Research Article


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Sodium montmorillonite (MMT) was chosen as the carrier; a serial of CdS/TiO$_2$-MMT nanocomposites with enhanced visible-light absorption ability was prepared by hydrothermal synthesis method combination with semiconductor compound modification method. The samples are characterized by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and ultraviolet-visible (UV-Vis) spectroscopy; the results showed that TiO$_2$ and CdS nanoparticles were loaded on the surface of montmorillonite uniformly. $N_2$ adsorption-desorption experiment showed that the specific surface area of TiO$_2$/montmorillonite nanocomposite made by this method can reach 200 m$^2$/g and pore-size distribution was from 4 to 6 nm; UV-Vis showed that the recombination of CdS and TiO$_2$ enhanced visible-light absorption ability of samples of TiO$_2$/montmorillonite and visible-light absorption ability increase with the increased of the adsorption of CdS.

1. Introduction

The bentonite is a kind of clay mineral mainly consisting of montmorillonite (MMT); the crystal structure of MMT is 2:1 layered silicates [1]. Pillared clay is a new mineral that used the high temperature resistant pillared agent with positively charged replaced the exchangeable positive ions in the montmorillonite, bridging the crystal structure of 2:1 layered silicates and put them open, and formed a kind of “layered and columnar” structure of two-dimensional passage [2]. Ti-pillared clay (Ti-PILC) has pore structure, large specific surface area, and thermal stability. Therefore, they are being used in many applications such as the preparation of catalyst, catalyst carrier, molecular sieve, adsorbent, environmental protection material, ion exchanger, conductive material, storage material, and nanocomposites [3–5].

At present, the preparation methods of TiO$_2$ pillared clay are Ti inorganic salt hydrolysis [6] or Sol-Gel method of Ti alkoxides [1]. But the particle size of hydrated titanium ion gel particles [TiO(OH)$_X$]$_n$ is only 1-2 nm, which is precursor of titanium oxide particles by the traditional method. The photocatalytic efficiency is relatively low; most of interlayer pores are micropores that hinder the contact between the substrate and catalyst for undersized titanium oxide between Montmorillonite interlayer. Next, the band gap of TiO$_2$ is wider (E$_g$ = 3.2 eV) and the efficiency of water used is low for it only can be excited at near ultraviolet, in which the wavelength is equal to or less than 387 nm in the sunlight.

The structure of Ti-pillared montmorillonite, which is prepared by hydrothermal synthesis method, is exfoliated. Which make some TiO$_2$ particles adsorb on the surface of montmorillonite enhanced visible-light absorption ability of the Ti pillared montmorillonite by using semiconductor CdS that has visible-light absorption ability as a photosensitizer, to improve the visible-light catalytic ability of composite catalyst.

2. Experiment

2.1. Material

2.1.1. Samples Purchased. Natural MMT with the purity 98% is supplied from Zhejiang Sanding Co., Ltd., China. TiCl$_4$, HCl, ethyl alcohol, and other chemical agents are purchased from Beijing Chemical Reagent Co., Ltd. And all the reagents used in the experiment were of analytical reagent grade.
Table 1: Specific surface area of CdS/TiO₂-MMT.

<table>
<thead>
<tr>
<th>Sample</th>
<th>BET specific surface area (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CdS-MMT</td>
<td>40.7789</td>
</tr>
<tr>
<td>CdS/TiO₂-MMT-0.5</td>
<td>212.1027</td>
</tr>
<tr>
<td>CdS/TiO₂-MMT-1.0</td>
<td>203.5253</td>
</tr>
<tr>
<td>CdS/TiO₂-MMT-2.0</td>
<td>198.4932</td>
</tr>
<tr>
<td>CdS/TiO₂-MMT-4.0</td>
<td>173.7505</td>
</tr>
</tbody>
</table>

2.1.2. Preparation of Ti Pillared Montmorillonite. TiCl₄ was put into 6 mol/L HCl aqueous solution gradually; dilute the solution to Ti pillared solution ([Ti] = 0.82 mol/L, [HCl] = 0.74 mol/L), aged for 96 h. Next, Ti pillared solution was put into 0.2% (mass fraction) sodium montmorillonite suspension according to the molarity of Ti in clay 20 mmol/g. We washed the sample with deionized water until without Cl⁻ after aged for 16 h. Centrifugal separation, put the produced sample in to the aqueous solution and then put the solution into high pressure reactor, continuously hydrothermal treatment at 160°C for 72 h. At last, a denoted as TiO₂-MMT sample was obtained after being centrifuged and washed.

2.1.3. Preparation of CdS/TiO₂-MMT. The CdS precursor solution was obtained after CdAc₂·2H₂O and CS (NH₂)₂ (the ratio of moles is 1:2) dissolved in 20 mL deionized water and ultrasonic processing for 5 min. Subsequently, the intensive mixed solution of TiO₂-MMT and the above precursor solution with 60 mL deionized water were put into a 100 mL high pressure reactor. After hydrothermal treatment at 160°C for 12 h, the produced samples were filtered, washed with deionized water and absolute ethanol in turn, dried, ground and denoted by the names CdS/TiO₂-MMT-0.5, CdS/TiO₂-MMT-1, CdS/TiO₂-MMT-2, and CdS/TiO₂-MMT-4 according to different concentration of CdS.

2.2. Characterization. The X-ray powder diffraction (XRD) (D/MAX2000) was used to determine the crystallite size and identity of TiO₂ and CdS in the samples. The particle diameter was calculated by characteristic diffraction peaks. Nitrogen adsorption-desorption test used Model ASAP2400 physisorption apparatus by Micromeritics Instrument Co., Ltd., USA. Samples were calcined at 200°C for more than 4 h under vacuum 113 Pa. The surface areas of samples were determined by using BET equation (Table 1); the pore size distribution treated by using the BJH method, the surface element valence, and energy level of samples were characterized by X-ray photoelectron spectroscopy (XPS) in a Perkin-Elmer, USA. The instrument condition: Mg Ka (1253.6 eV) source is X-ray, power is 300.0 W, spot size is 0.8 mm², the vacuum is 6.67 × 10⁻⁷ Pa, pass energy is 187.0 eV and 23.5 eV, and the CIs (284.6 eV) is the internal marked standard. The UV-Vis diffuse reflectance spectra of samples in the 200–800 nm range were recorded using U-3010 UV-Vis spectrophotometer.

3. Results and Discussion

3.1. XRD Characterization of CdS/TiO₂-MMT. The structure of the CdS/TiO₂-MMT was investigated by using XRD, and the spectrums are shown in Figure 1 (wide angle) and Figure 2 (low angle). It can be seen in Figure 1 that the characteristic diffraction peaks for anatase at 2θ values 25.3°, 37.8°, 47.7°, and 54.9° are observed from the XRD patterns of all the samples. The peaks appear at 28.0°, 36.9°, 43.7°, and 51.8° due to the cubic CdS particles. In addition, with the increase of CdS/MMT’s concentration (mmol/g), the intensity of the peak was enhanced. These facts indicate that the CdS particles have been loaded on the surface of montmorillonite. The small angle XRD spectrums of Na-MMT and Ti-MMT are shown in Figure 2. No obvious peak can be seen in the small angle XRD spectrum of Ti-MMT. The structure of Ti-MMT is called “delaminated” [7]; in other words, it is the mixture of TiO₂ particles and Ti-pillared montmorillonite (Ti-PILC),
which has some TiO$_2$ in the interlayer while others on the surface of montmorillonite.

3.2. Absorption Analysis of CdS/TiO$_2$-MMT to N$_2$. The N$_2$ adsorption-desorption isotherm of CdS/TiO$_2$-MMT is illustrated in Figure 3. It can be inferred that CdS/TiO$_2$-MMT has a mesoporous structure due to the isotherm of CdS/TiO$_2$-MMT with a prolate shape particularly, which states that most of the mesoporous in CdS/TiO$_2$-MMT are formed by montmorillonite flake. As a consequence, CdS always gathers on the surface but difficulty enters into the interlayer of montmorillonite without titanium existing as the exchanger. When the reaction system obtains both titanium exchanger and cadmium sulfide precursor at the same time, it is easy for CdS to enter into the interlayer of montmorillonite because the titanium exchanger enlarges interlayer spacing of montmorillonite by squeezing into it. As a result, pillar structure mesoporous material with TiO$_2$ and CdS in the interlayer was obtained. As Figure 4 shows, the size of mesoporous in CdS/TiO$_2$-MMT is concentrated among 4–6 nm, which declared CdS/TiO$_2$-MMT with quite uniform mesoporous. It can be seen that the specific surface area decreases with the increase of CdS content, which may be a result of the mesoporous blocked with too much TiO$_2$ and CdS in the interlayer of montmorillonite being meanwhile too much TiO$_2$ and CdS gathered on the surface of montmorillonite perhaps is the other reason for the specific surface area reduction.

3.3. XPS Characterization of CdS/TiO$_2$-MMT. The XPS spectrums of Ti2p3(A), Cd3d5(B), and S2p(C) in CdS/TiO$_2$-MMT-2 are shown, respectively, in Figure 5, and the XPS spectrum patterns were measured with binding energy C1s = 284.8 eV as the internal marked standard. The existence of Ti, Cd and S in CdS/TiO$_2$-MMT-2 is illustrated in XPS spectrums. Firstly, the two peaks, which binding energy are respectively 458.99 eV and 464.80 eV, are attributed as Ti2p$_{3/2}$ and Ti2p$_{1/2}$ (Figure 5(a)); thus, the existence of Ti$^{4+}$ in TiO$_2$ is demonstrated. Secondly, the peaks of Cd3d5 can be seen at 405.30 eV and 412.20 eV (Figure 5(b)) suggesting Cd$^{2+}$ in CdS. Thirdly, it can be seen that the peaks of S2p at 169.2 eV, which are thought to be the peaks of S within CdS. All the evidence shows clearly that CdS exists in CdS/TiO$_2$-MMT sample.

3.4. UV-Vis Absorption of CdS/TiO$_2$-MMT. Figure 6 shows UV-vis absorption spectrums of the resulting CdS/TiO$_2$-MMT samples. The visible-light absorption of the sample is enhanced obviously with the increase of CdS internal load. The absorption edge is in accordance with TiO$_2$-MMT when lacking CdS. Then the absorption edge spectral shift to nearby 600 nm, in other words, accord with CdS-MMT. The reinforcement of visible-light absorption ability can contribute to the increase of visible-light catalytic activity of sample.

4. Conclusions
CdS/TiO$_2$-MMT nanocomposite was prepared with the hydrothermal synthesis method, in which sodium montmorillonite was used as carrier and visible-light catalytic semiconductor CdS was used as photosensitizer. Both TiO$_2$ and CdS had been loaded on the surface of montmorillonite, which is demonstrated by the results of experiments. In the reaction system, with the increase of precursor CdAc$_2$·2H$_2$O, the CdS supported on the surface of montmorillonite is added; meanwhile the absorption edge of CdS/TiO$_2$-MMT shift’s to the direction of visible-light that enhanced the visible light absorption ability of CdS/TiO$_2$-MMT.
Figure 5: The XPS spectrums of Ti2p3 (a), Cd3d5 (b), and S2p (c) in CdS/TiO2-MMT-2.

Figure 6: Ultraviolet visible-light absorption ability of CdS/TiO2-MMT.

Disclosure

We confirm that the paper is authors owned work, and is original and unpublished, and is not being considered for publication elsewhere.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

References


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