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A comparative study of photocatalytic activity of ZnS photocatalyst for degradation of various dyes

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ABSTRACT

A simple chemical precipitation method is used to synthesize the cubic phase of ZnS nanoparticles. The crystal structure, phase purity, surface morphology, optical and photoluminescence properties, and photocatalytic activity of ZnS nanoparticles were studied using X-ray diffraction (XRD), fourier transform infrared (FTIR) spectra, Raman spectrometer, X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), UV–vis spectrophotometer, fluorescence spectrophotometer and 721 spectrophotometer. XRD, FTIR, Raman and XPS analysis indicates that the ZnS nanoparticles has a cubic phase with the cell parameter a = 5.406 Å without the presence of any other impurities. SEM image shows that the average particle size of ZnS nanoparticles is about 40 nm. Optical properties and photoluminescence experiment confirmed that the Eg value is found to be 3.21 eV and the emission spectra are made up of four emission bands at 345, 408, 444 and 510 nm under excitation wavelength at 290 nm. Photocatalytic experiment results indicate that the pure ZnS nanoparticles exhibits an obviously enhanced photocatalytic activity for degradation MO, and MR dyes than degradation MB, and XO dyes due to the ZnS nanoparticles can easily degradation the —N═N— bonds. Based on the electrochemical measurement and photocatalytic experiment, a possible photocatalytic mechanism for degradation of various dyes in presence of the ZnS nanoparticles are analyzed.

1. Introduction

Semiconductor photocatalysts has been attracting a great deal of research interest for a long time from the fields of electrochemistry, catalysis, and photochemistry due to its high chemical stability and photocatalytic activity [1]. Zinc sulfide (ZnS) is a well-known semiconductor photocatalyst, and exhibit a wide-band gap energy (3.2–4.4 eV), a large exciton binding energy (40 meV), a small Bohr radius and high activity [1]. Therefore, the ZnS semiconductor photocatalyst has attracted extensive attention due to its potential applications in flat-panel displays [2], ultraviolet-light-emitting diodes [3], photocatalysts [4], and infrared windows [5]. It is well known that the photocatalytic activity of the semiconductor photocatalyst highly dependent on their sizes, dimensions, defects and surface morphologies. Nanostructured ZnS are expected to exhibit

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enhanced photocatalytic activity which are usually absent in their bulk materials. Therefore, many efforts have been done on the preparation of ZnS nanoparticles.

Recently, various routes have been used to synthesize ZnS nanoparticles, includes solid-state reaction [6], wet chemical method [7,8], microwave irradiation [9,10], chemical co-precipitation method [11–13], reverse micelles method [14], spray pyrolysis [15], aqueous chemical method [16], UV-assisted approach [17], hydrothermal method [18], green chemical route [19], solvothermal method [20], and so on. Among these methods, the chemical co-precipitation method is a very good method for the synthesis of ZnS nanoparticles due to this route has some advantages includes high purity, low temperature synthesis, precise control over the stoichiometry, and high chemical homogeneity [21]. In addition, although the ZnS nanoparticles have been used to degradation of various dyes [22–26], however, no comparative study of the photocatalytic activity and photocatalytic mechanism has been reported yet for degradation of various dyes in presence of the ZnS nanoparticles. Therefore, it is interesting to synthesis and study the photocatalytic activity of the ZnS nanoparticles.

Herein, we have prepared the cubic phase of ZnS nanoparticles via a simple chemical precipitation method. The crystal structure, phase purity, surface morphology, optical and photo-luminescence properties, and photocatalytic activity of ZnS nanoparticles have been analyzed. Four different azo dyes includes methylene blue (MB), xylenol orange (XO), methyl orange (MO), and methyl red (MR) are used to study the photocatalytic activity of ZnS nanoparticles. Possible photocatalytic mechanism for of the ZnS nanoparticles for degradation of various dyes are proposed on the basis of the electrochemical measurement and photocatalytic experiment.

2. Experimental

2.1. Materials preparation

A simple chemical precipitation method is applied to synthesis the ZnS nanoparticles. According to the formula ZnS, 1M of $ZnCl_2$, 1 M of Na_2S and 0.015 M of capping agent were dissolved in the deionized water. The obtained mixed precipitates were washed about five to six times in double distilled water. Subsequently, above precipitates were separated by centrifugation at 4000 rpm and dried at 150 °C for 48 h in a thermostat drier.

2.2. Materials characterization

The phase purity of the ZnS nanoparticles was determined by means of X-ray powder diffraction (XRD) with Cu Kα radiation in λ = 1.5418 Å. Fourier transform infrared (FTIR) spectra were measured by a Bruker IFS 66 v/S spectrometer. Raman spectra were recorded using a Raman spectrometer. X-ray photoelectron spectroscopy (XPS) of the ZnS nanoparticles was characterized by a KRATOS X SAM 800 x-ray photoelectron spectrometer. The surface morphology of the ZnS nanoparticles was investigated by transmission electron microscopy (TEM). UV–vis diffuse reflectance spectra of the ZnS nanoparticles were measured using a UV–vis spectrophotometer. The UV–vis absorption spectra was obtained by Kubelka–Munk (K–M) theory. Excitation and emission spectra of the ZnS nanoparticles were measured by a SHIMADZU RF-5301PC fluorescence spectrophotometer. The electrochemical impedance spectroscopy (EIS) and Mott–Schottky plots of the ZnS nanoparticles was measured using a CST 350 electrochemical workstation.

2.3. Photocatalytic experiment

The photocatalytic experiments of the ZnS nanoparticles were investigated by the degradation of four azo dyes includes MB, XO, MO, and MR under visible light irradiation with λ = 550 nm and power of 18 W. The initial MB dye concentration was 50 mg/L with ZnS nanoparticles loading of 0.5 g/L. During the degradation process, in order to keep the mixed solution at ambient temperature, the water-cooling system is used to cooled the water-jacketed reactor. Subsequently, the concentration of azo dye at different time intervals were measured by a 721 spectrophotometer. The degradation rate of azo dye is calculate by following formula,

$$D\% = \frac{C_0 - C_t}{C_0} \times 100\% \quad (1)$$

Where C_0 and C_t are the concentration of azo dye before and after visible light irradiation, respectively. For comparison, the photocatalytic activity of the ZnS nanoparticles for degradation of XO, MO, and MR dyes and commercial P25 TiO_2 for photocatalytic degradation of MR dye was also presented under the same photocatalytic experimental conditions.

3. Results and discussion

3.1. Structural analysis

The XRD patterns for the ZnS nanoparticles are shown in Fig. 1(a). It can be seen that the synthesized ZnS nanoparticles exhibit peaks at 2 theta angles of 28.443, 47.850, and 56.879 corresponding to the (111), (220), and (311) planes, respectively. Three peaks can be attributed to the cubic of ZnS phase with the cell parameter a = 5.406 Å for ZnS nanoparticles (JCPDS file