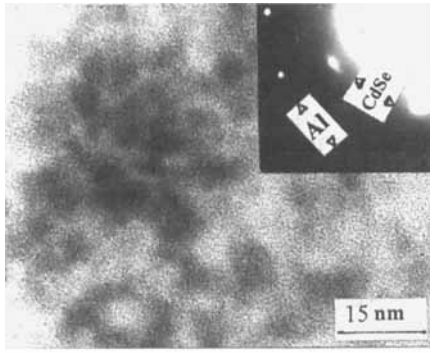

FIGURE 2 HRTEM photographs and ED pattern of CdSe nanocrystals self-assembled on aluminum surface.

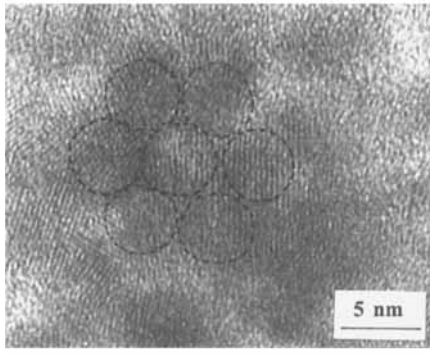

FIGURE 3 HRTEM photographs of several CdSe nanocrystals on aluminum surface. A structure of hexagonal close-packed could be seen.

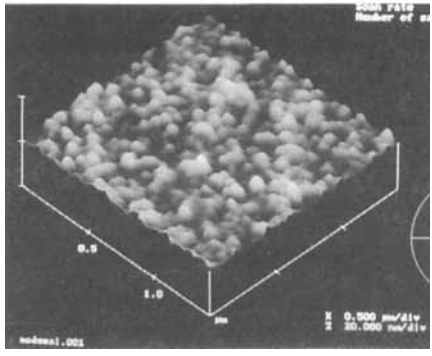

FIGURE 4 AFM image of CdSe nanocrystals bound to aluminum surface. It shows again that they are homogeneous without aggregation and their height are ~5 nm .
See Color Plate V at the back of this issue.

nanocrystals. The nanocrystals are all spherical and have a mean diameter of 4.2 nm which is estimated by measuring the size of the areas with lattice fringes. The most interesting results is that a structure of hexagonal close-packed which is an evidence of self-assembly has been observed in some regions of figure 3. It also be seen that the size of nanocrystals are uniform which is the necessary condition to form an ordered hexagonal close-packed structure. This result is similar with the report on CdS self-assembly by V. L. Colvin et al..[1]

When we carefully investigate a single CdSe nanocrystal image, two-dimensional lattice fringes show that: in one direction the distance between the planes is 0.32 nm while in the other direction is 0.36 nm, which agree well with those of wurtzite CdSe, $d_{(101)}$=0.329 nm and $d_{(002)}$=0.351 nm. In the inset of figure 2 there are two sets of ED patterns. The planar spacing of 0.36 calculated from the diameter of the first fringe is agreement with that of CdSe's (110) and (002) planes. The second ED fringe comes from aluminum's (111) plane.

The lateral size and self-assembly phenomena of CdSe nanocrystals on aluminum surface have been studied by TEM techniques. We used AFM to investigate the surface morphologies of self-assembled CdSe layer. From AFM image in figure 4 we can obtain that the average height of the nanocrystals bound to aluminum is ~5 nm which is consistent with the lateral size determined from HRTEM micrographs. It means that a monolayer of CdSe nanocrystsls were assembled on aluminum surface.

CONCLUSION

In conclusion, monodispersed semiconductor CdSe nanocrystals were made in inverse micellar solution and then assembled to aluminum surface by bifunctional linker molecules of mercaptoacetic acid. The studies of HRTEM, ED and AFM confirmed the formation of homogeneous monolayer of CdSe nanocrystals with hexagonal close-packed structure on aluminum surface.

Acknowledgment

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