Development of a visible-light sensible ZnS-ZnO photocatalyst and the enhanced photocatalytic activity of Pt/ZnS-ZnO under visible light irradiation

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Introduction

Recently, a lot of studies have been concentrated on the degradation of toxic organic compounds in waste water via photocatalysis of various semiconductors [1,2]. Especially, TiO_2 with anatase phase has been most widely investigated due to its acceptable photocatalytic activity and chemical stability. However, it is generally known that TiO_2 can barely absorb visible light due to its wide band-gap energy (3.2 eV) and this is one of the most serious obstacles associated with its further application [3].

To synthesize a visible-light driven photocatalyst, making solid solution between two semiconductors, which have large and narrow band gap, has been suggested [4,5]. In this study, ZnS and ZnO were adopted to synthesize a solid solution since they are cheap and easily obtained. Thus, a composite semiconductor of ZnS and ZnO was developed through co-precipitation and it was named as 'ZnS-ZnO'. We ascertained that ZnS-ZnO recorded much superior activity for degradation of an organic pollutant under visible light irradiation than both sole ZnS and ZnO. In addition, Pt was photodeposited on ZnS-ZnO to prohibit recombination of excited electrons, and we confirmed that Pt/ZnS-ZnO showed better activity than ZnS-ZnO.

Materials and Methods

The ZnS-ZnO photocatalyst was prepared through co-precipitation process of $Zn(NO_3)_2$ in a mixed solution of Na_2S and NaOH followed by drying and calcination at 400°C for 2h. Pt was deposited on ZnS-ZnO by irradiating the mixed solution of hexachloroplatinic acid (H_2PtCl_6) and the photocatalyst for ca. 5h. Result samples (ZnS-ZnO, Pt/ZnS-ZnO) were characterized by using XRD, FE-SEM, EDS, XPS, and UV-Vis DRS. 4-chlorocatechol (4-CC) was selected as an organic pollutant and a 300W ozone-free Xenon-arc lamp with a cut-off filter was adopted as a light source. A mixture of 4-CC and the samples were irradiated for 120 min to observe photocatalytic activities under visible light illumination.

Results and Discussion

According to DRS data shown in Fig. 1, the plots afford the threshold wavelength from 359, 397, and 520 nm for ZnS, ZnO, and ZnS-ZnO, respectively. This absorption features indicate that ZnS-ZnO has the most predominant visible light absorptivity among the semiconductors. This substantial red-shift of ZnS-ZnO seemed to occur due to the formation of solid solution between ZnS and ZnO. Calculated band-gap energies were ca. 3.5, 3.1, and 2.7 eV for ZnS, ZnO, and ZnS-ZnO, respectively. We were assured that this band-gap diminution has caused the advanced visible light absorptivity of ZnS-ZnO. Therefore, ZnS-ZnO recorded better activity for the degradation of 4-CC than sole ZnS or ZnO under visible light irradiation, as it was shown in Fig. 2.

We also developed the Pt/ZnS-ZnO photocatalyst by means of photodeposition process. Hexachloroplatinic acid was used as a precursor and 5 wt% of Pt was deposited on the ZnS-ZnO photocatalyst. According to photodegradation result shown in Fig. 2, we confirmed that Pt/ZnS-ZnO showed better activity for the degradation of 4-CC than ZnS-ZnO. It has been generally accepted that Pt particles deposited on various photocatalysts play an important role in trapping excited electrons, thus they prevent the electrons from recombinating [6,7]. When visible light is irradiated to the ZnS-ZnO photocatalyst, electrons in valence band would be excited into conduction band, and hydroxide radicals (·OH) should be formed via oxidation of water intermediated by holes. These hydroxide radicals are crucial since it breaks the phenyl group of 4-CC, however, the recombination of electron-hole pairs interrupts the formation of ·OH. The Pt particles are able to trap excited electrons, thus they relieve the recombination during the photocatalysis. Therefore, the enhanced photocatalytic activity of Pt/ZnS-ZnO occurred as it was shown in Fig. 2.

Significance

To the best of our knowledge, it was the first try to develop the ZnS-ZnO and Pt/ZnS-ZnO and apply them as visible-light sensible photocatalysts.

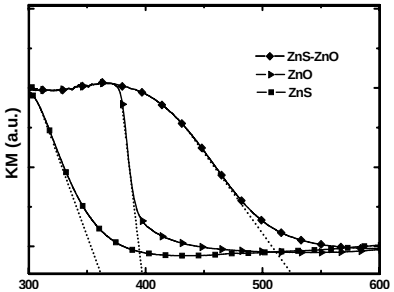

Figure 1. UV-Vis diffuse reflectance spectra (DRS) of ZnS, ZnO, and ZnS-ZnO

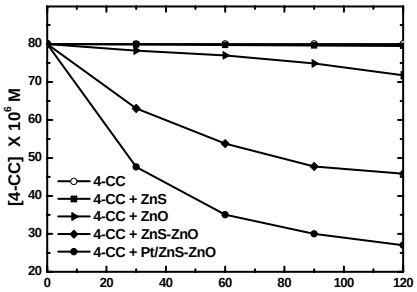

Figure 2. Photocatalytic activities of ZnS, ZnO, and ZnS-ZnO. 4-CC concentration = 80 mM, catalyst amount = 1 g l^{-1}.

References

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