

Experiment parts

1.1. Preparation of the photocatalysts

ZnO was prepared from the Zn(OH)₂ precursor which was prepared by neutralization. Na₂CO₃ was dissolved in water and mixed on an electromagnetic stirrer until the solution was clear. ZnCl₂ was added to the Na₂CO₃ solution and white Zn(OH)₂ precipitate started to appear. The Na₂CO₃ was in 50% surplus to ZnCl₂. The addition of ZnCl₂ was gradual because of CO₂ production. The mixture was stirred for 3 h, filtered and washed with deionized water until the pH was 7. The precipitate was dried overnight at 50 °C and powdered in a mortar.

Powdery g-C₃N₄ was prepared directly by heating of melamine. In detail, 5 g of melamine was placed in a covered alumina crucible and calcined in a muffle furnace at 620°C for 1 h with temperature increasing at the rate of 10 °C/min and 500°C for 4 h with temperature increasing at the rate of 10 °C/min.

In a synthesis procedure of g-C₃N₄/ZnO, the determined amounts of ZnO and g-C₃N₄ was dispersed in deionized water and evenly mixed (4 hours) and then dried in air at 60 °C. Finally, the mixture was sealed in a crucible with a cover, which was then maintained at 450 °C in a muffle furnace (the heating ramp is 15 °C/min) for 1 h, the atmosphere for the heating process is air.

The prepared nanocomposites (0.1 g) were deposited on a commercial support VUKOPOR (Lanik Ltd., Czech Republic). VUKOPOR is the Al₂O₃ foam (S. 1) with following parameters: specific surface area 0.6 cm²/g, apparent density of ceramic body 2.35 g/cm³, porosity of ceramic body 33 %. The utilized foam had height 1 cm and diameter 7 cm. The nanocomposites were deposited on the foam, which was previously dried in the oven (100 °C for 1 h), as follows: a sample was suspended in distilled water (10 mL) and the suspension was painted by a paint-brush on the foam and again dried under the same conditions.



S. 1 – Photo of the Vukopor® A

1.2. Characterization of g-C₃N₄/ZnO nanocomposite

Samples for zinc content determination were dissolved in concentrated HCl (p.a. purity Analytika Praha, Czech Republic), diluted with type 2 ultrapure water and analyzed by flame atomic absorption spectrometry (ContrAA 700, Analytik Jena, Germany) on Zn primary line (213.86 nm).

Atomic absorption measurements for the determination of real content of Zn were recorded with ContrAA 700 atomic absorption spectrometer (Analytik Jena, Germany), using flame atomization in acetylene/air flame in a 50 mm burner on Zn primary line (213.86 nm).

N₂ physisorption was realized in an automated volumetric apparatus 3Flex (Micromeritics Instruments, USA) after sample degassing at 150 °C for 24 h under less than 1 Pa vacuum. The adsorption-desorption isotherms of nitrogen were measured at -196 °C. The specific surface area (S_{BET}), was evaluated according to the classical Brunauer–Emmett–Teller (BET) theory for the p/p₀ range of 0.05–0.25.

Phase composition and microstructural properties were determined using X-ray powder diffraction (XRD) technique. XRD patterns were obtained using Rigaku SmartLab diffractometer (Rigaku, Japan) with detector D/teX Ultra 250. The source of X-ray irradiation was Co tube (CoK α , $\lambda_1 = 0.178892$ nm, $\lambda_2 = 0.179278$ nm) operated at 40 kV and 40 mA. Incident and diffracted beam optics were equipped with 5° Soller slits; incident slits were set up to irradiate area of the sample 10 x 10 mm (automatic divergence slits) constantly. Slits on the diffracted beam were set up to fixed value 8 and 14 mm. The powder samples were gently grinded using agate mortar before analysis and pressed using microscope glass in rotational sample holder and measured in the reflection mode (Bragg-Brentano geometry). The samples rotated (30 rpm) during the measurement to eliminate preferred orientation effect. The XRD patterns were collected in a 2 θ range 5° - 90° with a step size of 0.01° and speed 0.5 deg.min⁻¹. Measured XRD patterns were evaluated using PDXL 2 software (version 2.4.2.0) and compared with database PDF-2, release 2015.

UV–Vis diffuse reflectance spectra (DRS) were measured using a Shimadzu UV-2600 (IRS-2600Plus) spectrophotometer in the range of 220 to 1400 nm at laboratory temperature. Reflectance was re-calculated to absorbance using the Schuster-Kubelka-Munk's equation as follows (Eq. (2)):

$$F(R_{\infty}) = \frac{(1-R_{\infty})^{1/2}}{2R_{\infty}} \quad (2)$$

where R_{∞} is the diffuse reflectance from a semi-infinite layer. The obtained DRS spectra were transformed to the dependencies of $(F(R_{\infty}) \cdot h\nu)^{1/2}$ on $h\nu$ in order to obtain the values of energy of indirect absorption edges.

The infrared spectra of all samples were measured by potassium bromide pellets technique. Exactly 1.0 mg of sample was ground with 200 mg of dried potassium bromide. This mixture was used to prepare the potassium bromide pellets. The pellets were pressed by 8 tons for 30 seconds under vacuum. The infrared spectra were collected using FT-IR spectrometer Nexus 470 (ThermoScientific, USA) with DTGS detector. Following parameters were used for measurement: spectral region 4000-400 cm^{-1} , spectral resolution 4 cm^{-1} ; 64 scans; Happ-Genzel apodization. Treatment of spectra: polynomial (second order) baseline, subtraction spectrum of pure potassium bromide.

Raman spectra of all samples were measured using a 180 degree measurement technique without any sample preparation. Raman spectra were measured at dispersive Raman spectrometer DXR SmartRaman (ThermoScientific, USA) with CCD detector. The measurement parameters were as follows: excitation laser 780 nm, grating 400 lines/mm, aperture 50 μm , exposure time 1 second, number of exposures 500, and the spectral region 1300-150 cm^{-1} . An empty sample compartment was used for background measurement. Treatment of spectra: fluorescence correction (6th order).

The fluorescence spectra for the hydroxyl radicals' ($\bullet\text{OH}$) trapping test were carried out by a spectrometer FLSP920 Series (Edinburgh Instruments, Ltd.). The excitation wavelength was 325 nm and the terephthalic acid (TA) was used as a probe molecule to intercept $\bullet\text{OH}$ under visible light irradiation ($\lambda = 425 \text{ nm}$).

Morphology of particles was observed on a transmission electron microscope (TEM) JEOL 2010 HC (JEOL Ltd., Japan) with LaB_6 electron gun. The accelerating voltage of 200 kV was applied and micrographs were taken by a camera Tengra (EMSI). The samples were prepared by dispersion in ethanol and then sonicated for 5 min. One drop of this solution was placed on a copper grid with a holey carbon film and dried at room temperature.

Photoelectrochemical measurements were realized using a photoelectric spectrometer with a 150 W Xe lamp coupled with a potentiostat (Instytut Fotonowy, Poland). The photocurrent responses were recorded using a classical three electrode setup. The platinum wire and Ag/AgCl were used as the counter and reference electrodes, respectively. The photocatalysts powder was deposited onto indium-tin oxide (ITO) coated by polyethylene terephthalate and used as the working electrode. The solution of KNO_3 (0.1 M) was used as an

electrolyte solution. The photocurrent spectra were recorded within the range of 300-400 nm with the step of 10 nm in the potential range of -0.2 to 1.0 V (step 0.1 V).