一步水热合成铜纳米颗粒负载二氧化钛复合纳米管及其可见光催化活性

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摘要: 采用一步水热法合成了Cu纳米颗粒负载二氧化钛纳米管材料. 利用透射电子显微镜(TEM)、X射线衍射仪(XRD)、能谱仪(EDS)等对材料的相组成、形貌以及形成过程进行了研究. 制得的Cu-TiO₂复合纳米材料长度约为100 nm, 直径10–15 nm, 其上负载的Cu纳米颗粒尺寸约为5 nm. BET比表面积测试表明实验制备的Cu-TiO₂复合纳米管的比表面积为154.67 m²·g⁻¹. 通过调节水热反应时间和钛前驱体种类, 研究了该复合纳米管材料的形成机制. 结果表明: 非晶态的钛源对于成功一步合成Cu-TiO₂复合纳米管至关重要. 同时, 实验中观察到铜纳米颗粒的尺寸随水热反应时间延长而减小(反奥氏陈化过程), 这一现象有助于纳米颗粒的可控合成. 紫外-可见吸收光谱表明该复合纳米管在350–800 nm范围内有较强的吸收, 并在550–600 nm范围观察到Cu的表面等离子体吸收带. Cu-TiO₂界面处形成的肖特基势垒有助于加快光生载流子的输运, 提高光生电子-空穴对的分离效率. 光催化实验表明Cu-TiO₂复合纳米管在可见光下具有较高的催化活性.

关键词: 可见光催化; 二氧化钛; 铜; 一步水热法; 复合纳米管

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One-Step Hydrothermal Synthesis and Visible-Light Photocatalytic Activity of Ultrafine Cu-Nanodot-Modified TiO₂ Nanotubes

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Abstract: One dimensional titanate nanotubes modified with copper nanospheres were synthesized through a facile one-step hydrothermal process. Transmission electron microscope (TEM), X-ray diffraction (XRD), and energy dispersive spectrometry (EDS) were used to monitor the changes in the morphology and phases during the hydrothermal process. The diameter of the Cu-TiO₂ composite nanotubes was 10–15 nm and their lengths were ca 100 nm, the dimension of the covered Cu nanoparticles was about 5 nm. Brunauer-Emmett-Teller (BET) tests revealed the specific surface area of the Cu-TiO₂ composite nanotubes to be 154.67 m²·g⁻¹. The formation process and mechanism of the composite nanotubes were surveyed by adjusting the hydrothermal duration and titanium precursor. The results revealed that an amorphous titanium precursor is essential for the successful formation of this unique topography and phase composition. Anti-Ostwald ripening, a decrease in the dimensions of the copper nanospheres with hydrothermal time, was

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observed in the TEM images, which is of benefit to help keep the particles on the nanoscale. The UV-Vis spectrum of the as-prepared material exhibits a strong absorption at 350–800 nm in the visible band compared with commercial TiO₂ nanopowders. The plasmonic absorption of metallic copper particles between 550 and 600 nm is seen in the UV-Vis spectrum. Schottky barriers between copper-TiO₂ interfaces make this kind of material a potential agent in speeding up electron transport rates and slowing recombination rates. Photocatalytic experiments demonstrated this unique Cu-TiO₂ composite nanotube material has a high photocatalytic activity under visible-light irradiation.

Key Words: Visible-light photocatalysis; TiO₂; Cu; One step hydrothermal method; Composite nanotube

1 Introduction

Owing to their low cost, distinctive physical and chemical properties, anatase TiO₂ materials in nanoscale have been widely used as photochemical catalysts, solar energy converters, energy storage, and UV-absorbent materials. For example, dye-sensitized solar cells (DSSCs) made from anatase nanocrystalline have already yielded a power conversion efficiency of 12.6%, and a discharge capacity of 300 mAh · g⁻¹ has been reached when anatase is used as cathodes in lithium-ion batteries.^{1–9} Nevertheless, over the past decades, there has been persistent effort to resolve two main problems with pure anatase. First is that its energy gap (3.2 eV) is too wide to exploit more of the solar radiation spectrum. By adding impurities, metal, or nonmetal, to the TiO₂ matrix,^{10,11} its band gap can be tailored. Nitrogen-doped TiO₂ has also been shown to extend the absorption edge of TiO₂ photocatalysts out to 550 nm.^{12,13} However, catalytic performance under optical wavelengths is less than satisfactory.¹⁴ Furthermore, rapid charge-carrier recombination lessens the efficiency of TiO₂ to a great extent. More-rapid electron transport and slower charge recombination have been attained by synthesizing one-dimensional (1D) TiO₂ nanostructure material. Meanwhile, its optical absorption performance has not improved as much compared with regular TiO₂ nanospheres.^{15–20}

Recently, TiO₂ nanotubes loaded with noble metals (Au, Ag, Pt) have attracted attention because of surface plasmon resonances from the metal nanoclusters as well as the 1D structure. This unique material leads to both strong optical responses and efficient photon-excited charge-carrier separations. Superb properties have been obtained from metal-TiO₂ nanotubes. For example, Au-TiO₂ nanotube composite electrodes have been proven to be a promising platform for fabricating third-generation biosensors.²¹ In most cases, though, the hybrid nanotubes are prepared in two or more steps: first, synthesis of TiO₂ nanotubes by alkaline liquor hydrothermal or anode oxidation, and then reducing the mixture of metal salt and TiO₂ nanotubes. This makes the preparation complicated.^{22–24}

As is well-known, the Fermi level of copper is 4.65 eV, which is between gold (5.10 eV) and silver (4.26 eV), making copper an appropriate and cheap candidate to replace noble metals in modulating the band structure of TiO₂ nanotubes. In our present study, one species of Cu superfine nanoparticles

modified anatase TiO₂ nanotubes has been synthesized through a simple one-step hydrothermal method. The formation mechanism has been examined as well as the catalytic performance under visible light is investigated in this paper.

2 Experimental

2.1 Synthesis of Cu-TiO₂ nanotubes

All reagents were analytically pure and gained from Aladdin Inc. (Shanghai). In a typical experimental procedure, 0.5 g cuprous chloride (CuCl, 97.0%) was dissolved in 5 mL concentrated ammonia water to generate clathrate. Then 0.8 g ascorbic acid (C₆H₈O₆, 99.7%) and 1.4 g sodium citrate (C₆H₅O₇Na₃ · 2H₂O, 99.0%) were added into the solution above with a strong stir about 10 min. Dark brown homogeneous liquid was obtained. After that, 10 mL absolute ethyl alcohol mixed with 0.005 mol tetrabutyl titanate (C₁₆H₃₆O₄Ti, TBT, 98.0%) was added to the solution drop by drop and agitated for 15 min. 10 mol · L⁻¹ NaOH (96.0%, 35 mL) solution was introduced by dripping slowly before the final mixture was transferred into a 50 mL Teflon-lined stainless autoclave. The proportion between Cu and Ti species is 1:1 in the initial precursor solution, and both of their concentrations are about 0.1 mol · L⁻¹. After 24 h hydrothermal process at 453 K and cooled to ambient temperature, the as-prepared products were centrifuged in dilute nitric acid (HNO₃, 0.1 mol · L⁻¹), deionized water, and absolute ethyl alcohol several times to wash out of the impurities, and then dried in the air at 333 K. After the drying process, the products were annealed under argon and air at 723 K for 2 h, respectively. Parallel experiments were carried out to examine various synthetic parameters.

2.2 Characterization

The phase composition of the samples was determined on a Bruker D8-Advance X-ray diffractometer (Germany) with Cu K_α radiation (λ=0.15406 nm). The morphology of the prepared samples was investigated by transmission electron microscope (TEM, Hitachi H-600, Japan). Energy dispersive spectrometer (EDS, Bruker XFlash 5010 EDS Detector, Germany) was used to detect the elemental composition. Absorption properties of the products were recorded by TU-1901 UV-Vis Spectrophotometer (Beijing Pirkinje General Instrument Co., Ltd). The specific surface areas were carried out by the surface area analyzer (3H-2000-BET-M, BeiShiDe Instrument, Beijing).

2.3 Photochemical catalysis measurements

The visible-light source for the photocatalytic activity test is a 500 W Xe lamp with UV filter. Concentration of the catalyst is 1.0 mol · L⁻¹, and the initial methylene blue (MB) concentration is 40 mg · L⁻¹. Visible radiation intensity is 20 mW · cm⁻². The regular irradiation time for sampling is 10 min. After the specimen was filtered, the filtrate was analyzed by UV-Vis spectra (Shimadzu UV-1800 Spectrometer, Japan) for the absorption intensity using the values at 650 nm. Considering that MB is unstable under light irradiation, the blank test was carried out with no addition of any catalyst.

3 Results and discussion

3.1 Morphologies and phases of the composite nanotubes

TEM photographs of the as-prepared nanotubes before annealing are presented in Fig.1. Dispersive nanotubes are clearly seen covered by uniform superfine nanoparticles obtained after the hydrothermal process. Nanotube diameters and lengths are about 10–15 nm and 100 nm, respectively. The sizes of the superfine nanoparticles are about 4–6 nm. As copper atoms are heavier than the others in the sample, dark nanoparticles are identified as elemental copper and the nanotubes as titanium complexes. This unique nanostructure is superior to conventional 0D nanospheres and 1D nanorods or nanotubes with suppressed electron-hole pair recombination. At the junctions between Cu and TiO₂, Schottky barriers tend to form because the work functions and band alignments are different on each side.

These unique metal-semiconductor interfaces induce effective separation and transfer of photo-excited electrons and holes.²⁵ In addition, this tube-dot composite structure yields a much higher specific surface area per volume compared with other nanomaterials. Energy-dispersive spectroscopy (EDS) results indicate the presence of only Cu, Ti, and O in the sample. Besides cubic copper (JCPDS No. 04-0836), diffraction peaks near to that for H₂Ti₂O₅ · H₂O (JCPDS No. 47-0124) can also be identified from XRD patterns (see Fig.2(a)). After annealing under Ar at 450 °C for 30 min, the sample's XRD patterns (Fig.2(b)) transform into those for an anatase TiO₂ phase (JCPDS No. 21-2172). There are no diffraction peaks from CuO or Cu₂O in the spectra. Considering that the detection sensitivity of XRD for minor phases is 3%–5%, we conclude that the principal phases of the sample after annealing are pure copper and anatase. Little of Cu⁰ is oxidized into Cu⁺ or Cu²⁺. Results from EDS analysis of the sample annealed under Ar is shown in Table 1. Though EDS yields only semi-quantitative results, it does provide the relative content of elements with an error limit of ca 5%. From column five of Table 1, the atomic proportion of Ti and Cu is ca 31:27. This value is close to their initial 1:1 proportion. In contrast, the Ti/O atomic ratio is about 27:42, and this value is close to the stoichiometric proportion of TiO₂, indicating that little copper oxide remains in the composite nanotubes obtained.

3.2 Copper-TiO₂ nanotube formation

To understand how superfine copper nanoparticles cover the TiO₂ nanotubes, a series of experiments were performed in which hydrothermal reaction time was adjusted. TEM images

Fig.1 TEM images of 1D Cu-modified titanate nanotube sample at different magnifications

Inset in figure (a) is an EDS spectrum of the sample after annealing at 450 °C.

Table 1 Proportion of Ti, Cu, and O elements obtained from EDS spectrum

Element	Atom number	w ₁ /%	w ₂ /%	x/%	Error/%
Cu	29	44.52	49.77	30.78	1.2
Ti	22	29.62	33.11	27.18	0.9
O	8	15.31	17.12	42.04	2.3
Total		89.46	100.00	100.00	

w₁: unnormalized mass fraction; w₂: normalized mass fraction; x: atomic fraction

were taken for the morphology change at reaction time of 6, 12, and 18 h (Fig.3).

In the initial period of hydrothermal reaction (Fig.3(a)), a mixture of nanospheres and nanosheet-like substance is exhibited in the image. The sample agglomerates quite densely and a large distribution of particle sizes also appears in the image. After a six-hour reaction, nanoribbons with a regular shape can be seen in the image (Fig.3(b)) with only a few nanoballs attaching to ends of the nanoribbons. After a reaction time of 18 h, threadlike nanotubes, folded nanosheets as well as nanolayer structures coexist in the sample (Fig.3(c)), which presents a glimpse into the formation details of the titanate nanotubes.

Compared with the earlier samples, the nanotube structure is more obvious and many Cu nanoparticles are dispersed over the surface of the 1D materials. The sample obtained after 24 h hydrothermal duration is featured in Fig.1 and, as described earlier, shows nanotubes with maximal-attached densities of highly homogeneous Cu nanospheres.

As stated above, no anatase TiO₂ phase trace is detected but cubic copper phase is identified in each sample before sintering. In detail, XRD patterns of samples after hydrothermal durations of 6 and 12 h are similar to those of H₂Ti₃O₁₁ · H₂O (JCPDS No. 44-0131), see Fig.2(a). However, the crystal structures of products after longer reaction time are distinct; the diffraction peak at 36.1° disappears but the one at 28.4° appears, yielding patterns that are near to that of H₂Ti₂O₅ · H₂O (JCPDS No. 47-0124). This conversion may be attributed to an increase in TiO₆ octahedra during hydrothermal treatment.

In the XRD patterns of samples annealed at 450 °C for 30 min (Fig.2(b)), anatase TiO₂ is seen clearly to coexist with cubic copper in all the samples washed by hydrogen nitrate and no impurities are detectable. Remarkably, the product prepared

Fig.2 XRD patterns of samples without annealing (a) and annealing at 450 °C for 30 min (b) **Fig.3** (a-c) TEM images of samples with various hydrothermal treatment durations; (d) schematic of the Cu-TiO₂ nanotube formation mechanism; (e) histogram of Cu particle sizes under various hydrothermal treatment time

(a) 6 h, (b) 12 h, (c) 18 h

by hydrothermal treatment for 18 h exhibits no distinctive and typical diffraction peaks of anatase TiO₂, and this phenomenon may be explained as follows. Before annealing, the Ti species in the samples with a hydrothermal duration of 6 and 12 h are classified as H₂Ti₅O₁₁ · H₂O, whereas the samples with hydrothermal treatments of 18 and 24 h are H₂Ti₂O₅ · H₂O. Thus, the crystalline phases after 6 and 12 h annealing time are transformed from H₂Ti₅O₁₁ · H₂O and those after 18 and 24 h annealing time are from H₂Ti₂O₅ · H₂O. 18 h is a transition period (during the hydrothermal treatment) for H₂Ti₅O₁₁ · H₂O to H₂Ti₂O₅ · H₂O. With a more-disordered atomic arrangement than other samples, this sample has weaker diffraction intensity than other samples. In addition, because the diffraction intensity of copper is so strong, the diffraction peaks of TiO₂ are almost submerged into the background lines. As for the sample given 24 h hydrothermal duration and no HNO₃ washing, the diffraction pattern shows no trace of anatase as well, revealing that acid-washing is a necessary procedure in forming anatase TiO₂ phase nanotubes rather than titanate nanotubes.

Distinct from regular nucleate crystal and growth principles, the particle size of copper nanocrystals becomes smaller with longer hydrothermal treatment (Fig.3(e)). Average particle sizes diminish from 22.7 nm for 6 h, 16.9 nm for 12 h, and 9.7 nm for 18 h to 5.5 nm for 24 h. In typical conditions, particle formation includes producing nuclei, growth, and finally stabilization. Stabilization complies with Ostwald ripening: growth of larger particles accompanied by dissolution of smaller ones driven by differential solubility at highly curved interfaces. This process minimizes surface energy by lessening interfacial area, resulting in an increase over time of the average particle size.²⁶

In contrast, particle size for copper nanospheres shows the complete-opposite trend, so-called anti-Ostwald ripening. This astonishing phenomenon may be explained as follows. At the preliminary stage of the reaction, small tiny Cu particles of only several angstroms as well as larger porous clusters composed of these smaller Cu subunits are produced in solution. The interfacial energy between tiny Cu subunits is huge, and the system is highly unstable. Two spontaneous processes actually contribute to minimizing the system energy: larger Cu particles shrinking over the course of hydrothermal process and smaller Cu nanoparticles attaching to defective sites of the nanotubes. The interfacial energy could be the driving force in shrinking those larger clusters, forcing Cu nanocrystals to become smaller and rounder. As a consequence, the average Cu diameter appears to reduce over time.²⁷

Based on sample architecture observed from the TEM images, three main transformations occur during the 24 h hydrothermal process: (1) formation of titanate nanotubes, (2) reduction in copper nanocrystal diameters, and (3) surface adsorption of copper nanoparticles on the nanotubes (Fig.3(d)). The first transformation coincides with the classical formation mechanism of TiO₂ nanotubes. In the primary stage of the hydrothermal reaction, layered sodium titanate is preferentially formed,

and these nanosheet products are comprised of highly distorted TiO₆ octahedra.²⁸ Afterwards, to reduce the number of surface dangling bonds and to lower its system energy, these nanosheets are exfoliated from superimposed sodium titanate and then curled into nanotubes. The heat fluctuation in the aqueous solution may assist the rolling-up process. Thus, nanotube products constituted of sodium titanate are formed by exfoliation and rolling up into nanosheets. Alternatively, nanowires tend to form when the hydrothermal temperature increases to 180 °C and with reaction time as long as 24 h. However, in this experiment the nanotube products are still obtained successfully. According to Huang's theory,²⁹ titanate nanotubes were found to be an inevitable intermediate product. The nanotubes are bound to be transformed into nanowires when the hydrothermal duration increases. In detail, this transformation is a coarsening process induced by simultaneous Ostwald ripening (OR) and oriented attachment (OA).²⁹ In our case, though, tube bunching is not observed in all the samples, implying the OA mechanism plays a limited role in this hydrothermal process. This may be ascribed to the existence of copper nanoparticles in the reaction solution. During hydrothermal treatments, copper particles act as boundaries to isolate single nanotubes and obstruct parallel nanotubes from bunching up. Thus, the kinetic reaction rate slows down and the transformation from nanotubes to nanowires gets deferred.

Anatase TiO₂ nanopowders as titanium source had been performed to investigate influences of separate titanium sources on the product architecture. A typical TEM image of the sample is shown in Fig.4.

The premise of a vast majority of previous research has been to use crystalline structures as start-up material to synthesize TiO₂ nanotubes; essentially, crystalline TiO₂ would be able to delaminate into single-layer sheets, whereas amorphous TiO₂ raw materials would not form sheets.^{30,31} In this study, amorphous tetrabutyl titanate (TBT) has been used as precursors to produce composite nanotubes. Moreover, based on our previous experimental results, the role of crystalline TiO₂ is reversed in the formation process of these composite nanotubes.

As seen in Fig.4, the sample consists of nanotubes, nanosheet-

Fig.4 TEM image of the sample using anatase TiO₂ nanopowders as titanium source

ts, and some aggregates. The size of nanoclusters is more non-uniform than the TBT-prepared sample and much fewer nanoclusters adhere to either nanotubes or nanosheets. During alkali treatment of the crystalline TiO_2 raw materials, nanocrystals unfold into nanosheets, but the highly ordered atomic arrangement of nanocrystals creates fewer defects in the final product, leading to fewer binding sites for the copper superfine nanoparticles. The above analysis demonstrates that TBT is a better choice as a titanium source.

3.3 UV-Vis absorption of the samples

The UV-Vis absorption spectra of prepared samples (Fig.5) before and after annealing at 450°C , as well as the commercial anatase TiO_2 powders (C- TiO_2 , from Aladdin Inc.) show that samples composited with copper exhibit a significant improvement in absorption in the visible region compared with commercial TiO_2 . There are two absorption bands in the spectra. Samples after annealing reveal stronger absorption bands at wavelengths of about 320 nm along with a broad absorption band between 350 and 500 nm. The former is related to O $2p$ electron excitations to the Ti $3d$ level whereas the latter is ascribed to the emergence of Cu, in agreement with a former thesis.³² It is worth noting that for the as-prepared composite nanotubes there is a wide absorption range between 525 and 600 nm, and this range becomes broader after annealing. Based on some earlier reports,^{33–36} when uniform metal spheres are considerably smaller than the wavelength of light, a plasma absorption band will be produced. For copper, if the particle size is a little larger than 2–4 nm, the position of the plasma absorption band is around 550–600 nm. According to the preceding analysis, the particle size of copper reduces spontaneously to lower their interfacial energy. There are reasonable grounds to believe that this spontaneous process is continuing during annealing. Along with the decrease of the particle size, the plasma absorption band of copper broadens.

Particles after annealing are almost black in appearance (see photo inset in Fig.5). As Cu has a narrower band gap and higher work function than individual TiO_2 , Schottky barriers tend to form at the interfaces between Cu and TiO_2 . Thus, the Cu- TiO_2 composite particles reinforce the capability of the material to

Fig.5 UV-Vis absorption spectra and photos of the prepared samples

(a) TiO_2 nanopowders, (b) before annealing, (c) after annealing under Ar

absorb visible light and establish a charge carrier separation. These properties enable the composite Cu- TiO_2 nanotubes to have potential applications in strengthening photocatalytic and photoelectric characteristics necessary for use as solar cells.

3.4 Photocatalytic activity of the sample

Pure anatase displays high catalytic activity under UV light, but its catalytic performance under visible irradiation is unsatisfactory. A comparison of visible light catalytic activity between the Cu- TiO_2 composite nanotubes and mixed nanopowders is shown in Fig.6. Absorption of the substance is positively correlated with its concentration. Clearly, light irradiation leads to very slow degradation of methylene blue (MB). The composite nanotube has a more rapid decomposition rate than mixed nanopowders under visible irradiation. The MB concentration decreases with irradiation time; the degradation rate also grows rapidly.

As mentioned above, metal-semiconductor interfaces between Cu nanoparticles and TiO_2 nanotubes are beneficial for electron-hole pair separation. Cu superfine nanoclusters have strong optical responses. Optically generated electrons pass through Cu- TiO_2 interfaces onto anatase, inducing organic degradation within the composite material under visible irradiation. In brief, there are two principal reasons for higher photocatalytic activity in Cu- TiO_2 nanotubes than in Cu- TiO_2 nanopowders. The first is the influence of specific surface area. Specific surface areas of Cu- TiO_2 nanotubes and Cu- TiO_2 nanopowders have been characterized using Brunauer-Emmett-Teller analysis; results are 154.67 and $54.75\text{ m}^2\cdot\text{g}^{-1}$, respectively. A larger specific surface area in general leads to better adsorption and catalysis capabilities. Second, because TiO_2 does not adsorb visible photons directly, catalytic activity in the visible region has to depend largely on the Cu/ TiO_2 interfaces. The Cu- TiO_2 nanotubes provide innumerable Cu/ TiO_2 interfaces for transmission of photo-generated electrons. Although Cu powders and TiO_2 nanopowders are separated in the nanopowder mixture, loose physical contact creates only meager Cu/ TiO_2 numbers of interfaces in the catalyst. These factors give reasonable explanations of the photocatalytic experimental results.

Fig.6 Photocatalytic decomposition of MB with Cu- TiO_2 composite powders, nanotubes photocatalysts as well as the blank test under visible irradiation

4 Conclusions

In summary, 1D titanate nanotubes of diameter 10–15 nm, and length of ca 100 nm covered by 5 nm copper nanospheres have been initially synthesized through a simple one-step hydrothermal process. The phase of as-prepared material was converted after calcination for 30 min at 450 °C into anatase and cubic copper. The formation process indicates that there are three principal transformations occurring during the hydrothermal process: formation of titanate nanotubes, reduction in copper nanoparticle diameters, and surface adsorption of copper nanoparticles onto the titanate nanotubes. Acid washing agent was necessary in the final phases of material preparations and a TBT amorphous titanium source proved to be indispensable in the hydrothermal process. Intense absorption and high photocatalytic activity under visible light suggests that this unique architectural material has significant potential applications in many areas, such as environmental applications and solar cell technologies.

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