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Functional and eco-friendly nanocomposite kaolinite/ZnO with high photocatalytic activity

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ABSTRACT

Highly photoactive nanocomposites kaolinite/ZnO with various amounts of ZnO nanoparticles (10 wt.%, 30 wt.%, and 50 wt.%) were prepared using simple hydrothermal method. Calcination of the nanocomposites at 600 °C led to the kaolinite–metakaolinite phase transformation, to further growth of ZnO crystallites, and to significant increase of photodegradation activity. The nanocomposites were studied using X-ray fluorescence spectroscopy, X-ray powder diffraction, Fourier transform infrared, diffuse reflectance and photoluminiscence spectroscopies, scanning and transmission electron microscopies, BET analysis, and molecular modeling using empirical force field. Photodegradation activity was evaluated by the discoloration of Acid Orange 7 aqueous solution under UV irradiation. Leaching tests confirmed strong interaction between kaolinite matrix and ZnO nanoparticles, and, therefore, high stability of prepared nanocomposites.

1. Introduction

Zinc oxide (ZnO), a low-cost semiconductor having large band gap ~3.3 eV, belongs to the most studied and commonly used nanomaterials, mainly for its good photocatalytic, piezoelectric and antibacterial properties. ZnO nanoparticles (NPs) can be prepared via various methods (hydrothermal synthesis [1–4], coprecipitation method [5,6], sol–gel method [7,8], non-aqueous solution method [9], photolysis [10], solid state mixing of precursors [11], thermal decomposition of precursor [12], microwave assisted synthesis [13], vapor deposition techniques [14]) using various precursors (zinc chloride + sodium hydroxide [3,4,8,15], zinc chloride + ammonia [1,2], zinc acetate + sodium hydroxide [3,16–18], zinc acetate + lithium hydroxide [19], zinc acetate + octadecylamine [9], zinc acetate + oxalic acid [6], zinc acetate + acetic acid [20], zinc acetate + hydrogen peroxide [10], zinc nitrate + sodium hydroxide [3], zinc nitrate + citric acid [11], zinc nitrate + ammonia [2], zinc sulfate + sodium hydroxide [3], zinc sulfate + sodium carbonate [21]) and it is known that different reaction conditions give rise to a large scale of resulting morphologies [3,22].

Not only pure ZnO NPs are studied but also various polymer/ZnO composites attracted an attention of researchers: polyurethane/ZnO [5], polyaniline/ZnO [7,16], poly(methyl methacrylate)/ZnO [23]. Although these nanocomposites exhibit some interesting properties, possible release of NPs from polymer into the environment represents a serious problem.

Toxicity of NPs and their potential risk to the environment and human health is still vivid and open topic and a lot of studies dealing with toxicity of ZnO NPs to plants [24], animals [25,26], and human [27] have been reported. Many other studies can be found in exhaustive and comprehensive review published recently by Ma et al. [28]. Based on the results of more than 80 works, Ma et al. concluded that ZnO NPs have toxic effects in both aquatic and terrestrial organisms (microorganisms, algae, plants, aquatic and terrestrial invertebrates, aquatic vertebrates), and for certain species, the toxicity can occur at concentrations as low as less than 1 mg dm^{-3}. This suggests that ZnO NPs, if reaching sufficient level in natural environments, can cause significant risk to the environmental biota [28].

For these serious and compelling reasons, an attention should be focused on nanocomposites in which the ZnO NPs are anchored on suitable solid matrices restricting the movement of NPs but not suppressing their unique properties.

Yang et al. [1] pepared ZnO NPs on pure Cu substrate, Collard et al. [19] synthesized SiO$_2$ substrate from tetraethyl orthosilicate, and Ding et al. [29] studied ZnO/graphene oxide nanocomposite but these approaches are quite expensive and used matrices cannot compete with clay minerals, i.e. layered silicates (phyllosilicates),

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that are abundant and widely available, chemically stable, non-toxic and very cheap.

Bentonite [17], pure montmorillonite [4,8,21], and palygorskite [20] have been succesfully used for the preparation of ZnO-based nanocomposites.

However, although the kaolinite has been found as a suitable matrix for metal oxide NPs [30–32], the preparation of kaolinite/ZnO nanocomposite has been reported only by Ananthakumar et al. [13] (a mechanical mixture of kaolinite and pre-synthesized ZnO NPs).

Therefore, we decided to prepare kaolinite/ZnO nanocomposite and to test its photocatalytic activity. Using a simple hydrothermal method the composites containing 10 wt.%, 30 wt.%, and 50 wt.% of ZnO were prepared. Samples were characterized by X-ray fluorescence spectroscopy (XRFS), X-ray powder diffraction method (XRPD), Fourier transform infrared spectroscopy (FTIR), UV–VIS diffuse reflectance spectroscopy (DRS), photoluminiscence spectroscopy (PLS), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and BET analysis. Molecular modeling using empirical force field has been carried out in order to study structure of nanocomposite and adhesion forces between kaolinite and ZnO NPs. Photocatalytic activity of the composites was evaluated by means of photodegradation of Acid Orange 7 (AO7) model solution. AO7 exhibits the highest absorbance at the wavelength of 485 nm. This maximum corresponds to a double bond between nitrogen atoms in azo group which is cleaved first in the degradation process. Absorbance of intermediate products emerging during the AO7 degradation is minimal at the wavelength of 485 nm [33]. This fact allows direct measurement of the concentration of AO7 using VIS spectrophotometer. Therefore, an efficiency of the photocatalyst can be easily quantified.

2. Preparation and characterization methods

2.1. Preparation of the samples

ZnO NPs were synthesized by the reaction between zinc chloride (anhydrous pure, Lach-Ner, Czech Republic) and sodium hydroxide (G.R. Micropearls, Lach-Ner, Czech Republic) at the molar ratio of Zn^{2+}:OH^- being 1:5. The aqueous solution of prepared zinc chloride was mixed with sodium hydroxide solution and vigorously stirred at 40 °C for 30 min. Kaolinite/ZnO nanocomposite (KAZN) was prepared by addition of the aqueous mixture of zinc chloride and sodium hydroxide solutions into the aqueous suspension of kaoline KKAF (LB MINERALS, Czech Republic) followed by continuous stirring at 100 °C. The mixture was allowed to react for 5 h. The precursors/kaolin ratios were chosen so that the composites contained 10, 30, and 50 wt.% of ZnO. The resulting solid phase was separated by decantation, washed several times with distilled water until the conductivity of filtrate reached the value lower than 100 μS cm^{-1}, and finally dried at 105 °C for 24 h [4]. Such obtained composites are denoted as KAZN1X where 1 means drying at 105 °C and X is the amount of ZnO in the sample (1 for 10 wt.%, 3 for 30 wt.%, 5 for 50 wt.%). The stability of composites was evaluated using leaching test according to the Council Decision 2003/33/EC, i.e. 10 g of composite was added into 100 ml of demineralized water, the solution was shaked for 24 h at 20 °C and, finally, the amount of released Zn was determined.

Composite was calcined at various temperatures (200–1000 °C) for 1 h. Calcined samples are denoted as KAZNTX, where T represents the calcination temperature and X has the same meaning as in the case of dried samples (i.e. the amount of ZnO). For example, KAZN65 was calcined at 600 °C and contains 50 wt.% of ZnO. Based on the results of photodegradation activity test, only dried samples and samples calcined at 600 °C were deeply characterized.

2.2. Characterization methods

2.2.1. X-ray fluorescence spectroscopy

Chemical composition of samples was determined using energy dispersive fluorescence spectrometer (XRFS) SPECTRO XEPOS (SPECTRO Analytical Instruments GmbH) equipped with 50 W Pd X-ray tube. For this measurement, samples in powder form were pressed into tablets using wax as a binder.

2.2.2. X-ray powder diffraction

X-ray powder diffraction (XRPD) patterns were recorded under CoKα irradiation (λ = 1.789 Å) using the Bruker D8 Advance diffractometer (Bruker AXS) equipped with a fast position sensitive detector VÅNTEC 1. Samples in powder form were pressed in a rotational holder and reflection mode was used for all measurements. Phase composition was evaluated using PDF 2 Release 2004 database (International Centre for Diffraction Data).

2.2.3. Fourier transform infrared spectroscopy

FTIR spectra were recorded in the range from 400 to 4000 cm^{-1}. Samples were measured by the ATR technique with diamond crystal on an FTIR spectrometer Nicolet 6700 (ThermoNicolet, USA).

2.2.4. UV–VIS diffuse reflectance spectroscopy

UV–VIS DRS was used for a qualitative description of the differences in the band gap shift depending on the amount of ZnO in the studied composites. UV–VIS DRS of the powder samples placed in a 5.0 mm quartz cell were registered using spectrophotometer CINTRA 303 (GBC Scientific Equipment) equipped with a reflectance sphere. Obtained reflectance spectra were transformed to Kubelka–Munk coordinates (KM) and then expressed using Tauc plot [34] showing the relation $(\mathrm{KM} \times hf)^{1/2} = f(hf)$. Energies of band gap ($E_g$) were evaluated using method described in [35].

2.2.5. Photoluminiscence spectroscopy

Room temperature photoluminescence spectra (PL) of KAZN samples were recorded using FLS920 (Edinburgh Instruments Ltd.) spectrometer at room temperature. Spectrometer was equipped with 450 W Xenon lamp source (excitation wavelength λ = 340 nm). Because of high intensities of calcined samples, 395 nm filter was used for the measurement of middle part of spectra.

2.2.6. Electron microscopy

The morphology of samples was observed on a scanning electron microscope (SEM) Hitachi SU6600 (Hitachi Ltd., Japan) and a transmission electron microscope (TEM) JEOL 2010 HC (JEOL Ltd., Japan). Accelerating voltages were 5 kV and 160 kV for SEM and TEM, respectively.

2.2.7. BET analysis

Before the measurement, all samples in powder form were degassed at 105 °C for 3 h. The measurement was carried out by nitrogen adsorption in a NOVA 4000e (Quantachrome Instruments, USA) nitrogen sorption apparatus. SSA was determined by multipoint BET method using adsorption data in the relative pressure range of 0.1–0.3.

2.2.8. Evaluation of photodegradation activity

Photodegradation activity of the prepared composites was evaluated in a liquid phase, using discoloration of AO7. In order to achieve the adsorption equilibrium in the first part of the experiment, the suspension containing 0.05 g of the photocatalyst, 65 ml of demineralized water, and 5 ml of the AO7 aqueous solution ($c_0 = 6.259 \times 10^{-4}$ mol dm^{-3}) was stirred in the dark for 60 min. After 1 h of the adsorption period in the dark, the suspension was