



Facile synthesis of ultrafine CuS nanocrystalline/TiO₂: Fe nanotubes hybrids and their photocatalytic and Fenton-like photocatalytic activities in the dye degradation



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ABSTRACT

Interface-induced effect and large specific surface area of heteronano-structures are attracting much attentions due to applications in photocatalysis. In this work, ultrafine CuS nanocrystalline/Fe-doped TiO₂ nanotubes hybrids were fabricated with facile methods. The effect of the ratio of CuS to Fe-doped TiO₂ nanotubes (NTs) on the microstructural, optical and photocatalytic properties of the NTs and hybrids were studied. The NTs showed an actual Fe content of ~2.93 at % and an optical bandgap of ~3.00 eV. The bandgap of the hybrids were ~2.50–2.95 eV decreased with increasing CuS/NTs ratio. The specific surface area of the NTs was ~333 m² g⁻¹. Whereas the hybrids showed remarkably larger specific surface area of ~794–1100 m² g⁻¹ than the NTs because of well controlled formation process of CuS nanoparticles. The sunlight-excited degradation experiments of malachite green in the water indicated that the photo- and photo-Fenton-like catalytic activity of the hybrids was higher than that of the NTs and increased with increasing CuS/NTs ratio. The quasi-kinetic first-order rate constant was in the range of ~0.260–1.181 h⁻¹ and increased to ~3.932–10.597 h⁻¹ in the present of the H₂O₂ aqueous solution with a concentration of 20 ml l⁻¹. The high photocatalytic activity of the hybrids was mainly ascribed to the narrow bandgap, large specific surface area and effective heterojunction.

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1. Introduction

Nano-TiO₂ materials as a photocatalyst have been widely studied for potential application in environment decontamination. To acquire high photocatalysis and mineralization in decomposing various harmful substances in gas or liquid, a large number of efforts were made to enhance the light absorption of the TiO₂ materials. Doping nitrogen [1,2], sulfur [2,3], and some metal cations [4,5] were usually used to narrow the bandgap of TiO₂. The Fe doping has been reported to be effective in enhancing photocatalytic activity [4–9] and mineralization [9] of TiO₂ and more effective than other metal cations [5]. Our previous study [10] revealed that the photo- and Fenton-like photocatalytic activities of the Fe-doped TiO₂ nanotubes are obviously greater than that of the undoped TiO₂ nanotubes and increased with increasing actual Fe content to 3.86 at.%. The effect of Fe doping can be ascribed to the bandgap narrowing of TiO₂ [10] and/or photogenerated electrons/holes from Fe impurity energy levels [11,12].

Because high surface-to-volume ratios, it has been reported that the TiO₂ nanotubes are of an enhanced photocatalytic properties with respect to any other form of TiO₂ [13,14]. TiO₂ nanotubes and nanotube arrays have been produced by a variety of methods. These methods include using a nanoporous alumina as template [15], sol-gel transcription using organo-gelators as templates [16,17], seeded growth [18], hydrothermal processes [19–21], and anodization route [22–25].

To further enhance the photocatalytic property, various heterojunction nanostructures of two and three semiconductors, which can promote effective separation between photogenerated electrons and holes, are widely attended. Copper sulfide is a significant binary compound semiconductor that has some unique characteristics: (i) narrow direct and indirect bandgaps, (ii) high absorption coefficient in sunlight, (iii) nontoxic and abundant in nature, and (iv) low cost. Recently, some CuS-cororated TiO₂ hybrids have been reported to be of high photocatalytic activity [26–29]. However, CuS-cororated TiO₂: Fe hybrids, especially CuS-cororated TiO₂: Fe nanotubes hybrids, have not been reported in previous literature. Thus, structuring the heterojunction nanostructures between CuS

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and Fe-doped TiO₂ nanotubes might be reasonable for excellent photocatalytic activity.

Malachite green as an alkaline green dye usually exists in the wastewater produced from printing and dyeing industry. This dye has toxicity to human and environment because it is a carcinogenic substance. Naphthol green B is also light noxious to human and environment. Thus, they must be removed for wastewater treatment and environment purification.

In this work, we focus on (i) the fabrication of Fe-doped TiO₂ nanotubes (NTs) and CuS/NTs hybrids and (ii) the effect of CuS/NTs ratio and operation parameter on the photocatalytic and Fenton-like photocatalytic activities of the NTs and hybrids in the degradation of dye in the water.

2. Experimental section

2.1. Synthesis of the Fe-doped TiO₂ nanoparticles and nanotubes

The Fe-doped TiO₂ nanoparticles (NPs) were synthesized by a sol–gel process. First, butyltitanate (C₁₆H₃₆O₄Ti) and ferric nitrate (Fe(NO₃)₃·9H₂O) were dissolved in ethanol according to molar ratios of Fe/Ti = 3 at.%. Into which, citric acid about 1.5 times molar of the metal cations, as a chelating agent, was added. The solutions were then stabilized with a little acetylacetone (~1 ml) to prevent the hydrolysis of butyltitanate and then expanded to 100 ml with ethanol. After constant ultrasonic stirring for 30 min, transparent gel with Ti cation concentration of 0.1 mol l⁻¹ were formed. The gel solutions were dried at 80 °C for 12 h to fully volatilize low-boiling organic component and then 150 °C for 7 h. As-dried gels were calcined at 450 °C for 2 h in air. Subsequently, the Fe-doped TiO₂ nanotubes were fabricated by hydrothermally treating the as prepared NPs in 10 mol l⁻¹ NaOH aqueous solution at 110 °C for 24 h, on basis of the method reported in previous literature [19,20]. The products were filtered, washed repeatedly with deionized water until washing liquid near neutral, and then dried at 80 °C for 3 h. Finally, the products were crystallized at 400 °C for 1 h. Soft products with yellow color were obtained.

2.2. Synthesis of the CuS/Fe-doped TiO₂ nanotubes hybrids

The CuS/Fe-doped TiO₂ nanotubes hybrids were fabricated by successive ionic adsorption and reaction method. First, the Cu²⁺ solution was prepared by dissolving the cupric acetate (Cu(CH₃COO)₂·H₂O) in deionized water, while thioacetamide (C₂H₅NS) was dissolved in deionized water in another beaker. Second, the 0.5 g NTs was ultrasonically suspended in 50 ml deionized water. Under constant ultrasonic condition, one drop of the Cu²⁺ solution and the thioacetamide solution were alternatively dropped into the NTs suspension. Because very large solubility product constant of CuS, the formation of CuS in the solution containing Cu²⁺ and S²⁻ ions is very fast and thereby the thioacetamide is rapidly decomposed. After each dropping, a time span of 0.5 min was taken to realize full homomixing of Cu²⁺ cation and thioacetamide, adsorption of Cu²⁺ cations on the NTs, and/or reaction between the Cu²⁺ and S²⁻ ions. Above process was repeated until the CuS/NTs molar ratio equals 0.025, 0.050, 0.075, and 0.100, respectively. The mixed suspensions were then filtrated and washed with deionized water by several times. Finally, the products were dried in an oven at 80 °C for 6 h.

2.3. Characterization of the synthesized nanoparticles, nanotubes and hybrids

The crystal phases of the TiO₂ NPs, and NTs, and hybrids were identified at room temperature using an X-ray diffractometer (XRD,

CuK_{α1}, λ = 0.15406 nm, Model No: D/Max-2200PC, Rigaku, Japan). The morphology and X-ray energy dispersive spectra (EDS) of the NTs and hybrids were analyzed using a transmission electron microscopy (TEM, Model No: JEM-3010, Japan). Raman spectra of the samples were collected using a spectrophotometer (Model no: Renishaw-invia, U.K.) at a laser excitation wavelength of 532 nm. Fourier transform infrared spectra (FTIR) were determined by an infrared spectroscopy (Model no: Vector-22, Bruker, Germany). Diffusion-reflection absorption spectra of the NTs and hybrids adhered on glass substrate by a transparent adhesive were measured on a UV–vis spectrophotometer (Model No: Cary100 UV–Vis, Agilent, USA) in the range of 350–900 nm. Specific surface area of the NTs and hybrids were measured by N₂ absorption method on a surface area analyzers (Model no: Gemini VII2390, Micromeritics Instrument, Shanghai, China).

2.4. Photocatalytic and photo-Fenton-like catalytic properties of the hybrids

Malachite green and naphthol green B dyes were used as substrate to study the photocatalysis of the NTs and hybrids. Photocatalysis experiments were performed at a room temperature of ~27 °C in sunlight irradiation with average intensity of ~900 W m⁻². The malachite green aqueous solutions with concentrations of 5 × 10⁻⁶ mol l⁻¹ and initial pH = 5 and 7 were first prepared. In each experiment, 50 mg photocatalysts and 50 ml malachite green aqueous solution were added to a glass breaker. To study the effect of H₂O₂, 1 ml H₂O₂ aqueous solution (H₂O₂: 30%) was added into such other two systems, in order that H₂O₂ aqueous solution content equals 20 ml l⁻¹. After different irradiation times, ~3 ml solution was taken out and subsequently measured for their light absorbance at ~617 nm on a spectrophotometer (Model No: 752N, China). The solution after the test was returned to the breaker to maintain the normal volume of the solution under the test. With same method, the photodegradation of the naphthol green B aqueous solutions with the concentrations of 5 × 10⁻⁶ mol l⁻¹ and initial solution pH = 7 and 9 were also carried out in the sunlight irradiation with average intensity of ~900 W m⁻².

In the period of first hour of the above photocatalytic experiments, the oxidation-reduction potentials (ORP) of the malachite green aqueous solutions with and without the photocatalysts were measured on an oxidation-reduction potential tester (ORP-286, China). Their difference was used as a determination of the ORP of the nanotubes and hybrid surfaces in the process of the dye photodegradation.

The quasi-kinetic first-order rate constant (*k*₁) were calculated with the kinetic relation between the concentration (*C*) of the dye aqueous solution and the photocatalytic reaction span (*t*) given by the following relation [6–8]:

$$\ln \frac{C_0}{C} = k_1 t \quad (1)$$

In which, *C*₀ is the initial concentration of the dye aqueous solution.

3. Results and discussion

3.1. Crystal phase and microstructure of the NTs and hybrids

Fig. 1 shows the XRD pattern of the synthesized TiO₂ NPs and NTs. The XRD peaks of the NPs correspond to the anatase phase (JCPDS: 21-1272). The initial NTs are also anatase. The annealing crystallization only leads to slight peak enhancement. The average

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