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Preparation and characterization of ZnS nanoparticles deposited on montmorillonite

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ABSTRACT

ZnS nanoparticles were prepared and deposited on montmorillonite (MMT) in the presence of cetyltrimethylammonium (CTA). UV spectrometry and transmission electron microscopy (TEM) proved the formation of nanoparticles with diameters ranging from 3 nm to 5 nm. Selected-area electron diffraction (SAED) patterns revealed the presence of romboedric ZnS. The band gap energy of nanosize ZnS was estimated at 3.89 ± 0.03 eV. Photoluminescence spectra exhibited a strong emission band between 300 nm and 600 nm explained by the vacant ZnS nanostructure.

The prepared ZnS–montmorillonite nanocomposite (ZnS–MMT) was used for the photocatalytic reduction of CO_2 providing a considerably high efficiency that exceeded 5–6-fold the results of commercial TiO_2 Degussa P25. The main reaction products were hydrogen and methane. Methanol and carbon oxide were also observed in about 7-fold lower amounts. The stability of ZnS against oxidation was confirmed by the determination of sulphate using capillary isotachophoresis.

1. Introduction

It has been found that an activity of photocatalysts can be improved by a decrease of their particle size because of an increase in their specific surface area. Nanosized photocatalysts including semiconductors have been used in many industrial applications.

In general, oxidation and/or reduction on a semiconductor nanoparticle begins with the excitation of an electron from the valence band to the conduction band. In this manner, a hole in the valence band is generated. Charge carriers (electrons and holes) can be trapped in surface or deep traps or they can recombine non-radiatively or radiatively producing heat or photoemission, respectively. Finally, they can take part in reduction or oxidation reactions with electron acceptors or donors adsorbed on the surface of photocatalysts.

Zinc sulphide is a semiconductor with a wide direct band gap energy about 3.7 eV. It appears to be a very promising material for photocatalysis due to the rapid generation of electron–hole pairs by photoexcitation and highly negative reduction potentials of excited electrons. The preparation of ZnS nanoparticles often involves using an organic/surfactant stabilizer. Cetyltrimethylammonium (CTA) [7–9], sodium bis(2-ethylhexyl) sulfosuccinate [10,11], L-cysteine, mercaptoethanol [12] and other stabilizers [13–17], or different polymer assistants [18–20] were used to prevent the particles agglomeration keeping their size in the nano-range.

CO_2 is a greenhouse gas representing the largest contribution of human activities. Since CO_2 is a rather inert and stable compound, the reduction of CO_2 is difficult. To convert it by force, severe conditions of high pressures and high temperatures are required. The reduction of CO_2 using photocatalysts is one of the most promising methods because CO_2 can be reduced by the UV radiation at room temperatures and atmospheric pressure. The reduction products are the valuable chemicals, such as methanol, ethanol, and methane that make this method an attractive option to conventional CO_2 removal methods.

The use of ZnS nanoparticles for the photoreduction of carbon dioxide has been described in several papers. The photoreduction was performed in the presence of 2-propanol [21,22], in water [18,23,24] and water with NaH_2PO_4 [25,26], methanol dehydrogenase [27], 2,5-dihydrofuran [1] and triethanolamine [28]. The main products were formic acid and hydrogen [21], formate [1,18,26–28], acetone and formic acid [22,25], four-carbon and two-carbon acids [23] and formaldehyde and ethanol [24].

The SiO_2 matrix was covered with different amounts of ZnS [1], which led to its higher catalytic efficiency. Also, several studies dealt with using montmorillonite as a catalyst support [2–6]. A catalyst prepared by the deposition of semiconductor nanoparticles on montmorillonite (MMT) and/or within the MMT interlayer should combine the effects of both nanoparticles and MMT.

The aim of this work was to prepare ZnS nanoparticles deposited on an inert support like MMT and examine their properties including the photoreduction of carbon dioxide. To produce very small and uniformly dispersed nanoparticles, CTA was used during their formation. ZnS nanoparticles were characterized by the UV and photoluminescence spectrometry, X-ray diffraction and TEM. The CO_2 reduction products were analysed as well.

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2. Experimental

2.1. Materials and chemicals

The used chemicals were of analytical reagent grade: Zinc acetate ($Zn(OAc)_2$), zinc nitrate, zinc sulphate, sodium sulphide, cetyltrimethylammonium bromide (all from Lachema, Czech Republic). Water deionized by reverse osmosis (Aqua Osmotic, Czech Republic) was used for the preparation of all solutions. The TiO_2 photocatalyst Degusa P25 was purchased from Precheza (Czech Republic). TiO_2 properties are given in Table 1.

Na^+-rich montmorillonite SWy 2 (Crook County, Wyoming) with CEC of 1.21 ± 0.06 meq g^{-1} determined by the saturation with NH_4^+ [29] and by the analysis of released metals (Na^+, K^+, Ca^{2+}, Mg^{2+}) was used for adsorption experiments. The structural MMT formula was $(Na_{0.40}K_{0.02}Ca_{0.01})$ $(Al_{1.31}Mg_{0.39}Fe^{3+}_{0.25}Ti_{0.02})$ $(Si_4)O_{10}(OH)_2$ as calculated from the results of X-ray fluorescence analysis. The <5 μm fraction of MMT separated by sedimentation was used. Specific surface area of MMT was determined by the nitrogen adsorption at 46 m^2 g^{-1}.

2.2. Preparation of ZnS nanoparticles

In a typical procedure, 50 mL of the aqueous solution of Na_2S (15 mmol L^{-1}) and CTA (20 mmol L^{-1}) was added drop-wise to 250 mL of the aqueous solution of $Zn(OAc)_2$ (2 mmol L^{-1}) under vigorous stirring. The pH values of the solution, in which ZnS particles were formed, were between 6 and 7. The molar ratio between zinc and sulphur precursors was set to 1:1.5 in order to increase the amount of S^{2-} ions available for the ZnS production and to form particles with low defect structure [9,30]. An optically transparent dispersion with a slight blue coloration originated. 300 mL of this dispersion containing 0.5 mmol ZnS was then shaken with 0.5 g of MMT for 24 h. The resulting ZnS–MMT nanocomposite was filtered, washed a few times with deionized water and dried at 60–70 °C.

ZnS nanoparticles were also prepared under different conditions to study the effect of preparation on their size. Molar ratios between zinc and sulphur (1:1–1:3) and Zn and CTA (1:1–1:3) were changed during the procedure as well as different zinc precursors, such as zinc nitrate and zinc sulphate. Also, in contrast to the above typical procedure mentioned, the zinc acetate aqueous solution was added drop-wise to the aqueous solution of Na_2S and CTA. It caused the pH value of the solution, in which ZnS particles were formed, was between 9.5 and 11.5.

2.3. Used methods for characterization of ZnS–MMT

2.3.1. UV–VIS spectrometry

UV–VIS spectra of ZnS dispersions were measured in 1 cm quartz cuvettes by an UV–VIS spectrometer Lambda 35 (Perkin Elmer, USA).

2.3.2. Atomic absorption spectrometry

The amounts of zinc in ZnS–MMT were measured by atomic adsorption spectrometer (AAS) AA280FS (Varian Inc., Austria) with flame acetylene–air atomization after its dissolution in a mixture of $HClO_4$, HNO_3 and HF [31].

2.3.3. Sulphur analysis

The total content of sulphur in ZnS–MMT was determined by elemental analysis (EA) based on the combustion of samples using CS-244L instrument (LECO, USA) equipped with an IR detector.

2.3.4. X-ray powder diffraction

X-ray powder diffraction study was performed by a powder diffractometer (INEL, France) equipped with a curved position-sensitive detector PSD 120 MB/11 (reflection mode, Ge-monochromatized, Cu $K\alpha_1$ radiation). XRD patterns were taken in an ambient atmosphere under constant conditions (1500 s, 60 kV, 55 mA).

Table 1
Selected characteristics of TiO_2 photocatalyst.

Sample	P25
S_{BET} (m^2 g^{-1})	50
Average diameter (nm)	26
TiO_2 content (%)	99.4
Anatase (%)	75
Rutile (%)	25

Note: Average values were given by the manufacturer, % (w/w).

2.3.5. Transmission electron microscopy

Transmission electron microscopy was carried out on a JEOL JEM 3010 microscope operated at 300 kV (LaB_6 cathode, point resolution 0.17 nm) with an EDX (Energy Dispersive X-ray) detector attached. Micrographs were recorded on a CCD camera with the resolution of 1024 × 1024 pixels using the Digital Micrograph software package. Powder samples were dispersed in ethanol and the dispersions were treated in ultrasound for 10 min. A drop of the very dilute dispersion was placed on a holey-carbon-coated copper grid and allowed to dry by the evaporation at room temperatures. Selected-area electron diffraction patterns were evaluated using the Process Diffraction software package [32].

2.3.6. Photoluminescence spectrometry

Photoluminescence (PL) measurements were performed at a home-made apparatus. Powder samples were placed on quartz substrates and the fluorescence was excited using a cw He–Cd laser at λ = 325 nm. The laser beam (power of about 1 mW) was focused by 10 cm lens onto a front side of samples; the photoluminescence light was collected under about the 45° geometry and focused on an entrance slit of the grating spectrograph with a CCD camera. The spectral resolution of the apparatus was about 0.5 nm. The measurements were performed at room temperatures.

2.3.7. Capillary isotachophoresis

An isotachophoretic analyzer EA 102 (Villa-Labeco, Slovakia) in the column-coupling configuration was employed. Capillaries were made from a fluorinated ethylene–propylene copolymer: a pre-separation capillary 90 × 0.8 mm ID and an analytical capillary 200 × 0.3 mm ID. Both capillaries were equipped with contact conductivity detectors and, in addition, analytical capillary was equipped with an UV detector. The driving current was 250 μA in the pre-separation capillary and 50 μA in the analytical capillary. Sampling was performed with a 30 μL sampling valve.

2.4. Photocatalytic reactivity experiment

The photocatalytic reduction of carbon dioxide was carried out in a home-made apparatus shown in Fig. 1 [33]. The reduction was carried out in a stirred batch annular reactor with a suspended catalyst illuminated by the UV 8 W Hg-lamp (254 nm) with the energy flux of 4.4 mW/cm^2. The CO_2 diffusion from the gas phase through the gas–liquid interface in a laboratory batch slurry reactor was eliminated by saturating the aqueous solutions of 0.2 mmol L^{-1} NaOH with pure CO_2 before the start of reactions [34,35]. During this step, pH decreased from 11.8 to 6.6.

The ZnS catalyst loading of 1 g L^{-1} was chosen to avoid concentration gradients in a bulk of stirred liquid with the catalyst dispersion due to a scattering effect of light as a result of the high catalyst