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Preparation and Photo-catalytic Activity of Cu-Supported Nano-TiO₂

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Abstract: Cu-supported nano-TiO₂ catalyst was prepared by forced hydrolysis method under mild condition. The morphology, composition and optical absorption properties of the samples were characterized by means of scanning electron microscope (SEM), X-ray photoelectron spectroscopy (XPS) and UV-Vis diffuse reflectance spectroscopy (UV-VIS DRS). Visible photocatalytic activity of the samples was investigated by photocatalytic degradation experiment on methyl orange. The results indicated that nano-TiO₂ was about 20nm in size with the main form of anatase, and photo response range was significantly broadened after it was loaded on the surface of Cu. The sample possessed high visible light catalytic activity, with the degradation rate of methyl orange reaching 94% under simulated natural light.

Key Words: Nano-TiO₂, Cu, Carrier, photodegradation

1. Introduction

Since Fujishima reported the photocatalytic reaction of water on N-type semiconductor TiO₂ electrode in 1972^[1], unceasing investigations on photo-catalytic features of TiO₂ have been going on^[2]. Nano-TiO₂ semiconductor of powders and thin films possess excellent chemical and physical properties, exhibiting a wide range of application prospects such as sensors, photo-catalysts, self-cleaning materials, photocells and antibacterial materials^[3-6]. However, it is to be noted that there also exist some crucial technical drawbacks for TiO₂ used as photo-catalyst, such as low utilization of solar energy, low conductivity and easy recombination of electron-hole pairs produced by photo-excitation^[7,8]. Meanwhile, it is difficult to split up and reprocess the nano-TiO₂ powder in practical use. Thus immobilizing TiO₂ on a suitable carrier renders it's possible to solve the above problems and increase its catalytic activity by means of synergistic effect. Carriers are commonly used include glass, silica gel, activated carbon, graphene, and metals, etc^[9-12].

Studies reveal that when semiconductor is in contact with metal, Schottky energy barrier effect can be generated. The photogenerated electrons flow from the semiconductor to the metal, which can effectively prevent the recombination of electron-hole pairs in the semiconductor, with the carrier metal being considered as an effective electron capturing trap^[13]. Since the work function of Cu is smaller than the TiO₂ band gap (<387 nm), the photogenerated electrons will flow to Cu, and the holes remain on the surface of the TiO₂ crystal grains when the nano-TiO₂ is supported on the surface of Cu, thereby preventing the recombination of electron-hole pairs and improving the photo catalytic performance of TiO₂. In addition, it is possible to enhance the visible light response of TiO₂ through the combination of semiconductor and metal, making it possible for TiO₂ to degrade organic pollutant under visible light. Yuzhu Jiao and co-workers^[14] prepared TiO₂ film modified by Pt. It was found that TiO₂ has excellent absorption in the visible region (> 420 nm), and more than 90% phenol could be degraded photocatalytically in 13h. In the previous report from Guangjun Chi^[15], Ni/TiO₂ photocatalytic composite with antibacterial function was prepared by electroplating method using stainless steel as the matrix. It was found that the antibacterial rate of the composite was above 95%. Wenfang Wang and co-workers^[16] prepared and studied the micro-structure and properties of Cu/TiO₂ composite coating. Jun Yan and other authors^[17] found that the light absorption threshold of the sample had a redshift from 397.5nm to 448.9nm after preparing TiO₂ on the surface of Cu, which can be attributed to a new energy level appearing below the conduction band after supporting of Cu, resulting in the narrow band gap and red-shift absorption. However, it should be noted that in ref 17 butyl titanate was chosen as raw material for the preparing of TiO₂ on the surface of Cu. Meanwhile a large amount of ethanol was used as organic solvent during the preparation. It is difficult to control the process due to the high reactivity of butyl titanate. In addition, high cost and pollution both render the process unattractive.

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In this paper, Cu-supported nano-TiO₂ was prepared using forced hydrolysis method in a solution of H₂O, with TiSO₄ as raw materials. The surface morphology, chemical composition and optical absorption properties of the prepared samples were characterized. The visible light catalytic activity of the sample was investigated with methyl orange as the pollutant.

2. Experimental

Titanium sulfate used in the experiment is chemically pure (Shanghai Chemical Reagent Co., Ltd.). The purity of Cu powder is 99.5% (Shanghai Jiuling smelting Co., Ltd.). Ammonia, concentrated nitric acid are all in analytical purity and commercially available.

Firstly, TiSO₄ of 2g is dissolved in 50ml distilled water. Then pH value of the TiSO₄ solution was adjusted to 7-8 by adding NH₃·H₂O. A large amount of white precipitate produced in this process was separated by centrifugation after the reaction was completed. The white precipitate was repeatedly washed with distilled water for 3-4 times, and then dispersed into 1 mol/L HNO₃ solution. The mixture was then transferred into a three-necked flask, and was stirred at about 70 °C in water bath to produce TiO₂ sol.

Cu powder was immersed in dilute sulfuric acid to remove the oxide layer on the surface. 100 ml of distilled water, 0.1g of vitamin C and 10 g of Cu powder were added to a three-necked flask equipped with stirring device, and were heated to reflux, followed by dropwise addition of TiO₂ sol under vigorous agitation. After the mixture was further heated to re-flux for 1 hour, Cu powder was separated and washed successively with distilled water and ethanol, and dried under vacuum at a constant temperature (65 °C).

The surface morphology of the samples was observed by XL30S-FEG field emission scanning electron microscopy (FE-SEM). The ultraviolet-visible diffuse reflectance (UV-VIS DRS) spectra of the powders were obtained on Perkin Elmer-Lambda 35 UV-Vis Spectrometer. The test of the sample's XRD was carried out on a powder X-ray diffractometer (Rigaku Dr. Max-2400) using Cu K α radiation. The chemical composition of the sample was analyzed by X-ray photo electron spectroscopy (XPS; ESCASystem;PHI1600X).

The photocatalytic performance of the sample was tested with methyl orange as a contaminant. The visible light source was simulated with a Philips ordinary fluorescent lamp with a power of 25 W. The distance between the sample and the light source was 100 cm, and the target could be uniformly illuminated by the light source. 0.5 g of the sample was laid on a glass container, and 25 ml of methyl orange solution (15 mg/L) was added. The sample was taken out at intervals, and the absorbance of methyl orange at 465 nm was measured on a spectrophotometer (Shimadzu Corporation 1501). The degradation rate of methyl orange was calculated according to Beer's law.

3. Results and discussion

3.1 Surface topography of the sample

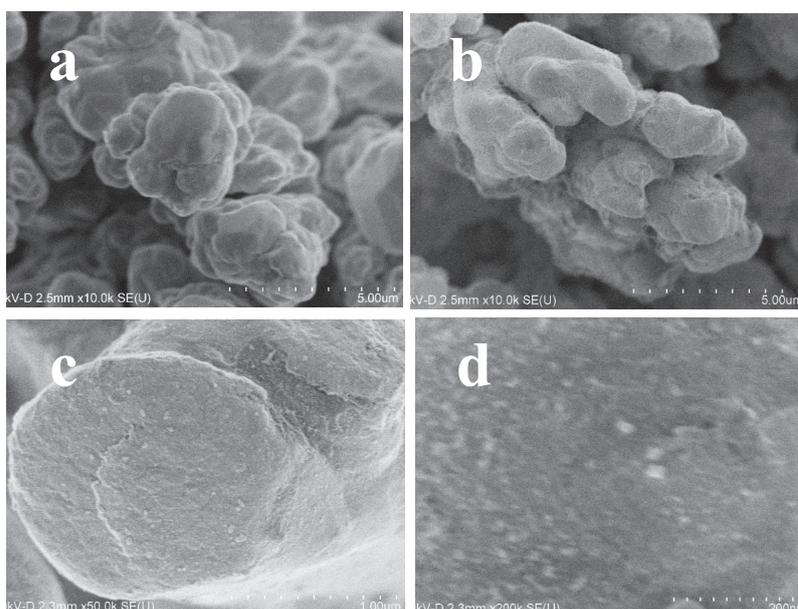


Figure 1. SEM images of Cu particle (a), Cu-Supported Nano-TiO₂ (b, c and d)

The surface morphology of Cu particle and Cu-Supported nano-TiO₂ was microscopically analyzed by field emission scanning electron microscopy (SEM), as shown in Fig.1. It can be observed from fig.1(a) that Cu particle displays an irregular particle stacking state with smooth surface. Fig. 1 (b), (c), (d) provides pictures of different magnification of Cu particle surface with the presence of TiO₂. As shown in the images, the surface of Cu particle is covered with sediments composed of particles of different sizes. In the enlarged photo (fig.1d), the particle is about 20nm in size. The results indicate that nano-anatase TiO₂ particles can be obtained by forced hydrolysis method with titanium sulphate as raw materials. Due to the low phase conversion temperature and short crystallization time, the prepared TiO₂ particles, featuring large specific surface area^[18], are easy to deposit on the surface of Cu particle to form a coating layer.

3.2 Surface chemical compositions of the samples

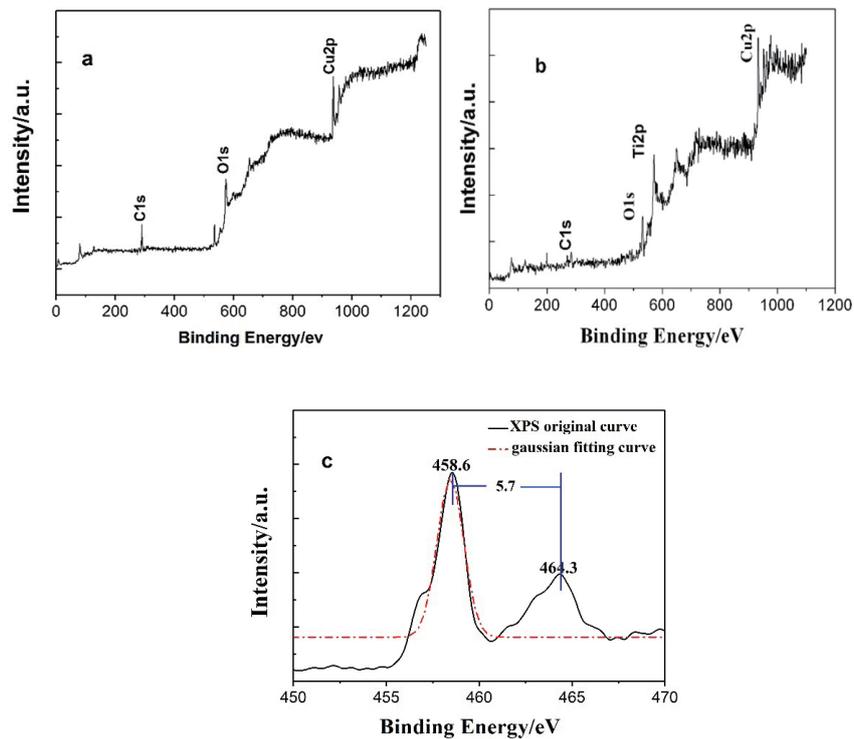


Figure 2. XPS of Cu particle (a), Cu-Supported Nano-TiO₂(b) and Ti2p(c)

The surface chemical composition of the sample is presented in Fig. 2. As presented in Fig. 2(a), C1s, O1s and Cu2p peaks appear on the surface of Cu particle, indicating that the surface is mainly metallic Cu with oxidized component such as Cu²⁺. C, O, Ti and Cu elements appear on the surface of the sample loaded with TiO₂, as shown in Figure 2(b). Figure 2(c) shows the spectrum of the Ti2p in the sample, in which Ti2p1/2 and Ti2p3/2 appear at 458.6eV and 464.3eV, respectively. The Ti2p3/2 and Ti2p1/2 spin-orbital-splitting is about 5.7eV, and the ratio of the two peaks remains about 0.5, indicating the presence of Ti⁴⁺^[19].

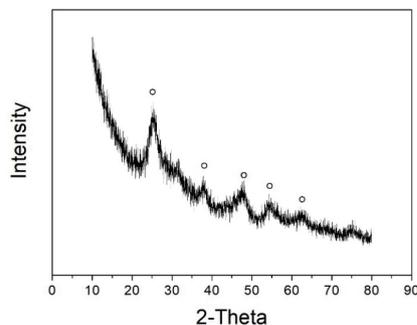


Figure 3. X-ray diffraction patterns of TiO₂

In order to further determine the structure of TiO₂ on the surface, TiO₂ powder was prepared by forced hydrolysis under the same conditions without Cu powder. The XRD spectrum of the prepared TiO₂ powder was shown in Fig.3. The sample diffraction peaks are shown to appear at 25.5°, 37.3°, 47.9°, 54.1°, and 61.1°, corresponding to the (101), (004), (200), (105) and (204) crystal faces of anatase respectively, which indicates the crystal structure of the prepared TiO₂ is anatase (JCPDS No. 99-0008)^[20]. Based on the results of SEM and XPS analysis, it can be reasonably concluded that the Cu-supported anatase nano-TiO₂ sample has been successfully prepared.

3.3 Performance of light absorption of the sample

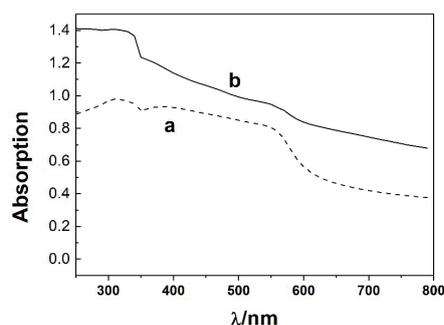


Figure 4. UV-VIS DRS results of Cu particle (a) and Cu-Supported Nano-TiO₂(b)

The UV-Vis diffuse reflection spectrum of the metallic Cu powder (a) and the Cu-supported TiO₂ sample (b) prepared in the experiment were shown in Fig.4. Cu exhibits a strong absorption of light from 400 nm to 550 nm, and the absorption rate gradually decreases as the wavelength increases; TiO₂ itself exhibits noticeable light absorption in the ultraviolet region and almost no absorption in the visible region, while Cu-supported nano-TiO₂ sample, performs a high absorption rate for both ultraviolet and visible light, forming a broad and strong range between 200 nm and 800 nm. The absorption of visible light is partially attributed to the doping effect of Cu²⁺ ion, which will expand the photo response range of TiO₂.

3.4 Photocatalysis performance of the sample

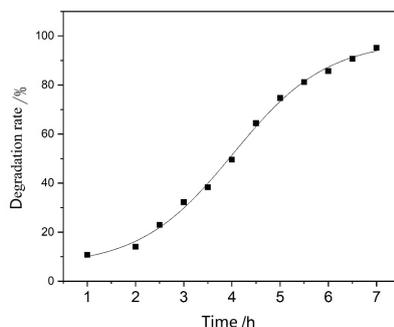


Figure 5. Photo-degradation rate of methyl orange

To investigate the visible light degradation ability of the prepared samples, we selected the aqueous solution of methyl orange with a typical azo-dye molecular structure as the contaminant. Fig. 5 shows the experimental results of degradation of methyl orange, indicating that the sample has a fairly high degradation effect on methyl orange solution under simulated natural light, and the degradation rate reaches above 94% after 7 hours. In view of the relatively low utilization of natural light for TiO₂ itself, however, the light absorption range may be expanded due to the doping effect of Cu²⁺ ion. During the preparation process TiO₂ doped by Cu²⁺, was inevitably produced on the surface of metallic Cu particle. Thereafter impurity energy levels mainly composed of Cu-3d would be introduced near the fermi surface after Cu²⁺ doping, which would form extra energy level to accept the transition of Ti 3d electrons under the visible light irradiation^[21]. Photogenerated electrons could transfer to metallic Cu particle, thus effectively prolonging the life of photogenerated holes, which could be responsible for the fact that the sample can effectively degrade organic under visible light irradiation.

4. Conclusion

Cu-supported Nano-TiO₂ catalyst was synthesized by forced hydrolysis method with TiSO₄ used as main raw materials. It was found that anatase nano-TiO₂ of about 20 nm has been successfully prepared on the surface of Cu particle. The visible light photo catalytic activity of the sample was investigated by photo-degradation reaction of methyl orange. The results indicated that the sample display highly photo catalytic degradation activity under visible light, and the degradation rate of methyl orange reached more than 94% after 7 hours.

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