Optical and photocatalytic properties of ZnO nanorods and ZnO/Ag nanocomposites

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В данном исследовании изучалась корреляция оптических и фотокаталитических свойств наностержней ZnO и нанокомпозитных материалов ZnO/Ag. Наностержни ZnO синтезированы при низких температурах гидротермальным методом, а наночастицы Ag – методом полиолов. При покрытии поверхности наностержней ZnO наночастицами Ag интегральная интенсивность спектра ФЛ наностержней ZnO уменьшилась в два раза. Однако было замечено, что эффективность деградации органического красителя нанокомпозитных материалов ZnO/Ag была в 2.2 раза выше, чем у наностержней ZnO. Обнаружено, что миграция носителей заряда через границы раздела наностержней ZnO и наночастиц Ag обусловлена уменьшением интегральной интенсивности ФЛ и повышением фотокаталитических свойств после покрытия поверхности наностержней ZnO наночастицами Ag.

Ключевые слова: наностержни ZnO, наночастицы Ag, фотолюминесценция, дефекты, фотокатализ.

In the study, the correlation of optical and photocatalytic properties of ZnO nanorods and ZnO/Ag nanocomposite materials were investigated. ZnO nanorods were synthesized at low temperatures by the hydrothermal method, and Ag nanoparticles were synthesized using the polyol method. When the surface of ZnO nanorods was coated with Ag nanoparticles, the integral intensity of the PL spectrum of ZnO nanorods decreased by 2 times. However, it was observed that the degradation efficiency of the organic dye of ZnO/Ag nanocomposite materials was 2.2 times higher than that of ZnO nanorods. It was found that the migration of charge carriers through the interfaces of ZnO nanorods and silver nanoparticles was caused by a decrease in PL integral intensity and an increase in photocatalytic properties after the surface of ZnO nanorods was coated with Ag nanoparticles.

Keywords: ZnO nanorods, Ag nanoparticles, photoluminescence, defects, photocatalysis.

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I. Introduction

Nanostructured semiconductors are of great interest due to their extraordinare physico-chemical properties, which differ from their bulk counterparts. Despite its high bandgap energy (3.37 eV), low photocurrent density and low energy transfer efficiency, ZnO is still a very important material in many fields due to its unique crystallographic structure, high electrochemical stability, high electron mobility, large binding exciton energy [1-3]. There is a growing interest in the fabrication of nanocomposite materials based on ZnO nanostructures and the study of their fundamental properties. When ZnO nanostructures are coated with various

noble metal nanoparticles, their optical, electrical, and antibacterial properties can change. These changes will enable one to create compact light sources, chemical sensors, nanocomposite materials with unique hybrid properties that are promising for use in energy accumulation and storage and photocatalytic devices. Among the noble metals, silver is a promising metal for photocatalytic and energy conversion due to its stability, high electrical conductivity, low cost, and nontoxicity [4-5].

Typically, a photoluminescence (PL) spectrum of ZnO nanostructures consists of two parts: a near band edge (NBE) emission centered at around 380 nm and defect-related emission bands in the visible range [6]. The PL spectrum of a ZnO/Ag nanocomposite material also consists of two emission bands, as typically observed in ZnO nanorods. In the study [7], the authors noted that when the surface of hydrothermally synthesized ZnO nanorods are coated with silver nanoparticles, the intensity of the emission band in the UV range increases and the intensity of the emission band corresponding to defects in the visible range decreases. Similar results have been reported in [8, 9]. In the study [10], the authors noted that Ag nanoparticles had no effect on the PL spectrum of ZnO. But Munavar et al. [11] in the ZnO surface covered with Ag nanoparticles observed a simultaneous decrease in the intensity of the two emission bands in the PL spectrum. Despite the large number of research devoted to optical and photocatalytic properties of ZnO nanostructures, many questions remain open.

This work reports a systematic study of dependence of the optical and photocatalytic properties of ZnO nanorods and ZnO/Ag nanocomposites. We have synthesized 1D ZnO nanorods using a low-temperature hydrothermal method and Ag nanoparticles using polyol method. The relationships between luminescence properties of ZnO, ZnO/Ag and photocatalytic characteristics have been revealed and discussed. Our studies showed that the PL properties of the samples were correlated with the photocatalytic properties, and that an increase in the PL intensity led to a decrease in the photocatalytic efficiency of the sample.

II. Experiment

ZnO nanorods have been synthesized on stainless steel grid by hydrothermal route [12]. Before ZnO nanorods are grown, a seed layer is formed on the surface of the substrates. Dip coating method had been applied to prepare ZnO seed layer on substrates because of its low cost and easy approach. All the reagents (Sigma-Aldrich, 99%) used in the experiment were analytically pure and used without further purification. Zinc acetate dehydrate ($ZnC_4H_6O_42H_2O$) was dissolved into ethanol with stirring at room temperature for obtaining a clear homogenous solution. The stirred solution is taken in a beaker and the substrates are dipped in the solution with low velocities using a handmade automatic dip coating system and dried in air at room temperature.

Growth of ZnO nanorods is carried out in the following order: the aqueous solutions of zinc nitrate hexahydrate ($Zn(NO_3)_26H_2O$) and hexamethylenetetramine ($C_6H_{12}N_4$) were prepared. The resulting suspension was transferred into a Teflon-lined stainless steel autoclave. The substrates with the ZnO seed layer were placed on the bottom of the autoclave. Finally, the autoclave was sealed and put into the water thermostat bath. The hydrothermal reaction is carried out at 90°C for 5 hours.

In this study, silver nanoparticles are synthesized using the polyol method. In the synthesis of silver nanoparticles, 30 ml of Ethylene Glycol (EG) is first heated to 70°C, then 700 mg of Polyvinylpyrrolidone (PVP K30) is added and mixed for 10 min using a magnetic stirrer. The prepared solution is removed from the oven and cooled to room temperature. After the solution has cooled, 100 mg of silver nitrate ($AgNO_3$) added and stirred at room temperature for 30 min. Then the solution is placed in a preheated oven at 140°C. After 5 minutes, the solution is removed from the oven and cooled to room temperature. The synthesized silver nanoparticles were separated from the solution at 13.000 rpm using a centrifuge.

Absorption spectra of the samples are detected using a UV/VIS-5100 spectrophotometer. The emission spectra of ZnO nanorods were obtained using a photoluminescence set-up coupled to 0.75 m monochromator with diffraction grating and high sensitive photomultiplier tubes. As excitation source, a longitudinally pumped nanosecond pulse N_2 laser emitting at 337 nm (pulse duration ~6 ns, P ~15 kW, repetition rate 100 Hz) was used. Emission spectra were recorded using a boxcar integrator with a gate width of 40 ns. The morphology of the ZnO nanostructures was examined using a scanning electron microscope (SEM) ZEISS EVO MA10.

III. Results and discussion

Morphology and particle size of the synthesized ZnO nanorods are shown in Fig. 1. As can be seen,

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the hydrothermal growth method provided to synthesis a high density of uniform nanorods on stainless steel grid. These ZnO nanorods possess spindle-shaped and hexagonal form and their length and diameter are 15−20 and 0.8−1.2 μm, respectively. Nanorods are located chaotically and have predominantly horizontal positions on the substrate.

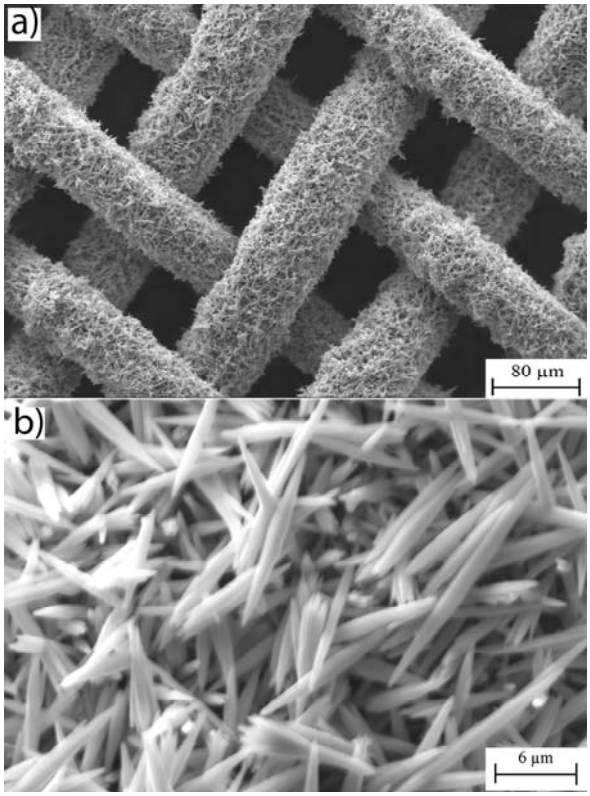


Figure 1. SEM images of ZnO nanorods obtained by scanning electron microscope.

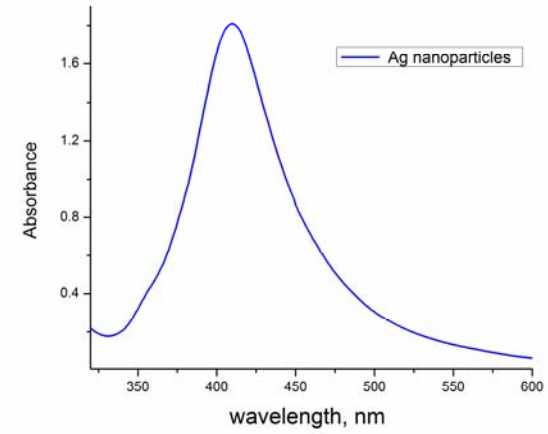


Figure 2. The absorption spectrum of the colloidal solution of the synthesized silver nanoparticles in ethanol.

The absorption spectrum of the colloidal solution of the synthesized silver nanoparticles in ethanol is given in Fig. 2. In the absorption spectrum of the synthesized silver nanoparticles, an absorption band at a wavelength of ~410 nm was observed. This absorption band belongs to the surface plasmon resonance (SPR) of silver nanoparticles [13-16]. In the study [14], the authors reported that when silver nanoparticles have around 30 nm in size, their maximum absorption band corresponding to SPR with a wavelength of 411 nm. Therefore the size of the synthesized silver nanoparticles is around 30 nm on the average and they have a spherical shape. The narrow absorption spectrum indicates that there is no significant difference between the sizes of the nanoparticles.

The surface of ZnO nanorods synthesized on the surface of stainless steel grid by hydrothermal method was coated with silver nanoparticles using dip-coating method. The photoluminescent and photocatalytic properties of the fabricated ZnO/Ag nanocomposite material were investigated. Figure 3 shows the PL spectra of ZnO nanorods and ZnO/Ag nanocomposite material.

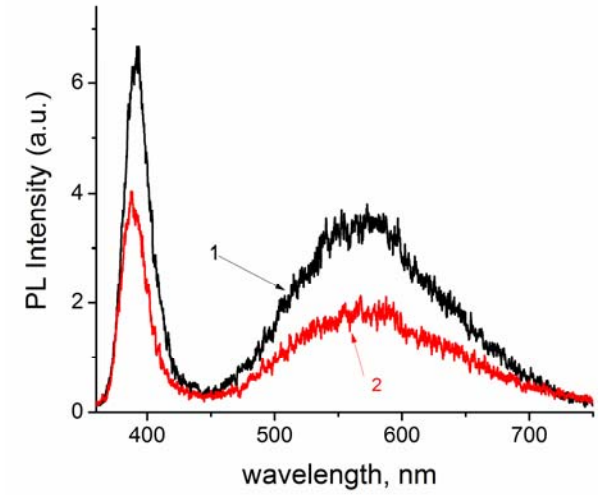


Figure 3. PL spectra of ZnO nanorods (1) and ZnO/Ag nanocomposite material (2).

Studies have shown that when as-grown ZnO nanorods are excited under UV light. PL spectrum of ZnO nanorods consist of two peaks: narrow and strong in the UV range and with weak and broad emission band in the visible range (Fig. 3, curve 1). The ratio of the maximum intensities of the emission peaks is 1.9. The PL spectrum contains a sharp UV peak located at 389 nm and a broad yellow emission band around at 570 nm. The UV peak was attributed to near band edge emission or free exciton of ZnO [7]. The yellow luminescence band can be attributed

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to intrinsic defects and/or their complexes. The yellow band is often observed in zinc oxide nanomaterials grown from aqueous solutions at relatively low temperatures and is usually attributed to interstitial oxygen or complexes formed with the participation of oxygen [17-18].

The photoluminescence spectrum of the ZnO/Ag hybrid heterostructure fabricated by coating the surface of ZnO nanorods with silver nanoparticles is shown in Fig. 3, curve 2. The photoluminescence spectrum of the ZnO/Ag nanocomposite material also consisted of two emission bands, such as ZnO nanorods. However, the intensity of the emission band in the UV field decreased by 1.6 times, and the intensity of the emission band corresponding to the defects in the visible field decreased by 1.9 times. The ratio of the maximum intensities of the emission bands is ~2.15. The increase in the ratio of the maximum intensities of the emission bands is caused by changes in the energy diagrams and Fermi levels of the charge transfer mechanisms of the charge carriers through the ZnO and Ag interfaces [11]. The extinction of PL integral intensity is followed by the Stenr-Volmer quenching based on the SPR phenomenon in silver nanoparticles [12].

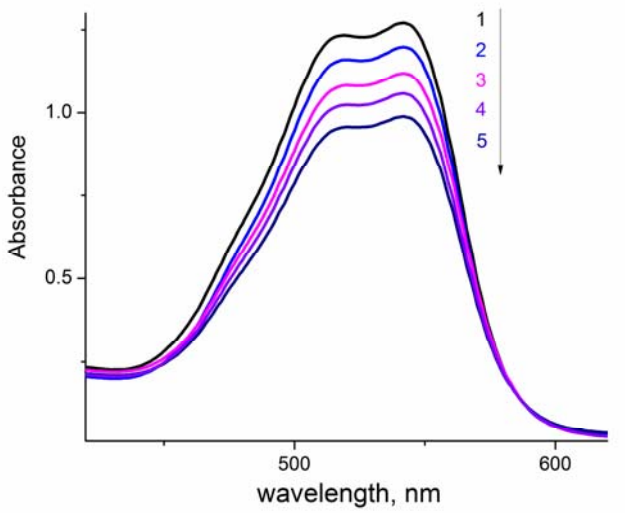


Figure 4. Absorption spectra detected at different times during the degradation of Corlon Red F3B dye when ZnO nanorods are irradiated with UV light: 1) 0, 2) 15, 3) 30, 4) 45, and 5) 60 minutes.

To study the photocatalytic properties of ZnO nanorods and ZnO/Ag nanocomposite material, 25 mg/*l* concentration solution of Corlon Red F3B dye in water was prepared and the absorption spectrum was determined (Fig. 4, curve 1). Illumination of the solution with UV light for half an hour showed that it could not degrade concentration of Corlon Red F3B dye. Degradation of the Corlon Red F3B dye occurred over time when ZnO nanorods were dropped into the solution and irradiated with UV light (Fig. 5, 2-5 curves). ZnO nanorods were irradiated with UV light, it was found that after 30 minutes and 60 minutes the concentration of the dye in the solution decreased by 12% and 23%, respectively. When the surface of ZnO nanorods was coated with silver nanoparticles, their photocatalytic efficiency was observed to increase significantly. The photocatalytic properties of ZnO/Ag nanocomposite material (Fig. 5) showed that the photocatalytic efficiency of ZnO/Ag nanocomposite material was ~1.89 times higher than that of ZnO nanorods, and that degradation of Corlon Red F3B dye by ~43% was observed when irradiated with UV light for 60 min.

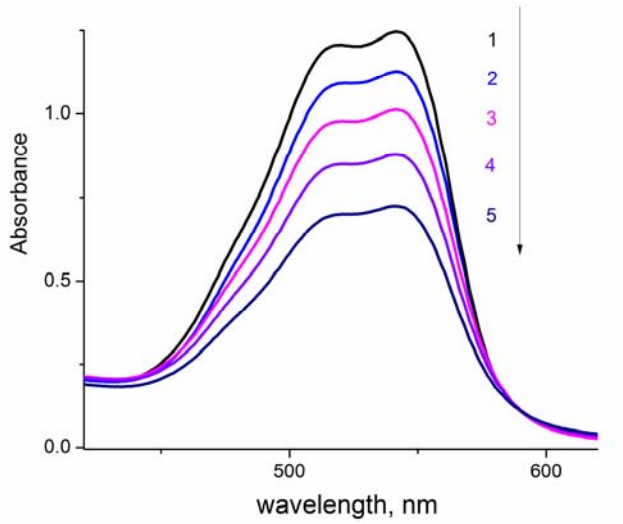


Figure 5. Absorption spectra detected at different times during the degradation of Corlon Red F3B dye when the ZnO/Ag nanocomposite is irradiated with UV light: 1) 0, 2) 15, 3) 30, 4) 45, and 5) 60 minutes.

The kinetic properties of the ZnO nanorods and the ZnO/Ag nanocomposite of the Corlon Red F3B dye decomposition mechanism under the influence of UV light were calculated using a first-order-pseudo-equation. Figure 6 below illustrates the kinetic properties of the photocatalytic process of ZnO nanorods and ZnO/Ag nanocomposites. As can be seen from the graph, the degradation process of Corlon Red F3B dye occurs almost according to the linear law. The value of the photocatalytic reaction apparent constant of Corlon Red F3B dye is $k_1 = 4.2\times10^{-3}$ min^{-1} for ZnO

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nanorods (Fig. 6, curve 1). The fact that the value of the photocatalytic reaction apparent constant of the ZnO/Ag nanocomposite is $k_2 = 9.5\times10^{-3}$ min^{-1} indicates that it takes ~109 minutes for the organic dye to completely degradation, and this value is 2.2 times smaller than the photocatalytic reaction apparent constant for ZnO nanorod. (Fig. 6, curve 2).

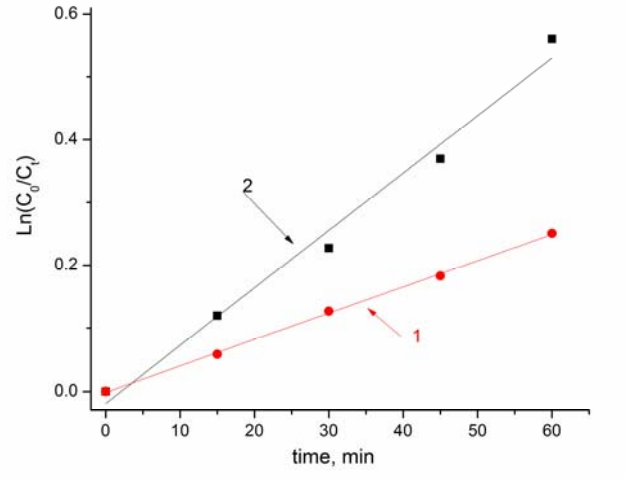


Figure 6. The kinetic properties of the Corlon Red F3B dye degradation mechanism calculated using the first-order-pseudoequation: 1) ZnO nanorods and 2) ZnO/Ag nanocomposites.

The increase in photocatalytic properties after the surface of ZnO nanorods is coated with silver nanoparticles is due to the migration of charge carriers through the interfaces of ZnO nanorods and silver nanoparticles. Under the influence of UV rays in ZnO nanorods electrons passing from the valence band to the conduction band gradually migrate to the surface. These excited electrons can easily pass without radiation to the energy level of the silver nanoparticles on the surface below the conduction band, which belongs to the SPR. As a result, the photogenerated electron-hole pair separates without recombination. This confirmation is supported by a ~2 times decrease in the PL integral intensity after silver nanoparticles are coated on the surface of ZnO nanorods. The separated electrons and holes actively participate in the oxidation-reduction reaction and serve to increase the photocatalytic efficiency.

IV. Заключение

We have synthesized 1D ZnO nanorods using a low-temperature hydrothermal method and Ag nanoparticles using polyol method. Correlation relationships between the optical and photocatalytic properties of ZnO nanorods and ZnO/Ag nanocomposites were determined. When the surface of ZnO nanorods was coated with silver nanoparticles, the integral intensity of the FL spectrum decreased by 2 times. However, it is observed that the degradation efficiency of the organic dye of ZnO/Ag nanocomposite materials was 2.2 times higher than that of ZnO nanorods. Due to the convenient state of the energy levels of ZnO nanorods and Ag nanoparticles, photogenerated electron-hole pairs can separate without recombination. The separated electrons and holes actively participate in the redox reaction and lead to an increase the photocatalytic efficiency.

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ZnO нанородлари ва ZnO/Ag нанокомпозитининг оптик ва фотокаталитик хоссалари

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Ушбу ишда ZnO нанородлари ва ZnO/Ag нанокомпозит материалларининг оптик ва фотокаталитик хоссаларининг ўзаро корреляцияси тадқиқ қилинди. ZnO нанородлари паст ҳароратда гидротермал усулда ва Ag нанозарралари полиол методи ёрдамида синтез қилинди. ZnO нанородлари сиртини кумуш нанозарралари билан қопланганда, ФЛ спектрининг интеграл интенсивлиги 2 марта камайиши содир бўлди. Шу билан бирга, ZnO/Ag нанокомпозит материалларининг органик бўёқни парчалаш самарадорлиги ZnO нанородларига қараганда 2.2 марта ортгани кузатилди. ZnO нанородлари сиртини Ag нанозарралари билан қоплангандан сўнг ФЛ интеграл интенсивлигининг камайиши ва фотокаталитик хоссаларининг ортишига ZnO нанородлари ва кумуш нанозарраларининг интерфейслари орқали заряд ташувчиларнинг миграцияси сабаб бўлиши аниқланди.

Калит сўзлар: ZnO нанородлари, Ag нанозарралари, фотолюминесценция, нуқсонлар, фотокатализ.

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