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HISTIDINE ASSISTED SYNTHESIS OF CdS HIERARCHICAL NANOSPHERES/CARBON NANOTUBES AND PHOTOCATALYTIC ACTIVITY

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A novel CdS hierarchical nanospheres with incorporated carbon nanotubes (CdS HNS/CNTs) were synthesized via biomolecule-assisted routes. The morphologies and structures were characterized by scanning electron microscopy, transmission electron microscope, X-ray diffraction, Fourier transform infrared spectra and UV-vis absorption spectroscopy. The results showed that CdS hierarchical nanospheres consisted of primary nanoparticles of about 10 nm in diameters and were indeed embedded with CNTs. The growth mechanism of CdS HNS/CNTs was proposed. Superior photocatalytic activity was observed for the CdS HNS/CNTs under visible light.

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1. Introduction

Photocatalytic has recently attracted a lot of attention [1] due to their potential in solve the environment crisis. With the band gap of 2.4 eV, CdS is among the most promising photocatalysts [2]. Usually, nanosized particles are expected to have high specific surface area, however, they are easily aggregated leading to reduction of the active surface area [3]. Hierarchical nanospheres, consisting of nanocrystals, combine the features of nanometer-scaled building blocks in one crystal and could overcome mentioned above disadvantage [4].

Many chemical methods for synthesis of hierarchical nanospheres have been demonstrated recently. For examples, Qu et al. describes an effective hydrothermal route for the synthesis of self-assembled CdS hierarchical nanospheres, which exhibited superior photocatalytic performance in photodegradation of eosin red [5]. As a new and environmentally friendly method, biomolecule-assisted routes for nanomaterials preparation have also attracted a lot of attention [6,7]. Amino acid contains multifunctional groups (such as, -SH, -NH_2, or -COO- group), which can promote the different morphology of metal sulfide nanoparticles by crosslinking between amino acids and disulfide bonds [8]. Apart from the other amino acids, L-Histidine has an imidazole side group, which can capture the metal ions from the solution and serve as a bio-compatible organic chelating agent [9]. Wang et al. reported a novel flower-like CdS nanostructure obtained via the L-Histidine-assisted method [10]. Hence, we believe that synthesis of CdS hierarchical nanospheres using L-Histidine-assisted routes should be successful as well.

Due to the fast charge carrier recombination, synthesis of stand-alone CdS nanoparticles is difficult [11]. Because of the unique tubular structure, high electrical conductivity and large surface areas, carbon nanotubes (CNTs) are ideal additives to promote charge separation in the nanocomposites [12-13]. Thus, synthesis of the hierarchical nanospheres integrated with carbon nanotubes is a logical step because CNTs as an electron acceptor can improve the charge separation in nanocomposites. To the best of our knowledge, there has been no reports on CdS

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hierarchical nanospheres integrated with CNTs obtained using a bio-compatible organic chelating agent L-Histidine.

In this paper, we developed an environmentally friendly strategy towards synthesis of composites consisting of CdS hierarchical nanospheres and carbon nanotubes using L-Histidine-assisted routes. L-Histidine chelates the metal ions and promotes the incorporation of hierarchical nanospheres with CNTs. The as-prepared nanocomposites showed excellent activity for visible light induced degradation of methyl orange (MO) dye.

2. Experimental details

For the synthesis of CdS HNS/CNTs 4 mmol of cadmium diacetate $Cd(AC)_2{\cdot}2H_2O$ (obtained from Sinopharm Chemical Reagent Co.) was dissolved in 50 ml deionized water. After that 10 mmol of L-Histidine was added followed by 0.02 g of acid-treated CNTs. The mixture was then stirred for 30 min. Finally, 4 mmol of thioacetamide (TAA, Sinopharm Chemical Reagent Co., Ltd.) was dissolved in the above solution. After stirring for another 30 min, the blended suspension was heated for 60 min in the microwave. The obtained precipitates were centrifuged, washed with water several times and dried under vacuum at 60 ℃ for 2 h. For comparative study, CdS hierarchical nanospheres (CdS HNS) were prepared using the same method but without the addition of CNTs. CdS nanoparticles were obtained using $Cd(AC)_2{\cdot}2H_2O$ and thioacetamide as precursors which were reacted in the water.

Samples were characterized by X-Ray diffraction (XRD), Scanning electron microscopy (SEM), transmission electron microscope (TEM), Fourier transform infrared spectra (FTIR) and UV-Vis diffused reflectance spectra.

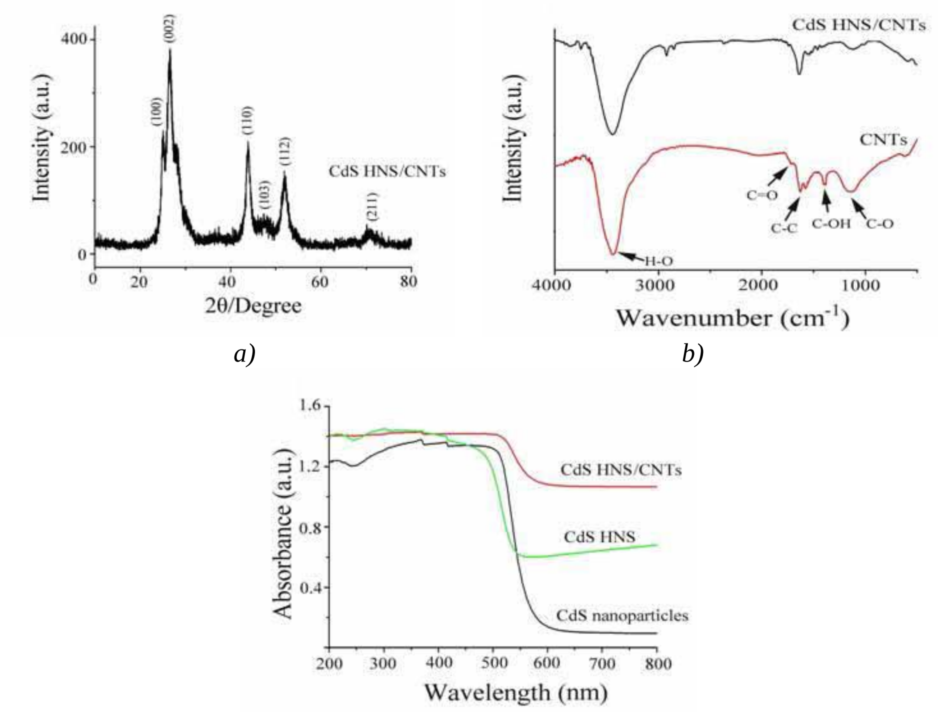
The photocatalytic performance of the samples was investigated under visible-light irradiation at room temperature. In a typical process, 50 mg of the composites and 100 mL of 5 mg/L MO solution were stirred together in a dark room for 30 min. Then the container with the solution was irradiated by a 300 W Xe lamp. The solution was sampled every 20 minutes and analyzed by UV-vis spectrophotometer.

3. Results and discussion

Fig. 1a displayed the XRD patterns of the CdS HNS/CNTs and the diffraction peaks located at 25.0°, 26.6°, 43.9°, 48.3°, 51.9°, and 70.1° were assigned to the (100), (002), (110), (103), (112) and (211) crystal planes of the CdS wurtzite phase (JCPDS No. 41-1049). The well-resolved broad diffraction peaks indicated the small CdS nanoparticles in the nanocomposites [14]. The small grain of CdS nanoparticles was due to the presence of the chelating agent L-Histidine, which captured the Cd ions from the blended solution and prevented the growth of the larger nanocrystals [10]. In addition, no characteristic peaks of the CNTs could be seen indicating good dispersion of CNTs in the nanocomposites [15]. Small CdS nanocrystals with the well-dispersed CNTs around them were very favorable for the transfer of photogenerated electron-hole pairs [15].

Fig. 1b showed the FTIR spectra of CNTs and CdS HNS/CNTs. For CNTs, it showed bands associated with C=O bond at 1713 cm^{-1}, C=C bond at 1633 cm^{-1}, C-OH bond at 1385 cm^{-1} and C-O bonds around 1124-1025 cm^{-1}. The peak at 3432 cm^{-1} could be assigned to the vibrations of the adsorbed water molecules [16]. Very weak peak intensity of the functional groups indicated that CdS nanocrystal hindered most of the functional groups at the CNTs surface, indicating the strong interaction between CdS and the groups [17]. A characteristic peak of Cd-S bending vibration at 567 cm^{-1} was observed. Thus, we conclude a strong interaction between the CNTs and CdS nanoparticles [18].

The diffuse reflectance UV-vis spectra of CdS nanoparticles, CdS HNS and CdS HNS/CNTs hybrid particles are presented in Fig. 1c. As expected, CdS nanoparticles showed the characteristic spectrum with the sharp absorption edge rising at 550 nm. After the formation of CdS HNS, the weak light absorption in the visible light range was enhanced indicating the smaller band gap for CdS grown with the L-Histidine assistance and more efficient utilization of visible light[15]. With the CNTs embedded, the light absorption range of the CdS HNS/CNTs composite expanded to a wider light region indicating that CNTs modified the surface of CdS and increased the surface electric charge in the hybrid catalysts [19]. Thus, combination of CNTs and CdS HNS might have a synergetic photocatalytic effect forming electron-hole pair in the visible light.

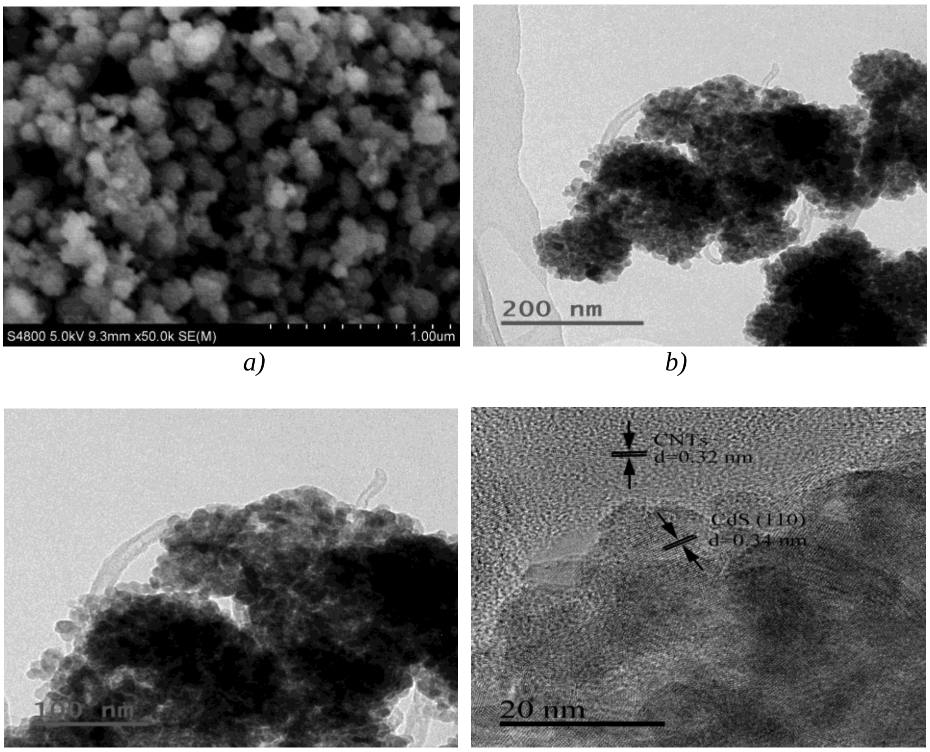


a) *b)*

c)

Fig.1.(a)XRD, (b)FTIR spectra, (c) UV-visible diffused reflectance spectraof the samples.

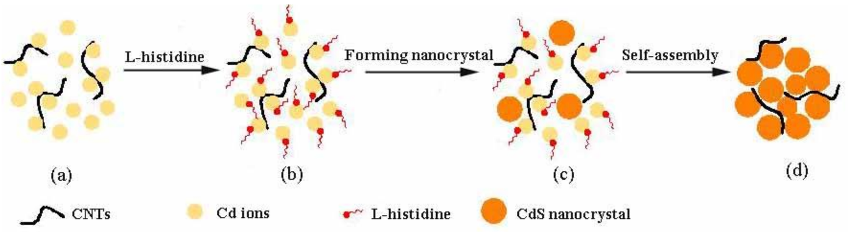
Fig. 2 displayed the SEM, TEM and HRTEM image of CdS HNS/CNTs nanocomposites. As can be seen from Fig. 2a, CdS HNS/CNTs had a homogeneous spherical structure with ~100-200 nm diameter. The CNTs were coated with well-dispersed CdS nanospheres indicating a good contact between CNTs and CdS. The representative TEM images of CdS nanospheres (Fig. 2b) showed hierarchical structures consisting of agglomerated nanocrystals with entangled CNTs on their surfaces (Fig. 2c). Some of CNTs were implanted within these nanospheres (as arrows in Fig. 2c): one side of CNTs were embedded inside the nanospheres and the other side were exposed to the surface. Fig. 2d shows an HRTEM image of the hybrid showing CNTs with diameters ~15-30 nm and thicker nanotubular morphology. Distances between adjacent lattice plane were 0.32 nm and 0.34 nm and could be assigned to the (110) facets of CdS and graphite, respectively.



a) *b)*

c) *d)*

Fig.2.(a)(b) SEM, (c)(d)TEM, (e)HRTEM images ofCdS HNS/CNTs.



Scheme 1. Schematic of the growth process of CdS HNS/CNTs.

Based on these results, we propose a formation mechanism of CdS HNS/CNTs (see Scheme 1). First, Cd ions were dissolved and CNTs were uniformly distributed in the solution (Scheme 1a). After the addition of L-Histidine, the imidazole rings of L-Histidine captured Cd ions to form Cd (II) bis-hitidinato complex (Scheme 1b) preventing release of active Cd^{2+} into the solution [10]. During the microwave heating, some of the cadmium ions were released forming small amount of CdS nanocrystals [20]. Gradually, more and more cadmium ions were slowly released into the solution forming abundance of CdS nanocrystals (Scheme 1c). Nitrogen atom in the imidazol ring of L-Histidine could form hydrogen-bond interaction between CdS nanocrystal and hierarchical nanospheres, thus assisting in this self-assemble [21]. CNTs imbedded themselves into these hierarchical nanospheres (Scheme 1d).

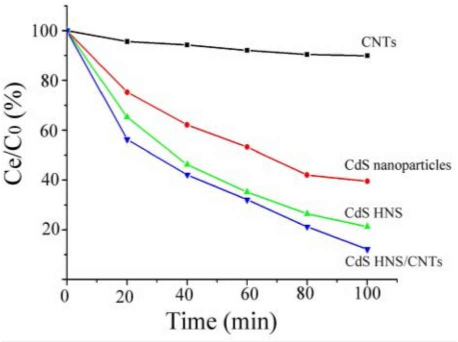
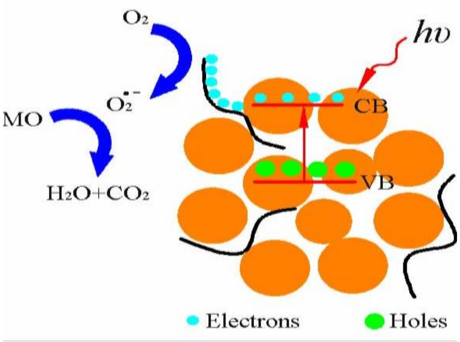


Fig. 3. Photocatalytic degradation efficiency of MO under visible-light.

The activities of different photocatalysts were measured by the photodegradation of MO in aqueous solution under visible light irradiation. As can be seen, CNTs has negligible photocatalytic activity. However, MO was degraded by the other three nanocomposites: CdS nanoparticles, CdS HNS and CdS HNS/CNTs. Among these, CdS HNS/CNTs showed the highest photodegradation activity. First possible explanation for this phenomenon is that hierarchical nanospheres could work as efficient photo-semiconductors because of their highly reactive surface. The second explanation is that CNTs act as ideal catalysts and facilitate charge transfer suppressing recombination of electron-hole pairs [22].



Scheme 2. The proposed mechanism of MO degradation.

The catalytic process of CdS HNS/CNTs is schematically presented in Scheme 2. Under visible illumination, electrons are excited from the valence band (VB) to the conduction band (CB) but due to the rapid electrons-holes recombination it does not leads to a high photocatalytic performance [23]. When CNTs are imbedded into the CdS HNS, the excited electrons can be shuttled into the CNTs, resulting in an effective charge separation in the nanocomposites. These excited electrons can react with oxygen yielding hydroxyl radical that could oxidize MO directly [24].

4. Conclusions

We demonstrated a novel environmentally friendly method to fabricate CdS HNS/CNTs nanocomposites using L-Histidine as a chelating agent. The growth mechanism of CdS HNS/CNTs was proposed. The imidazole ring of L-Histidine has a high affinity to Cd ions, which helps CdS nanocrystal formation. CdS nanocrystals self-assembled into the hierarchical nanospheres integrated with CNTs. Combination of CdS HNS and CNTs in one nanostructure had a synergistic effect on the degradation of MO under visible light. The CdS hierarchical nanospheres provided enough active sites so the CNTs could act as an electron transfer channel.

Acknowledgment

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