Composite Nano-structured Materials Consisting of CdS Clusters and Heteropolyanions $PW_{12}O_{40}{}^{3-}$

Degang Fu* and Yu Zhang
Key Laboratory of Molecular and Biomolecular Electronics of Ministry of Education, Southeast University, Nanjing 210096, P. R. China

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Composite nanocrystal materials $CdS/PW_{12}O_{40}{}^{3-}$ with an ordered structure formed by CdS clusters surrounded with dispersed $PW_{12}O_{40}{}^{3-}$anions were synthesized. The material has of a long period about 6.6 nm in agreement with the size sum of individual CdS cluster and $PW_{12}O_{40}{}^{3-}$ anion.

Cadmium sulfide has been widely used in the optoelectronic application since the 1950's. Because of its relatively broad energy gap (about 2.5 eV), pure and doped CdS nanocrystals are often used as photoconductor, as light emitter in the green region, and as solar cells and photocells.[1–3] On the other hand, the compounds of heteropolyanions also have many applications, such as catalysis in oxidation, alkylation, and hydrosulfurization reactions.[4,5] Heteropolyanions have several interesting properties. First, their redox properties could be easily adjusted by changing their composition. Second, their structure can be maintained even after receiving or losing several electrons. Furthermore, heteropolyanions are stable and can be used in solution or as solid materials. The reversible oxidation-reduction of heteropolyanions with no change in structures would be very attractive in electrochemical sensor and solar energy transfer devices.[6,7] Here, we report the synthesis of a new composite compounds of CdS nanoparticles with inorganic heteropolyanion $PW_{12}O_{40}{}^{3-}$ using a very simply and convenient process. It was found that the material contains oriented rod-like structures constructed by positively charged CdS clusters and $PW_{12}O_{40}{}^{3-}$ anions.

$CdS/PW_{12}O_{40}{}^{3-}$ hydrosol was prepared by mixing $Cd_3(PW_{12}O_{40})_2$ and Na_2S at 4 °C under stirring, the molar ratio of Cd^{2+}: S^{2-} being 10:7. The initial concentration of the CdS colloid was 4.12×10^{-4} M. In a typical experiment, 250 mL colloidal solution was carefully evaporated to 50 mL at 60 °C and then cooled to room temperature. The concentrated solution was centrifuged at the speed of 5×10^3 rpm. The upper solution was decanted out. The precipitation was dissolved with 20 mL hot water, then concentrated to 5 mL, cooled down to room temperature and centrifuged again. This operation was repeated three times to remove excess $PW_{12}O_{40}{}^{3-}$, Cd^{2+} and Na^+ ions. After washing three times, the concentrated solution was dried in vacuum. After sufficient evaporation of water, light brownred crystal-like solid films were formed.

TEM (Transmission Electron Microscopy) images of the colloidal solution evaporated on a carbon-coated, 300 mesh copper TEM grid were recorded on JEOL 2000-EX operating at 160 kV. The observation from TEM image shows that the nanoparticles with mean diameter of about 5 nm are linked into strips. The electronic diffraction pattern ($d_{111} = 3.25$ Å, $d_{220} = 2.00$ Å, $d_{311} = 1.70$ Å) indicated that the nanoparticles were CdS clusters with cubic zinc blende structure the same as found by previous authors.[8]

In the solid state, heteropolyanion compounds are ionic crystal.[9] $PW_{12}O_{40}{}^{3-}$ anion with large volume (about 1 nm in diameter) and charge, has the so-called Keggin structure which is relatively unaffected by its surrounding.[10,11] During the synthesis of the colloid, surface of CdS nanoparticles generally become Cd^{2+}-rich. As a result, $PW_{12}O_{40}{}^{3-}$ anions were surrounding CdS particles by electrostatic interactions. Because of the electrostatic repelling and the relatively large volume of $PW_{12}O_{40}{}^{3-}$ anions, $PW_{12}O_{40}{}^{3-}$ capped CdS nanoparticles may assembly with point-contacting mode to form linked 1D structures as shown by TEM image. The existence of $PW_{12}O_{40}{}^{3-}$ anions was verified by XPS (X-ray photoeletron spectroscopy) and infrared spectra of the powder sample of the crystal-like solids. XPS measurements were performed using a Britain VG ESCALAB MK-II electron spectrometer with Al Kα X-ray source of 300 W at pressures lower than 4×10^{-8} mbar. Considering the influence of charge up for semiconductor materials, all the XPS spectra were calibrated using the position of the C_{1s} peaks (285.0 eV) present in the spectra as a standard. The infrared spectra of the powder sample were recorded on a Nicolet 750 FT-IR spectrometer using KBr wafer. The infrared spectra of the sample indicate that the $PW_{12}O_{40}{}^{3-}$ anion still retains its Keggin structure while the XPS spectrum shows the peaks of CdS (Cd_{3d}:405.1 eV, S_{2p}:161.5 eV) and $PW_{12}O_{40}{}^{3-}$ (P_{2p}:133 eV, W_{4f}:35.7 eV,), and there is no characteristic peak of Na^+ at 1071.5 eV.

Earlier experiments with the compounds of $PW_{12}O_{40}{}^{3-}$ and its analogues showed that heteropolyanions can form ordered monolayers on highly oriented pyrolytic graphite.[12,13] or Ag surface.[15] The lattice constants of the monolayers vary with size of cations. To view the assembly behavior of composite $CdS/PW_{12}O_{40}{}^{3-}$ nanoparticles by AFM (Atomic Force Microscopy), we deposited one drop of the $CdS/PW_{12}O_{40}{}^{3-}$ hydrosol onto the mica sheet at 25 °C and then evaporated the solvent in air. The AFM images were obtained with NanoScope III (Digital Instruments) system in a constant force mode in air. Soft cantilevers are 200-μm long with an integrated pyramidal Si_3N_4 tip, exhibiting a spring constant of 0.12 N m^{-1}. Typical force was controlled on the order of 10 nN.

AFM images of the sample show that CdS nanoparticles are packed in an ordered pattern. They first assemble to form rod-like structures, and then the rods gather together along a direction. Much more interestingly such an oriented rod-like structure is also maintained on the crystal-like solid film as shown in Figure 1. The rods in 200 × 50-nm size were packaged in parallel mode to form an ordered structure. As we know, the stabilizer or surface capping reagent is very critical in the formation of ordered structures. In most organized structures of nanoparticles including 3D nanocrystals, organic agents such as trialkylphosphine oxide,[15] thiol,[16] quaternary ammonium salts,[17] and so on are usually used. Here, we have demonstrated that inorganic heteropolyanion can be used to form stable and ordered all inorganic nano-structures, which may be very useful in optoelcetronic application.

The structure of the CdS nanoparticles films was further characterized by XRD (X-ray diffraction). XRD experiments were done using a D/Max-RA rotating anode X-ray diffractometer with work voltage/current at 40 kV/150 mA. The diffractometer is equipped with a Kratky small angle diffraction device. Small angle diffraction experiment was performed with 2θ from 1 to 10°.

In the wide-angle region of XRD (Figure 2a) the CdS/$PW_{12}O_{40}{}^{3-}$ nanocrystallites exhibit three broad peaks ($d_{111} = 3.357$ Å, $d_{220} = 2.037$ Å, $d_{311} = 1.738$ Å), which were characteristic diffraction of CdS nanoparticles with cubic zinc-blend structures the same as that found from electron diffraction pattern of the sample. The broading of diffraction peaks includes several contributions such as the reduction of particle size and instrument function. The CdS mean diameter was estimated as 4 nm according to Scherrer's equation $D = k\lambda/(\beta\cos\theta)$.[18] The asymmetry of the peaks may arise from the size distribution of CdS nanoparticles.

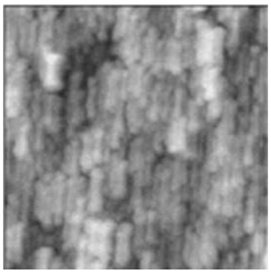

Figure 1. Surface AFM image of crystal-like solid film (size of area: 1 µm × 1 µm).

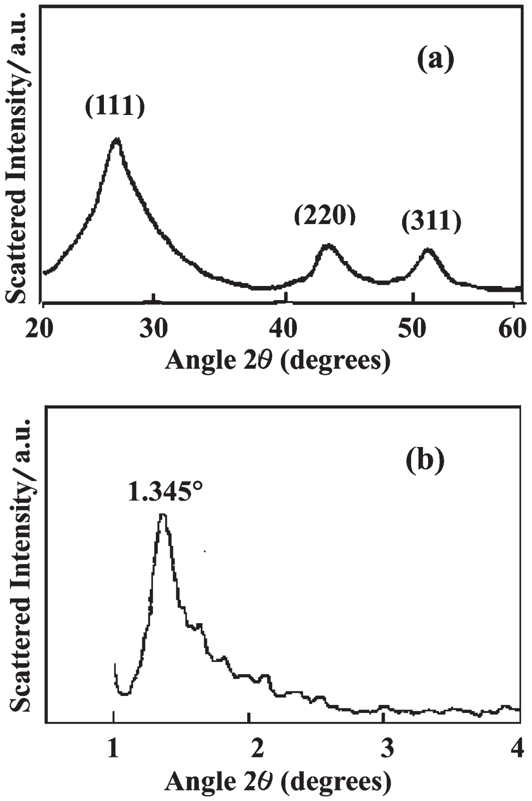

Figure 2. Powder X-ray diffraction pattern of crystal-like solid film: (a) wide angle, and (b) narrow angle region.

It should be noted that there is no diffraction peaks of heteropolyanion compounds in XRD spectra, indicating $PW_{12}O_{40}{}^{3-}$ anions dispersed in the crystal space formed by CdS nanoparticles. This fact agrees with the above suggestion that $PW_{12}O_{40}{}^{3-}$ anions absorbed around CdS nanoparticles. The oriented assembly of particles is revealed by small-angle XRD of the solid film (Figure 2b). A peak appears at 2θ of 1.3° means a long space period of 6.6 nm. This value is about the size sum of individual CdS cluster and $PW_{12}O_{40}{}^{3-}$ anion, reflecting that CdS nanoparticles and $PW_{12}O_{40}{}^{3-}$ anions have an ordered assembly along one direction in solid film.

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