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CdS nanodots preparation and crystallization in a polymeric colloidal nanoreactor and their characterizations

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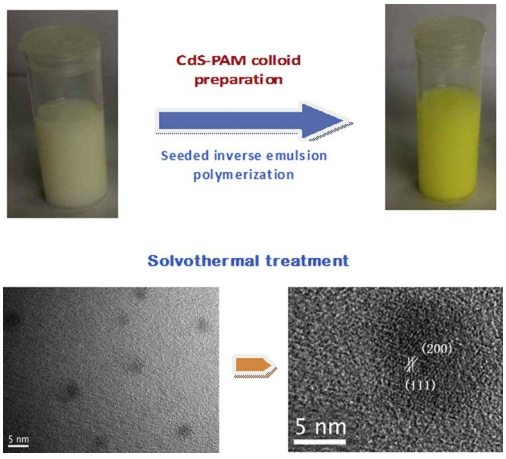
GRAPHICAL ABSTRACT



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ABSTRACT

Cadmium sulfide (CdS) nanodots in polymeric colloidal reactors were prepared by seeded inverse emulsion polymerization and then crystallized solvothermally. The cadmium sulfate ($CdSO_4$)-polyacrylamide (PAM) seeds were synthesized by inverse miniemulsion polymerization with $CdSO_4$ solution as a co-stabilizer. The prepared $CdSO_4$-PAM particles were used as polymeric colloidal reactors for the formation of CdS-PAM by feeding the mixed solution of sodium sulfide (Na_2S) and acrylamide. The effects of the feeding rate on the size, distribution and morphologies of particles were investigated. The influences of the solvothermal treating temperature and time on the crystallite size were characterized. The CdS was well formed and then crystallized in the PAM colloidal reactors. The crystals growth mechanism was taken under consideration. The crystallite size was calculated by the X-ray diffraction (XRD) data, and their morphologies were observed by transmission electron microscopy (TEM). The small CdS crystals showed a blue-shift on the spectra of ultraviolet visible absorption and fluorescence emission. The small CdS crystals displayed the desired property of photocatalytic degradation.

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1. Introduction

Cadmium sulfide (CdS) is a classic II−VI group semiconductor that is successfully applied in optics, electronics, photoelectron catalysis or transfer, infrared transmittance, among others [1–18]. There are many methods of CdS preparation, including sol-gel, vapor state processes, microemulsions, solid state reactions, precipitation, template method, and hydrothermal/solvothermal reactions [1–18].

Among these methods, microemulsion method refers to the isotropic and thermodynamically stable system with the action of surfactant, which can form well-distributed microemulsion particles as microreactors of tens nanometer size [3–6]. Wang et al synthesized monodisperse CdS particles by inverse microemulsion polymerization [3]. The particles prepared by microemulsion method have better dispersibility and better interfacial properties, but it has some disadvantages such as the excess demand for emulsifier and the harsh controlled conditions [3–6]. With the hydrothermal/solvothermal method, the crystal growth and self-assembly process is performed in the water/organic solvent at relatively high temperatures and pressures. The products have high crystallinity, high purity, and good dispersibility [6,7,16]. Jum et al prepared CdS nanowires by solvothermal method. But it is difficult to ensure the centralized distribution of the size of product [7]. Apart from above mentioned methods, the sol-gel method can be used for the preparation of many materials. But the material cost is high, and the reaction time is long. The product may have other residues, and there are many micropores in the gel [11,12]. Using the solid phase method, the material is difficult to mix evenly and the particles are easy to agglomerate [8]. Chemical deposition method can't control the crystal growth and growth rate of crystal nucleus; the prepared compounds are mostly polycrystalline or amorphous. The products prepared by template method are mostly polycrystalline materials, which limit the properties and applications of materials [13].

In order to reduce the shortcomings above, some emulsion polymerization methods are developed for nanocrystals synthesis, such as seeded emulsion polymerization and miniemulsion polymerization [19–27]. Liu et al used modified nano ZnO as seeds of microemulsion polymerization to prepare monodisperse core-shell ZnO/PS nanoparticles, which had the good UV absorption properties [19]. Two phases are dispersed evenly and the degree of phase separation is small, the initial rate of reactants can be controlled. The prepared nanocrystals have small size, regular morphology and narrow distribution. A miniemulsion is obtained by shearing a mixture comprising two immiscible liquid phases [21,22]. Cao et al prepared poly (HEMA, Hydroxyethyl methacrylate) latex particles from inverse HEMA miniemulsion polymerization and acted as nanoreactors. The Ag nanoparticles were formed in nanoreactors [23]. Wu et al prepared uniform size of PS/TiO_2 composite particles by miniemulsion polymerization [24].

In the present research, the CdS-polyacrylamide (PAM) nanoparticles are prepared by seeded inverse emulsion, and then nano CdS is crystallized solvothermally. Cadmium sulfate ($CdSO_4$)-PAM is synthesized by inverse miniemulsion polymerization to form the stable colloidal reactors. A mixed solution containing sodium sulfide (Na_2S, at equal molar quantity of $CdSO_4$) is diffused into colloidal reactor using a seeded inverse emulsion polymerization. CdS nanodots are formed by the reaction between $CdSO_4$ and Na_2S in PAM colloidal particles. The resultant CdS-PAM latex is incubated in a solvothermal vessel. The CdS crystallite size in the colloidal reactors can be controlled by using the different solvothermal treating temperature and time. The ($CdSO_4$)-PAM nanoparticles successfully act as colloidal reactors for the formation and crystallization of CdS. The ultraviolet visible absorption and fluorescence emission wavelength movement of the crystals are characterized. The effects of the solvothermal conditions on the growth mechanism of the crystals are investigated. Finally, the CdS crystals are used as a photocatalyst for dye degradation.

2. Experimental

2.1. Materials

Acrylamide (AM, 99.9% purity, monomer), $CdSO_4{\cdot}8/3H_2O$ and Na_2S (analytical purity) were purchased from the Chinese Medicine Group Chemical Reagent Co., Ltd. Ammonium peroxydisulfate (APS, initiator) and cyclohexane (analytical purity) were obtained from Wuxi Yatai Combined Reagent Co., Ltd, China. Methylthionine chloride and sorbitan oleate (Span-80, emulsifier) were purchased from J&K Scientific Chemical Co., Ltd. Dodecyl sodium sulfate (SDS, 95%) was purchased from Sigma-Aldrich, Inc (mainland). Distilled water was used in all experiments.

2.2. CdS-PAM nanoparticles formation and CdS crystallization

$CdSO_4$-PAM colloid were prepared by inverse miniemulsion polymerization. Typically, 0.40 g of $CdSO_4{\cdot}8/3H_2O$, 0.08 g of APS and 2.0 g of AM were dissolved at 8.0 g distilled water in the water phase; 1.60 g of the emulsifier Span-80 was dissolved at 50 g cyclohexane in the oil phase. The combination of water and oil phases was magnetically stirred for 15 min and then homogenized for 5 minutes (ultrasonic dispersion, 450 W, 85% amplitude) at a temperature of 5 °C. The obtained $CdSO_4$-AM miniemulsion and magnetic stirrer were poured into a 100 mL glass reactor and sealed. The sealed glass reactor was heated with a water bath and continuously stirred. In the reactor, the inverse miniemulsion polymerization was executed at 65 °C for 240 min. The final AM conversion was approximately 99% by residual monomer measurement (Gas chromatography method, GB/T12005.5-1989).

CdS-PAM colloid were prepared using seeded inverse emulsion polymerization. Based on the $CdSO_4$-PAM seeds prepared above, the mixed solution of 0.12 g Na_2S and 0.30 g AM dissolved in 2.00 g distilled water was fed into $CdSO_4$-PAM latex in batch or at fixed rates by the micro injection pump. After completing feed, the seeded emulsion polymerization was continuously carried out at 65 °C for 2 h. Thus, the CdS-PAM nanoparticles were obtained.

CdS crystallization was solvothermally treated in the next experiment. The CdS-PAM latex was transferred into a 100 mL Teflon lined autoclave. The solvothermal temperature was set at either 80, 100 or 120 °C, and the autoclave was heated for either 6, 12 or 24 h. After the solvothermal treatment was completed, the solvothermally treated CdS-PAM samples were cooled to room temperature.

The post-treating CdS-PAM nanoparticles process was as follows: The CdS-PAM colloid was separated by a high-speed centrifuge for 5 min; the bottom material was washed with warm cyclohexane and finally dried overnight at room temperature. The CdS nanoparticles were obtained for UV–vis absorption, XRD measurements and photocatalyst.

2.3. Characterization

2.3.1. Dynamic light scattering (DLS)

A laser particle size analyzer (DLS, Malvern 2000, British) was used to measure the size of the miniemulsion droplets or latex particles (volume-average diameter, D_v and z-average diameter, D_z) and their distribution (*PDI* intensity) at 25 °C.

2.3.2. Transmission electron microscopy

Transmission electron microscopy (TEM, JEM-2100, Japan), high-resolution transmission electron microscopy (HR-TEM, JEM-2100) and selected area electron diffraction (SAED) were used to observe the nanoparticles morphology and crystalline phase, respectively.

2.3.3. UV–vis absorption

The weighted CdS nanoparticles (0.001 g) were dispersed in 3 mL SDS aqueous solution (0.1% weight percent). The UV–vis absorption