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Journal of Photochemistry and Photobiology A: Chemistry 173 (2005) 185–194
Journal of Photochemistry and Photobiology A:Chemistry
www.elsevier.com/locate/jphotochem

Photochemical synthesis and optical properties of binary and ternary metal–semiconductor composites based on zinc oxide nanoparticles

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Received 15 October 2004; received in revised form 6 February 2005; accepted 9 February 2005
Available online 7 March 2005

Abstract

Photochemical properties of zinc oxide nanoparticles and their photocatalytic activity in the processes of the reduction of Cu^{2+} and Pb^{2+} ions as well as mixtures of Cu^{2+}–Ag^{+} and Cd^{2+}–Ag^{+} ions have been investigated. Optical properties of ZnO/Cu, ZnO/Pb, ZnO/Ag/Cu, ZnO/Ag/Cd and ZnO/Ag/Zn nanocomposites have been examined.

It has been found that a decrease in the size of ZnO nanoparticles from 6.0 nm to 4.4 nm results in the strengthening of quantum confinement of photogenerated charge carriers, growth of the band gap and the potentials of the conduction band and the valence band of the semiconductor. It has been found that ZnO nanoparticles smaller than $2R = 6.0$ nm photocorrode with the formation of metallic zinc when the colloidal solution is irradiated with the mild UV light. An increase in the potential of the conduction band electrons and the ability of ZnO nanoparticles to accumulate excessive negative charge have been supposed to be the principle reasons of advanced photochemical activity of ZnO nanoparticles with $2R < 6.0$ nm.

Mie theory has been applied to analyze the parameters of surface plasmon resonance bands of metallic copper in ZnO/Cu nanocomposites as well as to estimate an average size of Cu^{0} nanoparticles formed on the surface of the semiconductor.

It has been found that Cu(II) photoreduction rate increases substantially when Ag^{+} ions are present in the irradiated systems. Photocatalytic reactions in these systems result in the formation of ternary bimetallic ZnO/Ag/Cu nanocomposites.

It has been shown that Cd(II) ions, which are stable towards photoreduction on the surface of ZnO nanoparticles, can be co-reduced with Ag^{+} cations giving ternary ZnO/Ag/Cd nanocomposites with peculiar optical properties. Correlations between the conditions of co-reduction of metal cations and the parameters of partially disturbed silver plasmon bands in the optical spectra of colloidal ZnO/Ag/Cd and ZnO/Ag/Zn have been established.

Keywords: Photocatalysis; Photocorrosion; Photochemical synthesis; ZnO nanoparticles; Quantum confinement effects; Copper nanoparticles; Metal–semiconductor nanocomposites

1. Introduction

Photochemical reduction of the cations of some metals (for example, Ag, Au, Cu, Pt, Pd, Cd, etc.) induced by semiconductor nanoparticles (TiO_2, ZnO, SnO_2, CdS, ZnS, etc.) are of great interest not only as model processes for the investigation of photocatalytic properties of ultradispersed semiconductors, but also as one of the methods of the preparation of nanostructured metal–semiconductor composites [1–11]. An advantage of this method lies in the opportunity to control the composition of metal–semiconductor nanostructures through variations in the conditions of photochemical reaction [1,2,5,9,11–13]. This method can be successfully applied for the synthesis of multicomponent composites consisting of semiconductor nanocrystals and several metals in the form of alloy or "core–shell" structure [14].

Metal–semiconductor nanostructures manifesting properties of the semiconductor and the metal find wide application in photocatalysis due to the ability of metallic component to accumulate electrons generated at the absorption of light by the semiconductor component. Accumulation of

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doi:10.1016/j.jphotochem.2005.02.002

electrons within the metal "pool" of the nanocomposite improves primary charge separation and boosts photocatalytic [1–7,10–12,15,16] and photoelectrocatalytic [8,17] activity of the semiconductor.

In case of the semiconductor nanoparticles with quantum confinement effects, photochemical reactions can sometimes be performed, having no analogues in the world of bulk (micrometer) semiconductor crystals. The effects of quantum confinement may substantially affect both optical and photochemical properties of ultradispersed semiconductors [3,12]. These effects originate from the changes in energetic characteristics of charge carriers photogenerated in semiconductor crystals as small as exciton delocalization domain (typical range of this domain is 1–10 nm) [3,18]. Growth of absolute potentials of conduction band electrons and valence band holes, at a decrease in the size of nanoparticles, may lead to substantial increase in photochemical and photocatalytic activity of ultradispersed semiconductor. Cases, when size-dependent alterations of energetic characteristics of charge carriers give rise to redox processes, which are thermodynamically forbidden for bulk crystals of the semiconductor, are of particular interest. The vivid example of the latter phenomenon is the process of cathodic photocorrosion of zinc oxide nanoparticles (the bulk crystals of this semiconductor are stable towards the reductive photocorrosion [19]) resulting in the formation of composite ZnO/Zn nanoparticles. We also discuss some peculiarities of the photochemical synthesis of binary (ZnO/Cu and ZnO/Pb) and ternary (ZnO/Ag/Cu, ZnO/Ag/Cd and ZnO/Ag/Zn) nanostructures, evolution of their absorption spectra in the course of the synthesis and the effect of photoreduction conditions on the optical properties of the nanocomposites.

2. Experimental

ZnO nanoparticles in 2-propanol have been synthesized via the basic hydrolysis of zinc acetate (reagent grade) by sodium hydroxide (pure) at 0 °C [20–23]. In typical procedure, dry powdered $Zn(CH_3COO)_2$ (0.0915 g, 0.5 mmol) is dissolved at continuous refluxing in 60 ml of anhydrous twice-distilled 2-propanol at 50–60 °C. Resulting solution is diluted to 230 ml by 2-propanol and cooled to 0 °C again. Powdered NaOH (0.032 g, 0.8 mmol) is dissolved in 20 ml of anhydrous 2-propanol at 50–60 °C and then cooled to 0 °C. Solutions of sodium hydroxide and zinc acetate are slowly mixed at intense refluxing at 0 °C. After the synthesis, colloidal ZnO solution is heated for 2 h at 55–60 °C. Final colloidal ZnO solution has an absorption band with steep long-wave edge at 365–370 nm and contains spherical ZnO nanocrystals with the average diameter 5 ± 0.5 nm [20,21].

Colloidal solutions of zinc oxide in ethanol have been prepared in the same way from zinc acetate, sodium hydroxide in anhydrous ethyl alcohol. Solutions of Ag(I), Cu(II) and Pb(II) have been prepared from reagent grade $AgNO_3$, $CuCl_2$ and $Pb(CH_3COO)_2$.

Composite ZnO/Ag nanoparticles have been synthesized in ethanol and 2-propanol similar to [13] via photocatalytic reduction of $AgNO_3$ on the surface of ZnO nanoparticles. Irradiation of the solution containing $[ZnO] = 1 \times 10^{-3}$ M and $[AgNO_3] = 7.5 \times 10^{-5}$ M to 1×10^{-4} M up to complete conversion of Ag^+ ions results in the formation of ZnO/Ag nanocomposite with the average size of Ag^0 nanoparticles 1.8–2.0 nm [13].

Solutions have been irradiated in glass parallel-sided 1.0 cm cuvettes with the filtered light of 1000 W mercury high-pressure lamp. Glass 5.0 cm cuvette filled with water has been placed between the light source and the work cuvette to avoid heating of the latter. Light intensity was adjusted by calibrated metal semi-transparent filters and measured by ferrioxalate actinometry.

Optical spectra were registered using Specord M-40 double-beam spectrophotometer (spectral range 185–900 nm, resolution 0.1 nm, precision of absorbance measurements 0.005).

3. Results and disscussion

3.1. Synthesis, optical and photochemical properties of ZnO colloids; formation of binary ZnO/Zn nanocomposites

Basic hydrolysis of zinc acetate by sodium hydroxide in 2-propanol is well studied, reproducible and comparatively simple method of the preparation of colloidal ZnO nanoparticles [20–23]. We have found that analogous procedure may also be carried out in ethyl alcohol. The latter method has two advantages. First one lies in a possibility to synthesize more concentrated (up to 2×10^{-2} M) zinc oxide colloids as compared with 2-propanolic solutions, where ZnO nanoparticles become unstable already at $[ZnO] > 2 \times 10^{-3}$ M. The second advantage is simple control of the size of ZnO nanoparticles through variations in reagents' concentrations. Fig. 1 shows absorption spectra of ethanolic ZnO colloids of two different concentrations. At a decrease of zinc oxide concentration

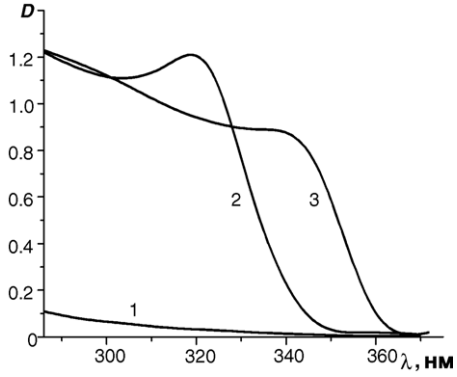

Fig. 1. Absorption spectra of colloidal ZnO solutions in ethanol after the mixing of the reagents (1), after 2 h ageing at 55–60 °C; $[ZnO] = 1 \times 10^{-3}$ M in (2) and 2×10^{-2} M in (3).