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Synthesis and photocatalytic properties of nanocrystalline Au, Pd and Pt photodeposited onto mesoporous RuO_2-TiO_2 nanocomposites

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ABSTRACT

Noble metals (Au, Pd and Pt) have been photodeposited onto hexagonal mesoporous RuO_2-TiO_2 nanocomposites to study their influence on the photocatalytic activity under UV and visible lights by determination of the formation rate of HCHO generated by photooxidation of CH_3OH in aqueous solution. X-ray diffraction (XRD) patterns and N_2 sorption isotherms reveal that highly crystalline TiO_2 and mesoporous structure have been formed with high surface area (150–180 m^2/g) and pore diameter ranging from 6.8 to 7.3 nm. TEM measurements show that the framework of the highly crystalline mesoporous RuO_2-TiO_2 is composed of anatase phase grown along [1 0 1] direction. The dependence of HCHO formation rate on the noble metals/RuO_2-TiO_2 nanocomposites, behaves quite differently depending on noble metals as electrons sink. Under UV light, the findings reveal that Pd/RuO_2-TiO_2 offers an improvement in term photooxidation rate of CH_3OH and photonic efficiencies over Pt/RuO_2-TiO_2 and Au/RuO_2-TiO_2. However, under visible light, the photocatalytic activity of mesoporous RuO_2-TiO_2 containing Au nanoparticles towards CH_3OH oxidation is remarkable and the photonic efficiency of RuO_2-TiO_2 has been improved two times. Pt and Pd nanoparticles could not be observed in any improvement in photocatalytic activity of RuO_2-TiO_2 under visible light.

1. Introduction

TiO_2 anatase can only be excited by UV irradiation ($\lambda < 380$ nm) because of its large band gap energy of 3.2 eV. Moreover, the rapid recombination of photoinduced electrons and holes greatly lowers the quantum efficiency [1]. Therefore, it is of great interest to improve the generation and separation of photoinduced electron–hole pairs in TiO_2 for further applications. The manipulation of semiconductor heterostructures is one of the effective methods for photoinduced electron–hole generation and separation in recent years [2,3]. Multiple-semiconductor devices can absorb a larger fraction of the solar spectrum, which is beneficial for the excitation of the semiconductor and thus the photoinduced generation of electrons and holes. Moreover, the coupling of two different semiconductors could transfer electrons from an excited small band gap semiconductor into another attached one in the case of proper conduction band potentials [4–6]. This favors the separation of photoinduced electrons and holes and thus improves the photocatalytic efficiency of semiconductor heterostructure dramatically.

The metal-semiconductor (MS) contact is one of the most widely used rectifying contacts in the electronics and photocatalysis applications [7]. When a metal and a semiconductor are joined to form MS interface, a significant redistrubtion of charge is expected to take place due to overlap of wave functions from two sides [7b]. Due to the technological importance of Schottky barrier and the most simple of the MS contact devices which are of the importance in the electron–hole separation, and, indeed, in the photocatalytic process. The nonideal behavior observed in Schottky barrier diodes has been generally attributed to the effect of interface states and the interfacial layer, which are present between metal contact and semiconductor. Thereby, the performance and reliability of Schottky barrier diodes generally depend on interface state density and their energy distribution [8]. Doping of noble metals (Au, Pd, Ag, Pt) with mesoporous TiO_2 photocatalysts was proposed to enhance the photocatalytic activity due to their different Fermi levels, characterized by the work function of the metals and the band structure of the semiconductors. Upon contact, a Schottky barrier can be formed between the TiO_2 and the noble metals, leading to a rectified charge carrier transfer [9–12].

3D mesoporous TiO_2 network acts as an antenna system transferring the initially generated electrons from the location of light

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