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Nanocomposites of SnO₂ and g-C₃N₄: Preparation, characterization and photocatalysis under visible LED irradiation

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ABSTRACT

Tin dioxide nanoparticles were prepared in the presence of graphitized carbon nitride (g-C₃N₄) forming nanocomposites with different contents of SnO₂ up to 40 %. G-C₃N₄ was synthesized by heating of melamine at 550 °C in the open air and Sn²⁺ ions were precipitated by sodium hydroxide in g-C₃N₄ aqueous dispersions. Resulting mixtures were dried by freezing at –20 °C and calcined at 450 °C to obtain SnO₂/g-C₃N₄ nanocomposites.

The nanocomposites were characterized by common characterization methods in solid state and in their aqueous dispersions using dynamic light scattering (DLS) analysis and photocatalysis. SnO₂ nanoparticles in the nanocomposites were found to have an average size of 4 nm, however, those precipitated without g-C₃N₄ had an average size of 14 nm. Separation of photoinduced electron and holes via heterojunction between SnO₂ and g-C₃N₄ was demonstrated by photocatalytic decomposition of Rhodamine B (RhB) under LED visible irradiation (416 nm) and photocurrent measurements. The most photocatalytically active nanocomposite contained 10 % of SnO₂. Graphitized carbon nitride was assumed to serve as a template structure for the preparation of SnO₂ nanoparticles with a narrow size distribution without using any stabilizing additives.

1. Introduction

Graphitic carbon nitride is a polymeric material based on melon units, which have already been synthesized by Liebig in 1834. The properties of g-C₃N₄ and related materials have been studied for a long time [1–4]. However, in 2006 Wang et al. [5] published a ground breaking paper about water photocatalytic splitting under visible light using g-C₃N₄, which has started a new interest of scientists in this material. It has extraordinary diamond-like properties, such as thermal, chemical and photochemical stability, due to tri-s-triazine (heptazine) (C₆N₇)-based on building blocks and strong covalent bonds between carbon and nitrogen atoms [2]. Nanoscale g-C₃N₄ has been synthesized as three-dimensional nanoparticles, two-dimensional nanosheets and one-dimensional chains [6]. An important advantage of g-C₃N₄ is its band gap energy of 2.7 eV, which enables absorption of visible light of about 460 nm. That is why various applications of g-C₃N₄ in photochemistry including photocatalysis have been studied [7–11].

However, the photocatalytic applications of g-C₃N₄ are limited by fast recombination of photoinduced electrons and holes, which causes low quantum efficiency. This drawback can be overcome by doping of g-C₃N₄ structures with anions and metal cations [9], by coupling with

metal nanoparticles [12,13] and semiconductor particles and nanoparticles of TiO₂ [14–17], ZnO [18], Al₂O₃ [19], SnO₂ [20], WO₃ [21,22], Ag₃VO₄ [23], BiVO₄ [24], BiIO₄ [25] etc. in order to separate photoinduced electrons and holes.

Tin dioxide is one of the materials having high electrical conductivity and optical transparency, which makes it suitable for various optoelectronic [26], solar cells [27], gas sensing [28], catalytic and photocatalytic applications [29]. It is a semiconductor with a wide band gap of 3.6 eV and, unfortunately, cannot be applied under visible light. Another disadvantage of SnO₂ is fast photoinduced electron-hole recombination [30].

Combination of g-C₃N₄ and SnO₂ could solve the problems of both semiconductors, especially for photocatalytic applications. In comparison with heterojunction photocatalysts like TiO₂/g-C₃N₄, SnO₂/g-C₃N₄ composites have been still less investigated [20,31–33]. The aim of this paper was to contribute to the knowledge of SnO₂ nanoparticles preparation, characterization of SnO₂/g-C₃N₄ nanocomposites and their application in photocatalysis under visible light. The influence of supporting g-C₃N₄ particles on the size of synthesized SnO₂ nanoparticles, which had not been referred by other authors, was observed.

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2. Experimental

2.1. Chemicals

All the chemicals used were of analytical reagent grade. Melamine was purchased from Sigma-Aldrich (USA), NaOH and SnCl₂ were purchased from Lach-Ner (Czech Republic). Water deionized by reverse osmosis (Aqua Osmotic, Czech Republic) was used for preparation of all solutions.

2.2. Preparation of g-C₃N₄

5 g of melamine was placed into a covered ceramic crucible at room temperature and heated in air in a muffle furnace. The heating temperature was gradually elevated with the heating rate of 20 °C min⁻¹ at the final temperature of 550 °C and kept for 2 h [34]. Then, the crucible was cooled to room temperature and a resulting product was ground into powder and characterized by several instrumental methods.

2.3. Preparation of SnO₂/g-C₃N₄ nanocomposites

For the preparation of SnO₂/g-C₃N₄ nanocomposites, 1 g of g-C₃N₄ and a certain mass of SnCl₂ were dispersed into 50 ml of distilled water using an ultrasonic bath for 10 min and then, a prepared dispersion was vigorously stirred on a magnetic stirrer for 1 h. In the next step, 25 ml of NaOH (c = 0.0531 mol l⁻¹) was added dropwise to the above given dispersion and the resulting mixture was vigorously stirred for 5 min. Afterwards, the mixture was collected by centrifugation (9000 rpm) for 10 min and washed by deionized water. The washing procedure was repeated twice. Then, the collected material was rapidly frozen at -20 °C and frozen water was removed by controlled sublimation [35]. The prepared powder was put into an aluminium crucible and heated at 450 °C for 2 h in the open air with the heating rate of 2 °C min⁻¹ and cooled naturally to room temperature.

The real composition of the SnO₂/g-C₃N₄ nanocomposites was determined by elemental analysis. Contents of C, N, and H were analysed by elemental analyser (CHNS-628) and the content of SnO₂ was calculated, see Table 1 (RSD = 5 %). In further text the content of SnO₂ in nanocomposites is always given in mass percentage but for simplicity it is denoted in “%”.

2.4. X-ray diffraction analysis

X-ray powder diffraction (XRD) was performed using a Rigaku SmartLab diffractometer (Rigaku, Japan) with detector D/teX Ultra 250. A cobalt tube (CoK_α, λ₁ = 0.178892 nm, λ₂ = 0.179278 nm) operated at 40 kV and 40 mA was used as a source of X-ray irradiation. Incident and diffracted beam optics were equipped with 5° Soller slits; incident slits were set up to irradiate the area of a 10 × 10 mm sample (automatic divergence slits) constantly. Slits widths for the diffracted beam were set up to fixed values of 8 and 14 mm.

Powder samples were gently ground using an agate mortar before analysis and pressed using microscope glass in a rotational sample holder and measured in a reflection mode (Bragg-Brentano geometry). The samples rotated (30 rpm) during measurement to eliminate

Table 1
Composition and labelling of tested SnO₂/g-C₃N₄ nanocomposites.

Theor. SnO ₂ (wt%)	Real SnO ₂ (wt%)	Labelling
2.5	2.4	2.5 % SnO ₂
5	5.4	5 % SnO ₂
10	9.7	10 % SnO ₂
20	18.3	20 % SnO ₂
40	39.5	40 % SnO ₂

preferred orientation effect. The XRD patterns were collected in the 2θ range of 5–90° with the step size of 0.01° and the speed of 0.5 deg min⁻¹. The XRD patterns were evaluated using PDXL 2 software (version 2.4.2.0) and compared with PDF-2 database, release 2015.

Crystallite size *L* was calculated according to Scherrer's equation for broadening *B*(2θ) (in radians) at half maximum intensity (FWHM) of a diffraction peak as

$$B(2\theta) = \frac{K\lambda}{L\cos\theta} \quad (1)$$

where λ is the wavelength of X-rays, θ is the Bragg's angle and *K* is a constant equal to 0.94 for cube or 0.89 for spherical crystallites. In this study *K* was rounded to 0.9.

2.5. Transmission and scanning electron microscopy

All transmission electron microscopy (TEM) analyses were performed on a Jeol JEM 1230 microscope operated at 80 kV, placed on a copper grid (400 mesh) coated with a Formvar film (1.5–3.0 wt% of polyvinylformaldehyde in chloroform), dried by a blotting paper and analysed after 2 days. The contrast of micrographs was improved by a 1 wt% solution of ammonium molybdate added to the samples.

High resolution electron transmission microscopy (HRTEM) was performed with a TITAN Themis 60-300 microscope (FEI) equipped with SUPER-X EDX windowless detector. The samples were dispersed in methanol, sonicated for 20 min and one drop was put on a copper grid with Holey carbon film. After drying in the air at room temperature the samples were analysed using an accelerating voltage of 60 kV.

Scanning electron microscopy (SEM) was performed using a microscope Quanta FEWG 450 equipped with detectors EDS Apollo X (EDAX), ETD and BSE and with a camera EBSD HIKARI (EDAX). Before the SEM analysis the samples were sputtered by gold (Polaron Range SC 7640) in argon atmosphere.

2.6. Physisorption of nitrogen

Total surface area (TSA) of the samples was determined using N₂ adsorption isotherms recorded at 77 K and calculated using the Brunauer, Emmett and Teller (BET) method using a 3Flex (Micromeritics Instruments, USA) apparatus after sample degassing at 150 °C for 24 h under less than 1 Pa vacuum. The adsorption-desorption isotherms were evaluated according to the BET theory for p/p° range of 0.05–0.25. External surface area (ESA) was calculated as a slope of *t*-plot and micropore surface area (MSA) was calculated as a difference of TSA and ESA. The pore sizes distribution was calculated by means of Barrett, Joyner and Halend (BJH) method using Broekhoff-De Boer model [36].

2.7. Dynamic light scattering analysis

Analysis of particle size distribution was performed by a dynamic light scattering (DLS) method using a Malvern Zetasizer Nano ZS (Malvern Instruments Ltd, UK) equipped with a 4 mW/633 nm laser. Theoretically, the DLS analyser is able to measure particle sizes in the range from 0.3 nm to 10 μm but, in reality, the particle sizes from 2 nm to 3 μm were reliably determined. Before each analysis, solid samples were dispersed by turbulent mixing in ultrasonic field with the intensity of 50 W l⁻¹ and placed into an optical 10 × 10 × 40 mm cuvette.

2.8. Fourier transform infrared spectroscopy

Fourier transform infrared (FTIR) spectroscopy was performed with a FT-IR spectrometer Nexus 470 (ThermoScientific, USA) equipped with a DTGS detector using the KBr pellets technique: 1.0 mg of each sample was ground with 200 mg of dried KBr. The measurement parameters

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