

Analysis of Light Absorption Properties of Composite Semiconductor Photocatalyst Materials

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ABSTRACT. *The solid material of coupled semiconductor WO-TiO₂ was prepared by a sol-gel method. The photocatalyst WO-TiO₂ supported metallic Cu was prepared by an isovolumic impregnation method. The surface structure, particle size and photo absorption performance of the materials were characterized by XRD, Raman, TPR, IR, TEM, XPS and UV-Vis. The experiment results show that 10wt%WO disperses on the surface of TiO₂ support with one monolayer of non-crystalline phase, average particle size of 1wt%Cu/10wt%WO-TiO₂ is about 15nm. Blue shifting of photo absorption edges is observed clearly after the addition of WO on the surface of TiO₂. The lattice WO forms and photo absorption performance decreases when the supporting amount of WO is more than that of the monolayer phase (>10wt%). The formation of bond W-O-Ti in the solid systems promotes the transfer of generating charge carriers between WO and TiO₂. Loaded metallic Cu accelerates the transformation from the tetrahedrally coordinated W species to the octahedrally coordinated W species.*

KEYWORDS: *Composite semiconductor, Photocatalyst, Material structure, Light absorption performance*

1. Introduction

Semiconductor heterogeneous photocatalysis is a new research field developed in the past 20 years. Scientists have done a lot of research on it, explored the principle of the process, and made efforts to improve the efficiency of photocatalysis. At present, among the semiconductor catalysts used for heterogeneous photocatalytic reactions, TiO₂ is most commonly used for its non-toxic, high catalytic activity and good stability. However, single TiO₂ semiconductor has disadvantages such as poor structural stability of active anatase at high temperature, high carrier recombination rate and low quantum efficiency. In recent years, studies have shown that dual compound semiconductor is the effective measure to improve the activity of photocatalyst, such as a MoO₃ TiO₂, TiO₂-ZnO and TiO₂-WO₃ etc,

born two semiconductor compound can make the light carrier transport and separation between different level semiconductor, extend the life of the carrier, thus improve the quantum efficiency, and semiconductor compound can change the size of the particles, the band gap of the semiconductor and the spectral absorption range adjustment. Schottky barrier effect can be generated when semiconductor surface and metal contact, carrier redistribution. The photogenerated electrons flow from the semiconductor to the metal, which can effectively prevent the electron-hole pair combination on the semiconductor, so the loaded metal is regarded as an effective electron capture trap. At present, there are many researches on precious metal loading such as Pt/Fe₂O₃/TiO₂ system. Few studies have been conducted on metal Cu-loaded composite semiconductors.

In this study, metal Cu was supported on the composite semiconductor TiO₂-pbO, and a series of characterization methods were used to study the influence of the structure of composite semiconductor on the photocatalyst's light absorption performance.

2. The experiment

1.1 Preparation of Catalyst

A certain amount of butyl titanate and anhydrous ethanol in the same volume were strongly stirred in 333K water bath to obtain uniform alcohol solution A. Different concentrations of lead acetate in aqueous solution B were prepared. Add concentrated hydrochloric acid to A, slowly drop human B solution into A solution to form A transparent sol, and continue to stir strongly until the gel is formed. The gel was left to age at room temperature for 24 h, dried, and washed to remove chloride ions (AgNO₃). Solution test), 773 K roast for 5 h. The solution was impregnated, dried, and roasted for 5 h at 773 K. The required solid material Cu/PbO-TiO₂ photocatalyst was obtained by reducing 5% H₂ / N₂ mixture at 623 K for 5 h. Among them, the mass fraction of Cu active component oxide was 1%, and the mass fraction of PbO was 5%, 10%, 15% and 20%, respectively, which were marked as CuPbT- 1, CuPbT - 2, CuPbT - 3 and CuPbT - 4.

1.2 Characterization of Catalyst

The phase structure of the catalyst was determined by BDX3300 X - ray diffractometer. Experimental conditions: radiated CuK_α, tube voltage 27.5kV, tube current 25mA, scan range 2θ=10~80. The catalyst was reduced with H₂ / N₂ mixed gas with a volume ratio of 5%. The reducing gas flow rate was 35 mL /min, the heating rate was 8K/min, and the bridge current was 120mA. The JEM-CX-II transmission electron microscope to observe the particle size of solid materials directly. The sample particles were ground into ethanol suspension solution, which was dispersed by ultrasonic shock and dropped on the surface of the copper mesh for observation. BET specific surface area of the solid material was determined by the

CHEMBET3000 pulsed gas chromatograph of Qualltachmm. RFS100 / S FT-Ra-man spectrometer of BRUKER company was used to determine the Raman spectrum of photocatalytic materials. The samples were tested with Lambda 35 uv-visible spectrophotometer from PE company, and the wavelength range was 250 ~ 1100 nm.

2. Results and discussion

2.1 Cu/Pbo-TiO₂ Catalyst Structure

Figure 1 shows the XRD patterns of CuPbT series catalysts calcined at different temperatures. As can be seen from figure 1, the calcined sample at 573K has no diffraction peak and is amorphous. At 673K, crystallization began, and obvious diffraction peaks appeared. The amorphous morphology was transformed into anatase structure. The diffraction peaks were all characteristic diffraction peaks of anatase TiO₂. With the increase of roasting temperature, the crystal shape tends to be perfect, and the diffraction peak is narrow and sharp. When the mass fraction of CuO and PbO were 1% and 10% respectively, the characteristic diffraction peaks of CuO and PbO did not appear, indicating that CuO and PbO formed monolayer or submonolayer dispersion on TiO₂ carrier, and this dispersion state was thermodynamically stable. Since the Pb²⁺ ion radius (0.119 nm) is much larger than the Ti⁴⁺ ion radius (0.061nm), the Pb²⁺ ion cannot partially replace the Ti⁴⁺ ion and infiltrate into the TiO₂ lattice, which can cause TiO₂. Lattice distortion and crystal symmetry decrease, so the peak intensity of anatase decreases and widens with the increase of Pb load in the XRD spectrum. When the PbO content is 20%, the characteristic peak of PbTiO₃ appears, and the crystal phase PbTiO₃ is generated, indicating that PbO accumulates on the TiO₂ grain surface in the form of composite oxide on the surface of TiO₂ carrier, forming the so-called second phase. Sample 873 K had rutile phase formation, and the crystal phase transition temperature was much higher than that of pure TiO₂ at 723K (not included in figure 1). This was due to the strain energy accumulated by the lattice distortion of TiO₂, which prevented the grain growth of rutile phase, thus inhibiting the phase transition of titanium dioxide.

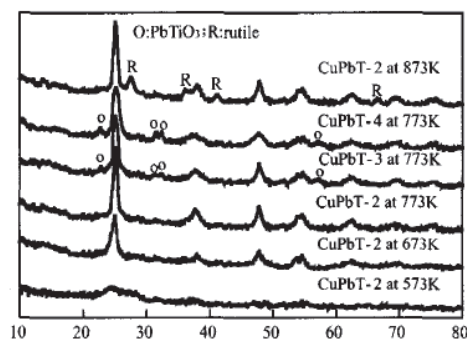


Fig.1 Xrd Patterns of Cupbt Series Catalysts Roasted At Different Temperatures

The TPR curve of catalyst is shown in FIG. 2. The reduction peak of 1% CuO/TiO₂ reduction curve at 493 K is the CuO reduction peak supported on TiO₂, and its peak temperature is lower than the reduction temperature of pure CuO, which is the small size effect caused by CuO's high dispersion on the surface of TiO₂ and small particle size. The 602 K reduction peak is attributed to the reduction of lattice oxygen in the cu-o-ti bond. The reduction peak of PbO appeared at 803 K, and the reduction temperature of PbO decreased by 30K when metal cu was supported, indicating that the introduction of cu promoted the redispersion of PbO on carrier TiO₂. When the PbO load exceeds 20%, a small reduction peak appears at 925k, which corresponds to the reduction of PbTiO₃, which is consistent with the XRD characterization results.

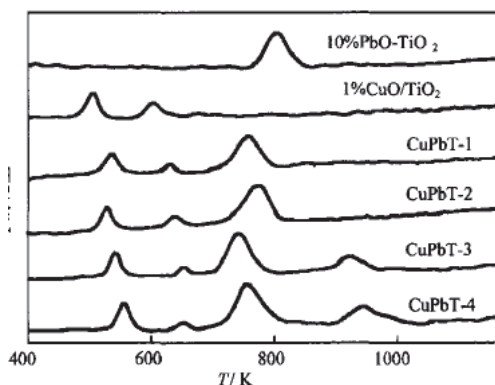


Fig.2 Tpr Spectra of Cupbt Series Catalysts

Figure 3 shows the Raman displacement peak of TiO₂. The Raman characteristic peak of anatase TiO₂ was observed in 145, 196, 39, 56, 16, 639 cm⁻¹. As can be seen from figure 3, when the PbO content reaches 20%, the crystal phase PbTiO₃ is generated, corresponding to the characteristic Raman peak of 83,207,287 cm⁻¹, which is consistent with the results of XRD and TPR.

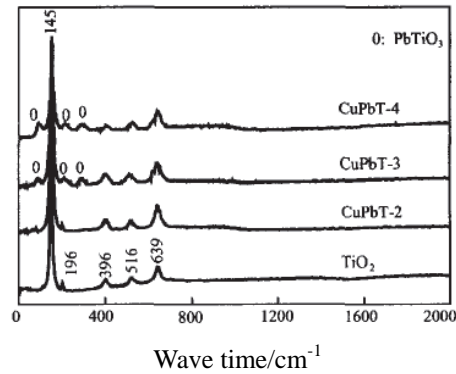


Fig.3 Raman Spectra of Solid Materials

2.2 The Absorbency of the Catalyst

FIG. 4 is a comparison of the light absorption properties of the prepared solid materials. It can be seen from figure 4 that TiO_2 has a better absorption performance in the ultraviolet region, and the visible part has almost no absorption. The absorption of the composite semiconductor in the ultraviolet region of 200-400 nm is close to that of TiO_2 , which indicates that the absorption performance of the composite semiconductor is similar to that of TiO_2 and superior to PbO (figure 4a-c). With the introduction of PbO , the absorption limit of the composite semiconductor was redshifted, and the absorption limit of the composite semiconductor was significantly blue-shifted after the supported metal coating, indicating that the band gap of TiO_2 was broadened and photogenic carriers with stronger oxidation and reduction ability were generated under ultraviolet light. The absorption of visible light by solid materials under the load of metal Cu is significantly increased, with the absorption rate above 0.5, indicating that metal Cu has a strong absorption of visible light. It is important to note that in the photocatalytic reaction, ultraviolet light as light source, electrons and holes for the electrons produce light students provide energy, the stronger the absorption ability, show that the higher light utilization efficiency, stimulate a hole on the more the number of electrons, the equivalent of improved the activity of photocatalytic oxidation, reduction, and improve the activity of reaction.

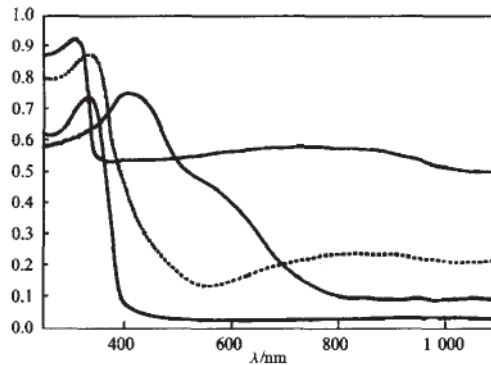


Fig.4 Uv-Vis Spectra of Solid Materials

As can be seen from FIG. 5, with the increase of PbO content, the absorption limit of the photocatalyst blue shifted. When PbO content reaches 10%, the absorption limit blue shifts to 364,310 nm and the ultraviolet absorption reaches 0.92. The PbO content continues to increase, the absorption limit is red shifted, and the absorption of ultraviolet part is significantly reduced. This is due to the fact that PbO is destroyed in the highly dispersed state of TiO₂ surface, and the appearance of PbTiO₃, a crystalline phase with poor photoactivity, leads to the decline of photocatalyst's absorption performance. On the other hand, the particle size of the composite solid material increases, the specific surface area decreases, and the composite semiconductor surface lacks center, resulting in the decrease of the optical quantum efficiency.

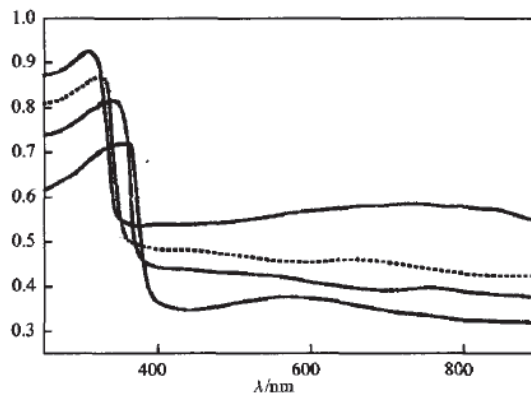


Fig.5 Uv-Vis Spectra of Catalysts with Different Pbo Contents

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