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We succeeded in preparing two kinds of RuS_2 nanoparticles with different solvents. Both the RuS_2 particles were coupled with TiO_2 particles to form different TiO_2/RuS_2/ITO films, respectively. In the electroassisted photocatalytic degradation of dodecylbenzene sulfonate (DBS), the TiO_2/RuS_2/ITO films exhibited improved photocatalytic efficiency compared to the TiO_2/ITO film and the TiO_2/RuS_2(in sulfolane)/ITO film showed higher efficiency than the TiO_2/RuS_2(in water)/ITO film did.

Keywords: TiO_2/RuS_2/ITO film; photocatalytic degradation; DBS

INTRODUCTION:

Photoelectrochemical conversion and photocatalytic degradation using TiO_2 nanoparticles have attracted considerable interest in recent year [1-3]. However, the efficiency of the photocatalysis is not high enough. One factor is that the TiO_2 system only utilizes the UV region of light. Another is the quick recombination between photoinduced charge carries. RuS_2 is a narrow band-gap semiconductor (Eg~1.85ev). Adding these particles to the TiO_2 system can be viewed as a promising method to extend the spectral response of the TiO_2 and restrain the

recombination between photogenerated charge carries [4,5]. The application of this method to the electroassisted photocatalytic degradation of pollutants has not been reported. Here, we monitored the photodegradation of DBS with single and coupled TiO_2 immobilized thin film electrodes assembly.

Experimental Section

Two kinds of RuS_2 particles are separately prepared by bubbling H_2S through $RuCl_3$ solutions with two solvents, *i.e.*, water and sulfolane. TiO_2/ITO, TiO_2/RuS_2(in sulfolane)/ITO and TiO_2/RuS_2(in water)/ITO films are fabricated by spreading the TiO_2 colloid and the mixture of 1.2g TiO_2 and 2mL(0.04mol/L) RuS_2 suspension on ITO glasses respectively, then dried in air and sintered at 703K for 30min.

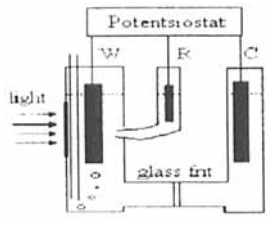

Fig.1 Schematic diagram of electro-assisted photodegradation: W. working electrode R.reference electrode (SCE) C. counter electrode (Pt wire).

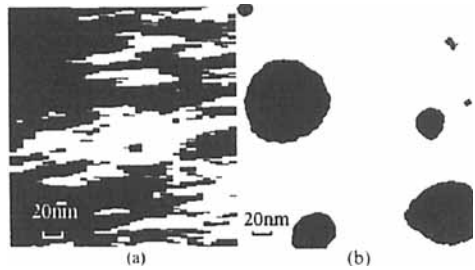

Fig.2 TEM Pictures of RuS_2 nanoparticles prepared in: a. sulfolane b. water

The schematic diagram of the photoelectrochemical cell used to degradate DBS (2.46×10^{-5}M, pH 9) is shown in Fig.1. An anodic bias of 0.6Vvs.SCE is applied to the electrodes and three kinds of thin film electrodes are utilized as working electrodes separately.

Results and Discussion

The TEM pictures of RuS_2 particles are shown in Fig.2. RuS_2 particles prepared

from sulfolane have regular sizes of about 10nm, and those from water vary in sizes from 10nm to 150nm. The result indicates that sulfolane, as a solvent, is better than water in preparing RuS_2 particles.

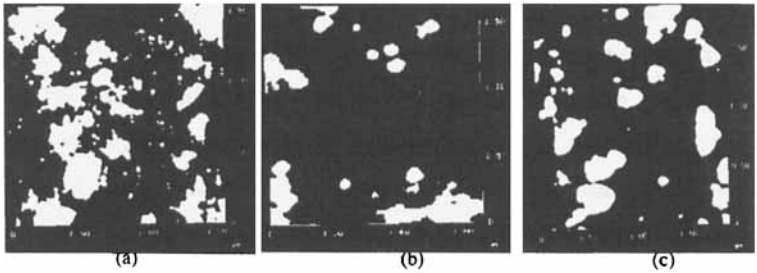

Fig.3 AFM images of different film electrodes: a. TiO_2/ITO electrode b. TiO_2/RuS_2 (in sulfolane)/ITO electrode c. TiO_2/RuS_2 (in water)/ITO electrode

The AFM images of electrodes are shown in Fig.3. Because of interconnected particles and pores, these electrodes have a kind of microporous structure, which is conducive to the reaction. The RuS_2 particles can be confirmed in TiO_2/RuS_2/ITO films. The particles are different from those in the TiO_2/ITO films. The degree of aggregation of coupled TiO_2/RuS_2 (in sulfolane) particles is lower than that of coupled TiO_2/RuS_2 (in water) particles in ITO glass.

Absorption spectra are shown in Fig.4. Single TiO_2/ITO film exhibits an absorption below 390nm corresponding to a band-gap of $\backsim$3.2eV. Coupled TiO_2/RuS_2 (in sulfolane)/ITO film displays an absorption in visible range, which greatly improves the ratio of light utilization.

Fig.5 shows that the photocatalytic reactions occur at a higher rate with the two coupled film electrodes. Semiconductors absorb visible light to produce photoexcited electrons in conduct band and holes in valence band. Photogenerated electrons from RuS_2 transfer into TiO_2 particles while holes remain in RuS_2 particles, preventing quick recombination between photogenerated electron-hole pairs. So the coupled system can improve the photocatalytic degradation efficiency.

Fig.5 also shows that efficiency of photocatalytic degradation of TiO_2/RuS_2 (in sulfolane)/ITO film is higher than that of TiO_2/RuS_2 (in water)/ITO film. The smaller the RuS_2 particles, the quicker diffusion of the electron from the bulk to the surface is, and the less possibility of recombination of electron and hole. Therefore the efficiency of separation of charges is higher. With the decrease in the sizes of coupled film particles, moreover, the number of atoms on the surface increases quickly, which leads to the improved efficiency of light absorption. Furthermore, larger surface area can promote the absorption of reaction. In summery, the photocatalytic efficiency of theTiO_2/RuS_2/ITO (in sulfolane) is higher.

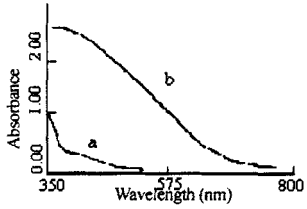

Fig.4 The absorption spectra of the working electrode (a) bare TiO_2 thin film electrode (b) coupled TiO_2/RuS_2 (in sulfolane)/ITO film electrode

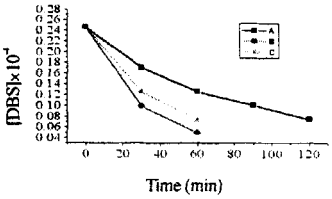

Fig.5 Dependence of DBS degradation rate on the different working electrode (a) single TiO_2 film electrode (b) coupled TiO_2/RuS_2 (in sulfolane)/ITO film electrode (c) coupled TiO_2/RuS_2 (in water)/ITO film electrode.

Acknowledgments

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