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Uniformly dispersed CdS nanoparticles sensitized TiO_2 nanotube arrays with enhanced visible-light photocatalytic activity and stability

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ABSTRACT

In this study, TiO_2 nanotube arrays (TiO_2-NTs) with various intertube spaces were fabricated in the electrolyte with different water contents and the CdS nanoparticles (CdS NPs) were further deposited onto the TiO_2-NTs as a sensitizer via a sequential chemical bath deposition (S-CBD) method. The FE-SEM, TEM, XRD and XPS results demonstrated that the CdS NPs were uniformly deposited onto the surface of TiO_2-NTs. It was found that higher water content in electrolyte was in favor of large intertube space and pore size and the uniform deposition of CdS NPs. The photocatalytic degradation of methyl orange was tested with the as-prepared CdS/TiO_2-NTs under visible light ($\lambda > 400$ nm). It was found that the photodegradation rate reached as high as 96.7% under visible irradiation for 180 min. In addition, a reasonable degradation rate of 75.8% was achieved even after 5 cycles, suggesting a good photocatalytic stability of the as-prepared CdS/TiO_2-NTs.

1. Introduction

In past several decades, photocatalytic degradation of organic pollutants in waste water using semiconductors has attracted much attention [1–3]. Titanium dioxide (TiO_2) has been regarded as one of the most promising photocatalysts because of its superior photocatalytic activity, high chemical stability, non-toxicity and low cost [4]. Up to now, varieties of TiO_2 nanostructures, including nanoparticles, nanospheres, nanorods, nanowires and nanotubes have been fabricated for their special physicochemical properties. Among the different geometric shapes, the highly ordered TiO_2 nanotube arrays (TiO_2-NTs) obtained by the anodization of Ti sheet attract more interest due to their large specific surface area and the precisely oriented nature of the nanotube arrays, which can improve the charge-collection efficiency by promoting the electrons/holes transport and slower recombination [5]. In addition, the aligned nanotube structure allows the absorption of radiation by reducing the loss of light reflection, since photons entering the nanotubes are less likely to escape due to multiple radiations scattering by the nanotube walls [6].

Nevertheless, there are still some drawbacks that limit the wide use of TiO_2 photocatalyst. One is the quick recombination of photon induced charge carriers [7] and the other is that the band gap of TiO_2 is so wide (3.0 and 3.2 eV for rutile and anatase phases, respectively) that its activation is only limited in the UV region, which accounts for only 4–5% of the spectrum of solar energy [8]. To overcome these two obstacles, various methods have been explored including the substitutional non-metallic doping (C [9], S [10], N [11,12], etc.), and novel metallic (Ag [13], Pt [14,15], Au [16,17] etc.) atoms doping. In contrast, the modification of TiO_2 with quantum dots (QDs) of narrow-gap semiconducting materials (CdS [18–21], CdSe [22,23] and Cu_2O [24,25]) is more promising as it can effectively improve the visible-light activity. CdS is normally considered as an important sensitizer since it has a narrow band gap (2.4 eV) with a slightly higher conduction band level than that of TiO_2 [7]. Hence, CdS, as a kind of photosensitive materials, can induce an efficient and longer charge separation by minimizing the electron–hole recombination in excited TiO_2. To date, many methods have been developed to deposit CdS nanoparticles (NPs) on TNTAs, such as electrodeposition [26,27] and sequential chemical bath deposition (S-CBD) [28–30]. However, the photocatalytic performance of TiO_2-NTs sensitized with CdS NPs is still insufficient and unstable because the distribution and aggregation of nano-sized CdS NPs sensitizer is coming to a challenge [6] which definitely degrades the photocatalytic performance and stability of the modified electrode. On the other hand, the CdS NPs sensitized TiO_2-NTs catalyst is commonly used in the form of powder, which is very hard to recycle. This shortage definitely limits its practical application.

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In this work, discrete TiO_2-NTs with large intertube spacing and pore size decorated with dispersed CdS NPs were prepared. The photocatalytic degradation of methyl orange (MO) under visible light was systematically studied using the whole sheet of CdS NPs sensitized TiO_2-NTs with the Ti subtract. The cycling performance of degradation of MO was also investigated to validate the stability of the photocatalyst.

2. Experimental

2.1. Fabrication of TiO_2-NTs

Highly ordered TiO_2-NTs were fabricated by the potentiostatic anodization method [31]. Ti foils (0.1 mm thickness, 99.6% purity) were degreased by sonication in acetone, highly pure water and ethanol for 15 min, 10 min, 5 min respectively, then dried in air. A two-electrode configuration including Ti foil and a piece of highly pure graphite ($50 \times 30 \times 5$ mm) acting as the anode and cathode. The electrolyte consisted of 0.1 M NH_4F dissolved in ethylene glycol (EG) with water content of 5, 8, 10 and 12 vol%. The anodization was performed under a constant voltage of 60 V. The anodization time was controlled to make the TiO_2-NTs with a length of about 10 μm. All experiments were carried out at room temperature unless otherwise stated.

After anodization, the samples were sonicated in EG for 60 s and then rinsed with highly pure water, dried in air to wipe off the debris on the surface of the TiO_2-NTs. Then the samples were annealed in air at 500 °C for 2 h with the heating and cooling rates of 1 °C/min.

2.2. Deposition of CdS NPs

CdS NPs were deposited by S-CBD technique [28]. Briefly, the as-anodized samples were immersed in a 0.02 M $CdCl_2$ solution for 30 s, rinsed in highly pure water for 60 s and then immersed in 0.02 M Na_2S solution for 30 s and rinsed again in highly pure water for 60 s to remove the excess precursor solution. Such an immersion cycle was repeated for 10, 15 and 20 times separately. Then the samples were annealed at 300 °C in Argon atmosphere for 2 h with the heating and cooling rates of 1 °C/min.

2.3. Characterization

The morphology was characterized by using a field-emission scanning electron microscope (FESEM, FEI Sirion 200) and a transmission electron microscopy (TEM, Hitachi H800). X-ray diffraction analysis (XRD, Rigaku D/Max-2500VL/PC, Cu $K\alpha$) was performed for crystal phase identification. The chemical states of the samples were analyzed by X-ray photoelectron spectroscopy (XPS, Thermo ESCALAB250).

2.4. Photocatalytic degradation of methyl orange (MO)

The photocatalytic degradation experiments were carried out on a XPA-7 photochemical reactor (Nanjing Xujiang Machine-electronic Plant, China) as shown in Fig. 1. A 250 W metal halogen lamp with a 400 nm filter was used as the visible light source. The distance

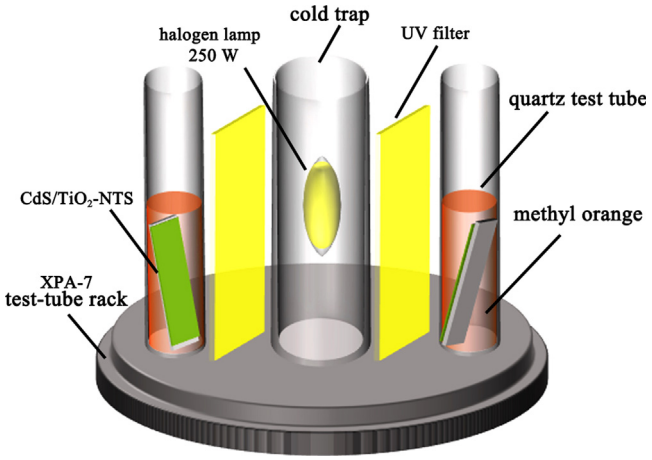

Fig. 1. Schematic diagram of the photocatalytic device for methyl orange degradation.

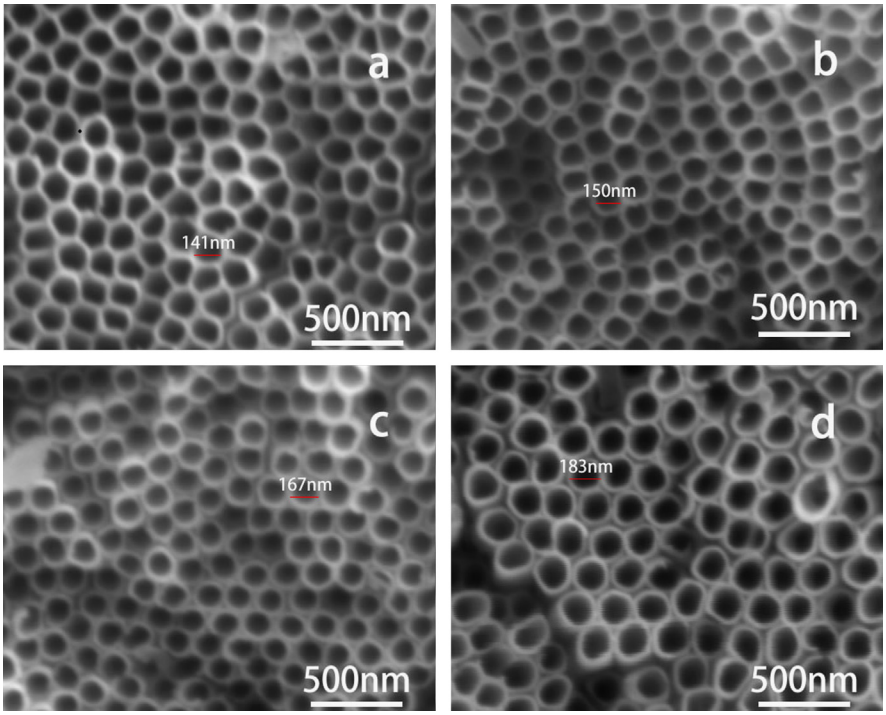

Fig. 2. Top-view FESEM images of as-prepared TiO_2-NTs with various water contents: (a) 5 vol%, (b) 8 vol%, (c) 10 vol%, (d) 12 vol%.