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ZnO/Ag hybrid nanocubes in alginate biopolymer: Synthesis and properties

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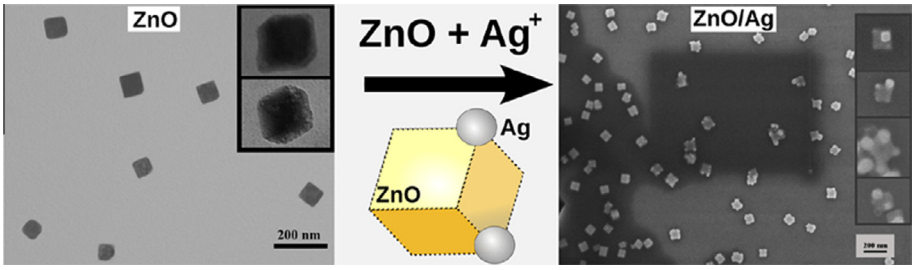
HIGHLIGHTS

- ZnO nanocubes were synthesized in the presence of alginate biopolymer.
- The nanocubes were used for the preparation of ZnO/Ag heterostructures.
- Spherical silver nanoparticles were formed on the vertices of ZnO nanocubes.
- ZnO/Ag heterostructures showed strong photocatalytic and antimicrobial activity.

GRAPHICAL ABSTRACT



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ABSTRACT

A procedure for the preparation of ZnO nanocubes in an alginate biopolymer was introduced. The obtained nanocubes were used for the preparation of ZnO/Ag heterostructures. High resolution scanning electron microscopy showed that reduction of silver salts in the presence of nanocubes results in the formation of spherical silver nanoparticles at their edges and vertices. UV–vis and photoluminescence spectroscopy revealed that alginate-ZnO/Ag nanostructures exhibit different optical properties compared to the starting alginate-ZnO system. The surface plasmon resonance peak of the silver nanoparticles dominates the absorption spectra of the ZnO/Ag hybrid particles, while at the same time the Ag nanoparticles quench the ZnO emission. The photocatalytic activity of the ZnO/Ag heterostructure was faster than that of the pure ZnO and further improved with increasing the concentration of silver. Both the alginate-ZnO and alginate-ZnO/Ag nanocomposites showed strong antimicrobial activities against gram-positive (*Staphylococcus aureus*) and gram-negative (*Escherichia coli*) bacteria.

1. Introduction

Investigations of metal–semiconductor hybrid nanostructures are of considerable technological importance but are also very attractive from a fundamental point of view. These nanomaterials often exhibit novel functional qualities, which make them suitable for applications in diverse areas such as catalysis, solar energy conversion, optoelectronics and biolabeling [1–6]. Until recently, a significant part of the research on metal–semiconductor heterostructures was dedicated to core–shell type nanoparticles, usually a noble-metal core covered with a semiconducting shell [7–12]. However, it has been shown that nanostructures of two or more distinct components and geometries other than core–shell (for example Au-CdS, Au-CdSe, Pt-CdS, Au-ZnO, Ag-ZnO [9,13–18]) may exhibit additional properties due to an anisotropic

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distribution of the surface functional groups and charges. These properties can be further adjusted by controlling the size and shape of the individual components in a particular nanostructure [19].

Zinc oxide is one of the most studied n-type semiconductors with a wide band gap (3.37 eV). So far, it has been synthesized into various morphologies such as rods, tubes, cones and disks [20–26]. In general, when a material has a well-defined anisotropic morphology, it is a good candidate for the site specific synthesis of hybrid nanostructures. For example, the photoreduction of Ag^+ ions on ZnO nanorods induced the preferential growth of Ag nanoparticles at one side of the rod [27]. On the other hand, reduction of Au salts in the presence of ZnO nanopyramids induced the formation of Au nanoparticles that were localized in the vicinity of the pyramid vertices [28]. In our previous study, it was found that an alginate biopolymer can be successfully used as a controlled environment for the growth of spherical ZnO nanoparticles [29]. Here, we show that a slightly different synthetic approach can result in the formation of ZnO nanocubes, which are then used as the starting material for the fabrication of ZnO-Ag hybrid nanostructures with site-specific position of Ag nanoparticles. The obtained ZnO-Ag nanohybrids were investigated by using structural and optical methods. Finally, it will be shown that these nanohybrids, besides interesting morphology, exhibit strong photocatalytic and antimicrobial activity.

2. Experimental

2.1. Synthesizes of ZnO nanocubes and ZnO/Ag nanohybrids in alginate matrix

In the present study we used alginate from brown algae with Mr. ~48,000–186,000 (Biochemica). Zinc acetate, sodium hydroxide and methyl orange were purchased from Merck. Silver nitrate was purchased from Centrohem. The alginate solution was prepared by dissolving 1 g of alginate in 100 mL of 0.01 M NaOH solution. In a typical synthetic procedure, the ZnO nanocubes in the alginate matrix were prepared by adding 5 mL of sodium alginate solution to a mixture of 0.8 mL of 1 M NaOH and 2 mL of 0.2 M Zn-acetate water solutions. The obtained mixtures were placed in a microwave (MW) oven and treated at 500 W for 1 min. The access of alginate was removed by fast centrifugation. In order to prepare the ZnO/Ag nanohybrids, 1 mL of 0.1 M $AgNO_3$ was added under slow stirring into 1 mL of the above obtained ZnO-alginate solution and heated at 60 °C for 9 min. Elemental analysis was performed on an inductively coupled plasma optical emission spectrometer (ICP-OES), Spectroflame. The concentration of silver with respect to ZnO was found to be 36.2 wt.%. For photocatalytic and antimicrobial activity testing (see below) several different samples were prepared by changing the initial concentration of silver. The concentrations of silver (per initial concentration of ZnO) in these additional samples were found to be 3.6, 15.1, 48.8 and 52.9 wt.%.

2.2. Characterization

X-ray diffraction measurements were performed on a Rigaku Ultima IV diffractometer (CuK_α radiation $\lambda = 0.154$ nm). Transmission electron microscopy (TEM) measurements were carried out on Phillips CM100 and JEOL 2010F electron microscopes with operating voltages of 100 and 200 kV, respectively. The samples were prepared by placing a drop of the ZnO- and ZnO/Ag-alginate nanocomposite water solutions onto a carbon-coated copper grid. High resolution scanning electron microscopy measurements were performed on a Zeiss NVision 40 CrossBeam FIB-SEM. UV-vis absorption spectra of a water solution of the ZnO and ZnO/Ag nanocomposites were obtained by using a Perkin Elmer Lambda 5 UV-vis spectrophotometer. The photoluminescence spectra of the same samples were recorded on a Perkin Elmer LS 3B spectrophotometer at a 320 nm excitation wavelength.

2.3. Photocatalytic activity testing

For photocatalytic activity testing, the ZnO/Ag nanohybrids with various Ag loadings were dispersed in 3.0 mL of the methyl orange aqueous solution (10 ppm) and sonicated for 30 min in the dark. The solutions were then placed in a quartz cell and irradiated by using an Osram Vitalux lamp at 300 W. The emission spectrum of the lamp simulates solar radiation. The lamp was posted at the distance of 50 cm above the top surface of the dye solution. Absorption spectra were recorded at certain time intervals.

2.4. Recycling of the ZnO/Ag photocatalyst

The recycling of the photocatalyst was tested on the ZnO/Ag sample with 48.8 wt.% of silver, since it showed the strongest catalytic activity. After the first photodegradation cycle (60 min of irradiation), the treated solution of the dye was centrifuged at 4000 rpm for 15 min to separate the photocatalyst. The liquid phase was removed and the solid phase containing the photocatalyst was carefully separated for reuse. After allowing it to dry at 45 °C, the separated catalyst was added again to a new identical batch of methyl orange solution. The whole procedure was repeated three times and the percentage of the photocatalytic reduction at the end of each cycle was reported.

2.5. Total organic carbon determination

The total organic carbon (TOC) was determined by using Lab-TOC Model 2100. Equal amounts of photocatalysts (with 48.8 wt.% Ag) were added into two glass tubes with 3.0 mL of the methyl orange aqueous solution (50 ppm) and sonicated for 30 min in the dark. The first solution was kept in the dark at room temperature, while the second was placed in a quartz cell and irradiated with an Osram Vitalux lamp for 60 min. After irradiation both samples were centrifuged for 15 min with 4000 rpm in order to remove the photocatalyst from the solution and the TOC was determined.

The percentage of TOC removal was used for the estimation of the efficiency of dye mineralization and it is defined by following expression [30,31]:

$$\text{TOC removal percentage} = \frac{\text{TOC}_0 - \text{TOC}}{\text{TOC}_0} \times 100 \quad (1)$$

where TOC_0 is the initial total organic carbon (prior to irradiation) and TOC is the total organic carbon after the irradiation.

2.6. Electron paramagnetic resonance (EPR)

Electron paramagnetic resonance spectroscopy was used for the detection of reactive oxygen species (ROS). It was carried out on a Bruker Biospin Elexsys II E540 15.0. As a spin trapper, we used 5-diethoxyphosphoryl-5-methyl-1-pyrroline-n-oxide (DEPMPO). For EPR analysis, 1.5 μL of the purified solution of DEPMPO was added in 45 μL of ZnO/Ag solution (48.8 wt.% Ag). The reported spectra were obtained after 30 scans. After that, the solution was irradiated with Osram Vitalux lamp for 20 min and EPR spectrum was recorded again. The spectrum was obtained after 5 scans.