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Invited paper

Synthesis and properties of zinc oxide photocatalyst by high-temperature processing of resorcinol-formaldehyde/zinc acetate mixture



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ABSTRACT

Novel stable ZnO photocatalyst prepared via simple high-thermal processing of resorcinol-formaldehyde/zinc acetate mixture was synthesized for photocatalytic purposes. As a reference, pure ZnO was obtained using $\text{Zn}(\text{CH}_3\text{CO}_2)_2$. The UV–vis spectra demonstrate an intensive absorption of composite ZnO within the visible region, in contrast to pure ZnO (white). The kinetic parameters of the diclofenac sodium photodecomposition reaction reflect higher activity of composite ZnO unlike pure ZnO and P25 (Evonik). Comparative study of bisphenol A degradation during Advanced Oxidation Processes involving ZnO and visible light irradiation demonstrated outstanding role of synthesized photocatalyst.

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1. Introduction

ZnO is well-known material widely used as pigment, photocatalyst, *n*-semiconductor and sensor that demonstrates high stability within a large range of pH (5.8–14). The latter is of key importance by designing photocatalytic ZnO systems, if they are scheduled to use in aggressive media. Moreover, they must preserve stability under the exposure of dark and photochemical corrosion. The presence of some organic pollutants in wastewater indicates their low susceptibility to biological treatment. Semiconductor photocatalysis is a newly developed approach, which can be conveniently applied for degradation of many organic pollutants. Semiconductors (such as TiO_2 , ZnO, Fe_2O_3 , and ZnS) are important for applications due to their electronic structure characterized by a relatively narrow bandgap. The main advantage of ZnO in comparison with TiO_2 is that it absorbs over a larger region of the UV spectrum.

Generally, the band gap (E_g) of zinc oxide is estimated to be 3.2 eV ($E_g = 3.34$ eV at room temperature [1]), while the positions of

E_v and E_c correspond to -0.5 and 2.7 eV (standard hydrogen electrode, pH 7), respectively [2–4].

The combination of wide-band gap ZnO with carbon materials often enables performing photocatalytic processes under the visible light irradiation. This irradiation is absorbed by carbon component of a composite. It is worth noting that the surface defects (V_{Zn}^0 , V_{O}^0) found in pure ZnO [5,6] and in places of contacts with carbon materials, stimulate spectral sensitization of this wide-band-gap semiconductor. It is no wonder that the introduction of carbon provokes the increase of a number of oxygen vacancies (V_{O}^0) responsible for the formation and accommodation of electrons at the donor levels in ZnO [7,8]. In that case, the Fermi characteristic energy level shifts toward the conduction band. There have been a lot of scientific evidences that conduction electrons can be brought into existence due to the ionization of the vacancies of more electronegative oxygen atoms in ZnO characterized by the Shottky atomic disordered structure. The authors [4] have proposed the quasi-chemical equations describing the ionization of oxygen donor levels and the creation of charged

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defects, whereas the two-step process takes place:



The thing that comes particularly strongly is the electrical conductivity of carbon materials (graphite, carbon nanotubes), which act as electrodes collecting generated electrons with subsequent transfer to reagents. In case of irreversible electron transition, it is possible to prevent the electron-hole recombination inside ZnO followed by the growth of the photochemical yield.

Within this paper, we focus on the spectral, morphological characteristics and photocatalytic activity of a novel stable composite ZnO material synthesized via pyrolysis of the resorcinol-formaldehyde/Zn(CH₃CO₂)₂ mixture in inert atmosphere with subsequent calcination at the temperature of 900 °C. To date, it has been proven that Zn²⁺ ions apt to the formation of complex compounds with the organic molecules before high-temperature processing [9,10]. Doping of ZnO structure with metals and non-metals are well-known and widely reviewed [11,12]. Such a feature of Zn²⁺ (3d¹⁰) is as considerable as that of Cu²⁺ (3d⁹). The complex compounds of both ions are characterized by similar stoichiometry and despite the filled 3d shell, Zn²⁺ is found in the Irving–Williams series of high-spin complexes. Since Zn²⁺ is of borderline acids according to the HSAB theory, this ion is easily bound to O-, N-, S-atoms without any preference. Thus, polymeric complexes with Zn²⁺ exhibit occurrence of covalent bonds in our case as well.

In the recent years a great progress is observed in both the number and type of new emerging pollutants [13] detected in environmental matrices. To this group are classified Pharmaceuticals and Personal Care Products (PPCPs). PPCPs are introduced into environment mainly with treated waste water [14]. PPCPs presence in the river water indicates for the insufficient removal during conventional waste water treatment. Diclofenac sodium, DCF (2-(2,6-dichloranilino)phenylacetic acid derivate), a non-steroidal, anti-inflammatory, analgesic agent is one of the PPCPs mostly detected in environmental matrices [15]. The presence of DCF was confirmed in waste water at the levels of 0.99 µg L⁻¹ [16]. DCF cannot be completely removed during conventional treatment as its removal potential is 10–50% [17]. The concentration of DCF in waste water treatment plant effluent can be really high (from 0.4 to 1 µg/L) [17]. Thus, there is a need to find new more efficient methods of the removal of PPCPs and, in particular, DCF from waste water.

Bisphenol A (BPA), 2,2-bis(4-hydroxyphenyl) propane, is another chemical vilely used and classified as Endocrine Disruption Compound [18,19]. Its environmental concentrations are relatively high up to 1.92–11.1 µg L⁻¹ in waste water [20]. The traditional methods of waste water treatment enabled to remove BPA to the unsatisfactory extent. BPA was noted in influents in waste water treatment plant at the levels 0.72–3.4 µg L⁻¹ and eliminated to 0.14–0.98 µg L⁻¹ (in effluents) [21]. The treat of BPA presence in the environment is its confirmed cancerogenic effect [22].

Advanced Oxidation Processes (AOP) offer a high level of the removal of many recalcitrant organic pollutants [23–26]. AOP base on the generation of the hydroxyl radicals chemically, physically and photocatalytically though the selection of the method can be easy considering both possibilities and cost. In the photocatalytic methods, TiO₂ is mostly applied [27]. ZnO possessing similar bandgap energy of 3.37 eV to TiO₂ can be successfully applied in photocatalytic purification methods [28,29]. However, the application of ZnO is connected with its UV activity and, therefore, requires expensive UV lamps. Additionally, the drawback of the application of ZnO is its fast lowered activity as a result of charge recombination [30]. Thus, it is necessary to modify ZnO toward the visible light activity [29].

2. Experimental section

2.1. Synthesis of pure and composite ZnO

Zinc acetate (Zn(CH₃COO)₂·2H₂O, chemically pure, 27 g) and resorcinol (C₆H₆O₂, pure, supplied by Khimlaborreactiv Ltd., Ukraine, 18 g) were mixed and dissolved in distilled water (104 mL) under constant stirring. Thereafter formaline (37 wt.% aqueous solution of formaldehyde, supplied by Khimlaborreactiv Ltd., Ukraine, 26 g) had been added to the reactor feed, whereupon the latter was mixed for 5 min in a magnetic stirrer. The formed solution cased into a plastic container was kept in a heat chamber at 85 °C. Consolidated dry light-brown gel was formed during 2 h. The dried composite gel was carbonized in a vertical reactor at 800 °C in Ar atmosphere. This has resulted in the formation of a composite consisted of porous carbon and ZnO (ZnO-C). Next step was to deposit a fine layer of the carbon composite onto an ovenware followed with annealing in the oxidizing atmosphere of oxygen at 900 °C for 3 h. As consequence of this procedure, a yellow-colored powder (labeled ZnO-N2) was obtained.

In the meantime, pure ZnO as a reference sample was prepared using Zn(CH₃CO₂)₂. The starting material (zinc salt) was calcined at 900 °C in air during 3 h, whereby powdered milky white ZnO (labeled ZnO-N1) was produced.

2.2. Characterization

The materials were characterized using UV-vis, diffuse reflectance spectroscopy (DRS), X-ray phase analysis, scanning electron spectroscopy (SEM), and photoluminescence (PL) spectroscopy methods.

The UV-vis and DR spectra were recorded using a Jasco V-660 spectrophotometer with a PIV-756 diffuse reflectance accessory in the range of λ = 200 ÷ 900 nm at a scan rate of 400 nm/min. ZnO was used as a reference sample. Supposing the Kubelka-Munk relation suitable to transform spectra of UV-vis to DR, the optical band gaps were calculated by means of the Tauc method to describe direct optical transition [31,32]. The respective plot was expressed in terms of (αhν)² vs. hν for a direct bandgap, where α is the coefficient of absorbance and hν is the photon energy.

Textural properties were analyzed by means of the low-temperature nitrogen adsorption-desorption (Micrometrics ASAP

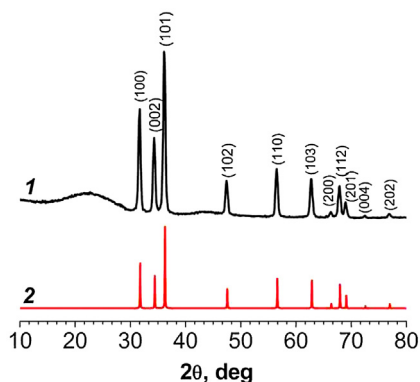


Fig. 1. XRD patterns of composite ZnO-C before pyrolysis at 900 °C (1) and standard crystalline ZnO (2).

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