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LETTER

# Thermoresponsive CdS@PNIPAM core–shell nanocomposite

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Design and synthesis of core–shell nanocomposites, with a shell of an organic material coating an inorganic nanocrystal core, have been thoroughly investigated due to their prospective applications in many fields, such as catalysis, photonics, electronics, optics, and biomedicine [1–6]. In the past decade, tremendous research efforts have been devoted to design nanoparticles with the surface coating layer sensitive to external stimuli, such as ionic strength, light, temperature, and pH value [7–10]. Poly(*N*-isopropylacrylamide) (PNIPAM) is a well-known thermo-sensitive polymer, exhibiting a lower critical solution temperature (LCST) at about 32 °C in water, and it is one of the most studied smart polymers to modify nanoparticles [11–13].

Generally, there are two approaches to covalently attach polymer chains to a solid surface. One is a "grafting to" method in which end-functionalized polymers are adsorbed onto the nanoparticles surface after polymerization. The other is a "grafting from" method, which usually involves the immobilizing of initiators onto the nanoparticles surface followed by in situ surface-initiated polymerization to obtain nanocomposites coated with polymer [14–16]. The route is practicable for the polymerization reaction of various monomers without any specific functional groups, which is required in the "grafting to" method. Up to now, many strategies have been developed to obtain thermoresponsive core–shell nanocomposite materials consisting of a core and a thermoresponsive PNIPAM shell based on the "grafting from" method [17–19].

For the "grafting from" method to prepare nanocomposite materials containing PNIPAM shell, it is pre-requisite to make use of the interaction between the inorganic nanocrystals (NCs) surface and the functional groups of organic molecules, such as silica particles and a silane coupling agent. Because of the ease of subsequent modification with silane to seed the radical polymerization of *N*-isopropylacrylamide (NIPAM), inorganic/PNIPAM core–shell nanostructures containing silica particles or silica-coated particles (such as metal, metal oxide) as cores have been most extensively studied [6, 18, 20]. However, the practical applications of the method have been seriously restricted for the toxicity, economy, and instability of silane. Furthermore, a layer of silica itself, formed between the metal oxide or metal core and PNIPAM shell, is chemical inert and has no any significance on the property and structure of nanocomposite. Thus, more general approach for the encapsulation of inorganic nanoparticles with thermoresponsive PNIPAM remains a difficult challenge for materials scientists, which may be critical for the tuning of properties of these core–shell nanomaterials.

Herein, we report a facile two-step route to prepare CdS@PNIPAM core–shell nanocomposite. Microemulsion system can be devised properly to synthesize a large variety of nanocrystals with different chemistries and properties and with low dispersity [4, 5, 21]. In our first step, nearly monodispersed CdS NCs with hydrophobic organic molecules absorbed on the surface were obtained in a microemulsion system under solvothermal condition. In the second step, Reversible addition and fragmentation transfer (RAFT) agent molecules were absorbed on the CdS NCs surface by ligand-exchange process followed by

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**Fig. 1** Dispersity of CdS nanoparticles in cyclohexane (*left*) and ethanol (*right*)

polymerization reaction. The polymerization was restricted on the surface of CdS NCs and core–shell nanostructures with CdS core and thermoresponsive PNIPAM shell have been synthesized through in situ polymerization method. TEM results show that the as-prepared CdS nanoparticles are nearly monodisperse and the thickness of PNIPAM layer is relatively uniform.

In a typical process to prepare CdS NCs, 10 mL water, 10 mL $C_2H_5OH$, 3 mL OA ($C_{17}H_{33}COOH$), and 100 mg NaOH were mixed together to form a transparent microemulsion. Then, 0.2 mmol $CdCl_2$ dissolved in 5 mL deionized water was added to the solution by stirring, getting an ivory-white latex emulsion soon. After 0.5 h of stirring, 0.3 mmol sulfur powder was added to above solution. The mixture was agitated for about 20 min and then transferred into a 45-mL autoclave, sealed, and heated at 160 °C for about 12 h. Then it was allowed to cool to room temperature naturally. The resulting bottom precipitates can be well dispersed in a nonpolar solvent (cyclohexane, chloroform, etc.) and then precipitated in a polar solvent (acetone, ethanol, etc.), as shown in Fig. 1.

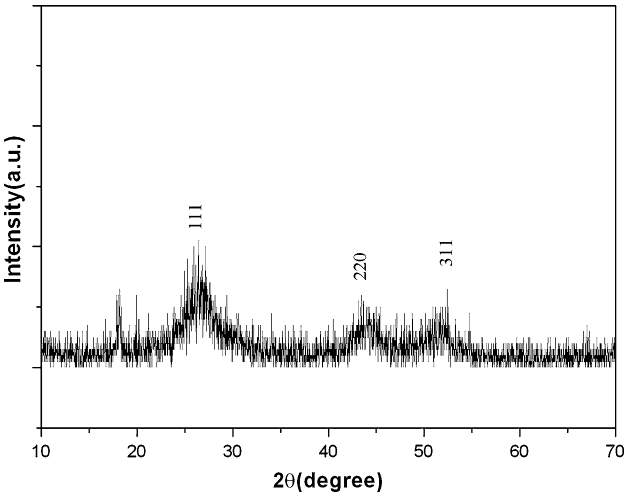


**Fig. 2** XRD patterns of CdS NCs

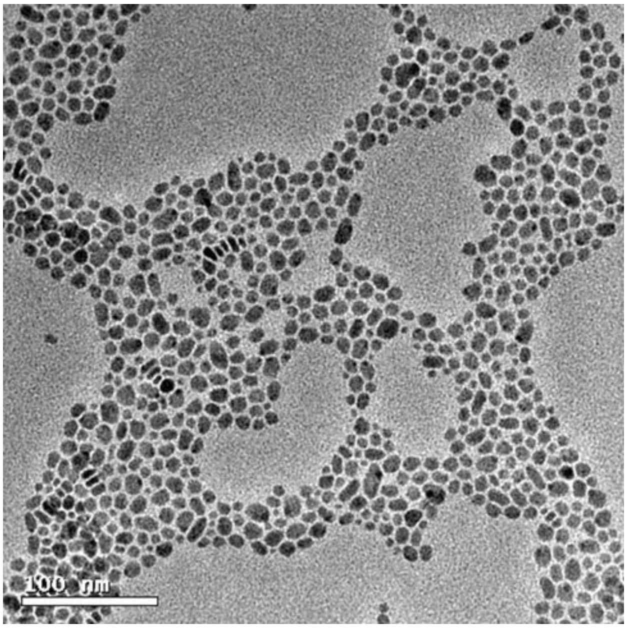


**Fig. 3** TEM image of CdS nanoparticles

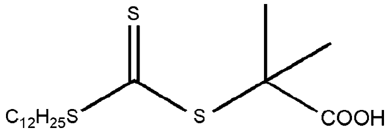
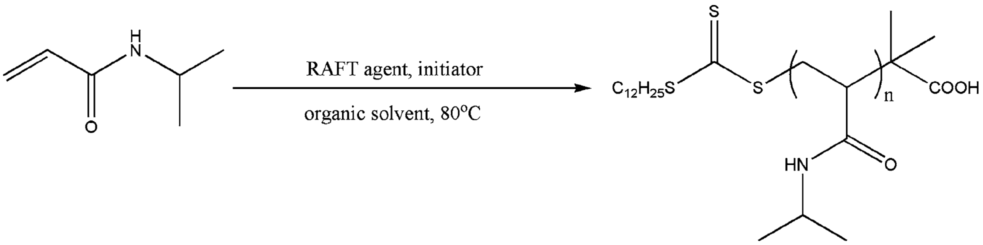


**Fig. 4** Scheme of the structure of the RAFT agent, *S*-1-dodecyl-*S*′-(α,α′-dimethyl-α″-acetic acid)trithiocarbonate

The as-obtained yellow precipitates were added into 50 mL cyclohexane and agitated for 12 h under ice-bath condition. The solution was then centrifuged at 4500 rpm for 30 min and the supernate was decanted. The precipitate was re-dispersed in 1.5 mL DMF containing 10 mg *S*-1-dodecyl-*S*′-(α,α′-dimethyl-α″-acetic acid) trithiocarbonate [22] followed by agitation for several days to get a transparent yellow solution. The DMF solution was then centrifuged at 2000 rpm for 5 min and the supernate was transferred a polymerization tube followed by adding *N*-isopropylacrylamide (NIPAM) (1.0 g) and azobis(isobutyronitrile) (AIBN) (1.0 mg). The tube was sealed under vacuum and placed in a thermostatted oil bath at 80 °C for 24 h. The reaction was stopped by opening the

**Fig. 5** RAFT polymerization reaction of PNIPAM



polymerization tube to air and cooled by ice bath. Then, the reaction solution was diluted with methanol and the resulting product was obtained by centrifuging in methanol (4500 rpm) for three times. Free PNIPAM is soluble in methanol and can be removed. The resulted products were dried under vacuum for 12 h at room temperature.

The crystalline phases of the CdS NCs were determined by X-ray powder diffraction (XRPD) by a Bruker D8 Advanced diffractometer with Cu K$\alpha$ radiation ($\lambda = 1.5416$ Å). The size and morphology of the CdS NCs were determined at 200 kV by a Hitachi H-800 transmission electron microscope (TEM).

Figure 2 shows the XRD pattern of the as-obtained precipitate in ethanol. All the reflection peaks of the XRD patterns can be readily indexed to a pure cubic phase of CdS with lattice constants $a = 5.82$ Å [space group $F\bar{4}3m$/ (216)] (JCPDS No. 02-0454). The $2\theta$ peaks at values of 26.5°, 43.9°, and 51.9° correspond to the crystal planes of [111], [220], and [311] of the crystalline CdS species, respectively.

The sizes and morphologies of CdS NCs were determined by low-resolution TEM. As shown in Fig. 3, the sample on the TEM grid shows morphologies of well-dispersed nanoparticles of approximately 15 nm.

Similar to our previously study [22], the $C_{17}H_{33}COO^-$ units absorbed on the surface of the nanocrystallites with the alkyl chains on the outside, through which the produced inorganic nanoparticles will gain hydrophobic surfaces. In our experiments, the as-prepared CdS NCs dispersed in cyclohexane easily and precipitated spontaneously from it after a long period of agitation due to the leaving of $C_{17}H_{33}COO^-$ units.

In the next procedure, CdS NCs were dispersed in DMF solution containing *S*-1-dodecyl-*S*′-($\alpha$,$\alpha'$-dimethyl-$\alpha''$-acetic acid) trithiocarbonate and the latter absorbed onto the CdS NCs surface via coordination interaction between the CdS NCs and carboxyl group (the structural formula of RAFT agent is shown in Fig. 4).

RAFT polymerization is widely used to prepare thermoresponsive PNIPAM among many synthetic methods, as shown in Fig. 5, in which *S*-1-dodecyl-*S*′-($\alpha$,$\alpha'$-dimethyl-$\alpha''$-acetic acid) trithiocarbonate and AIBN were chosen as RAFT agent and initiator agent, respectively. In our experimental system, the polymerization reaction were restricted within the surface of CdS NCs for the fact that RAFT agent necessarily to polymerization only existed outside the CdS NCs, thus formed core–shell nanocomposite with a shell of PNIPAM coating CdS NCs core.

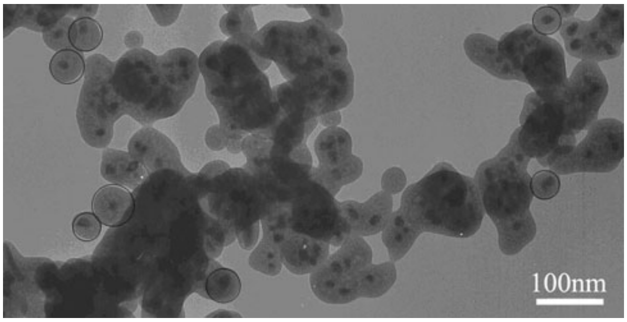


**Fig. 6** TEM image of CdS@PNIPAM nanocomposite

The morphologies of nanocomposite were investigated by low-resolution TEM. As shown in Fig. 6, the sample on the TEM grid shows clearly the CdS@PNIPAM core–shell nanostructures and each CdS NC was coated with a layer of PNIPAM with thickness of 25–30 nm which confirmed that the polymerization did happen within the confines of the surfaces of CdS NCs.

The thermal response of CdS@PNIPAM core–shell nanocomposite is simply illuminated in Fig. 7, wherein the colloidal suspension is transparent at 20 °C and becomes opaque at 32 °C. It should be noted that the opaque suspension does not precipitate due to the hydrophilic PNIPAM, which enhances the stability of the suspension. We suppose that the thermoresponsive CdS@PNIPAM core–shell nanocomposite may have potential application, for example, acting as a responsive catalyst.

In conclusion, we have demonstrated a facile way to synthesis CdS@PNIPAM core–shell nanocomposite. The polymerization was restricted on the surface of CdS NCs and CdS NCs coated with PNIPAM can be obtained. Furthermore, the good dispersity of CdS NCs in DMF avoided effectively the agglomerization during the polymerization process. The experimental results were supported by TEM and XRD in various aspects. We expect that this facile synthetic route to CdS@PNIPAM nanocomposite may be extended to the synthesis of other

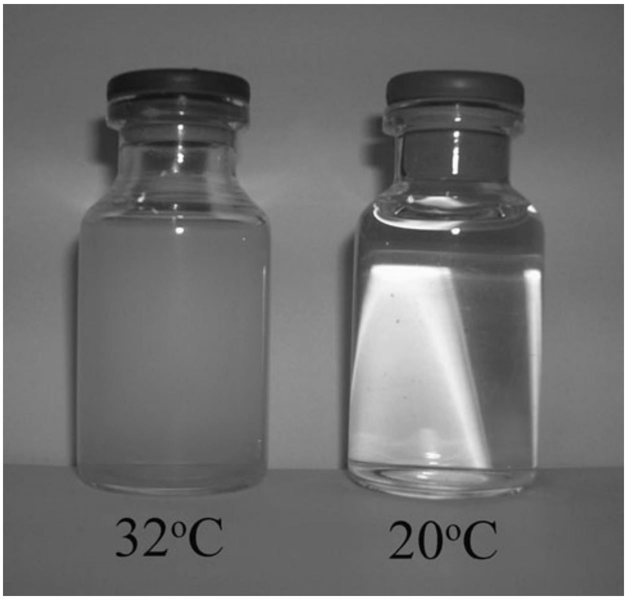


**Fig. 7** Thermoresponsive performance of CdS@PNIPAM nanocomposite in water

core–shell nanostructures with PNIPAM as shell and other inorganic materials as cores.

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