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Optical and photocatalytic properties of quasi-one-dimensional ZnO activated by carbon

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The 1-D $ZnO_{1-x}C_x$: nC nanocomposites and $ZnO_{1-x}C_x$ solid solutions synthesized by the thermolysis of $Zn(HCOO)(HOCH_2CH_2O)_{1/2}$ exhibit promising photocatalytic properties for the oxidation of toxic organic substances.

The ZnO-based compounds can be used as catalysts for the oxidation of toxic organic compounds to CO_2 and H_2O.[1] The doping of wide-band semiconductors by carbon and their transformation to a nanodispersed state can enhance their sorption properties and expand the spectral range of their photosensitivity.[2–4] The appeared surface defects may act as oxidation and sorption centers.[5,6] 1-D nanostructures, especially with a carbon covering, are used in hybrid solar batteries.[7,8] However, the formation of ZnO/C heterosystems in a quasi-one-dimensional state is technologically complicated and involves a number of high power input operations.[9] For the synthesis of ZnO-based tubular nanomaterials, we used the precursor method, where the oxide products inherit the shape of precursor crystals.[10,11] X-ray analysis, SEM, TEM, Raman scattering and EPR spectroscopy were used to demonstrate the formation of $ZnO_{1-x}C_x$: nC composites and $ZnO_{1-x}C_x$ solid solutions with high dispersity and high concentrations of intrinsic point defects like V_0^*. The optimal photocatalytic properties are regulated by the concentration of uncombined carbon and point defects.

The precursor complexes $Zn(HCOO)(HOCH_2CH_2O)_{1/2}$ were produced from $Zn(HCOO)_2$ with ethylene glycol.[11] The thermolysis of the precursors was performed in a helium atmosphere at 500 °C to result in the formation of the $ZnO_{1-x}C_x$: nC composite. According to X-ray diffraction analysis, the composite is isostructural to ZnO with a wurtzite structure. According to elemental analysis, $ZnO_{1-x}C_x$: nC contained 7.5 wt% carbon, including 6.8 wt% free carbon and 0.7 wt% combined carbon. The SEM and TEM images showed that the particles of $ZnO_{1-x}C_x$: nC are quasi-one-dimentional tubes with a mean diameter of about 200 nm [Figure 1(*a*)]. The electron-diffraction pattern of an individual $ZnO_{1-x}C_x$: nC tube exhibited the system of continuous Debye rings due to the nanodispersed polycrystalline structure of tubular aggregates [Figure 1(*a*), insert] with a crystallite size of ~15 nm. The TEM images demonstrated the dispersed particles of zinc oxide, which are surrounded by an amorphous carbon matrix [Figure 1(*b*)]. The Raman spectra exhibited two lines, which confirm the state of carbon as amorphous: strong D line at 1357 cm^{-1} is due to the C–C bond with sp^3 hybridization and G line at 1599 cm^{-1} corresponds to the vibrations of carbon atoms in the sp^2 hybridization. Zinc oxide was leached from the $ZnO_{1-x}C_x$: nC composite with formic acid on boiling, and the residual amorphous carbon retained the tubular morphology of the source material [Figure 1(*d*)].

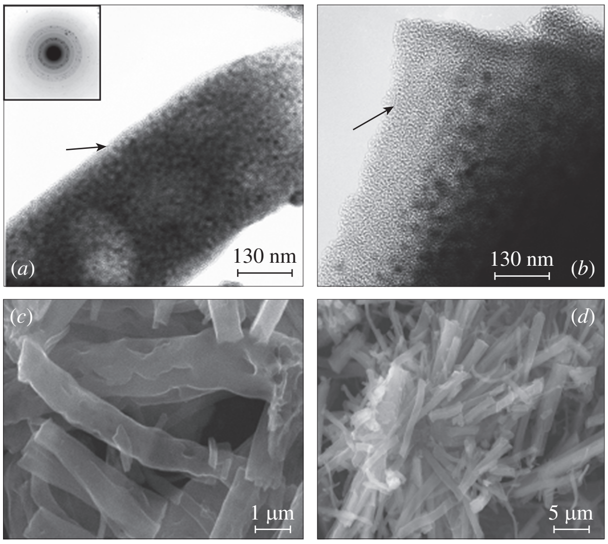

Figure 1 (*a*),(*b*) TEM image of the $ZnO_{1-x}C_x$: nC composite; SEM images of (*c*) $ZnO_{1-x}C_x$: nC and (*d*) carbon nanofibers after the dissolution of ZnO.

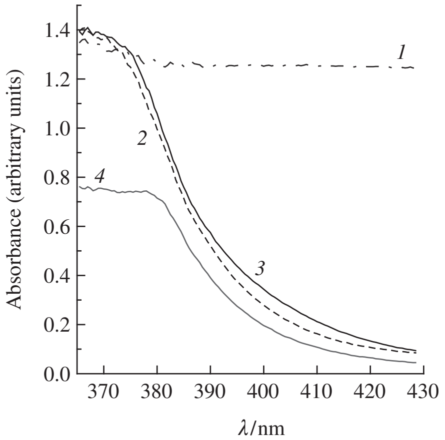

Figure 2 Absorption spectra of (*1*) $ZnO_{1-x}C_x$: nC and that after thermolysis in air at (*2*) 350, (*3*) 450 and (*4*) 600 °C.

For optimizing the concentration of free carbon, whose excess depresses the photocatalytic activity, the composite was stepwise calcined in air in a temperature range of 250–700 °C. The absorption spectra of $ZnO_{1-x}C_x$: nC composites calcined at temperatures below 300 °C did not show the features for ZnO absorption band edge (Figure 2). The concentration of carbon in these samples was ~5 wt%. In the absorption spectra of the samples calcined at 350 °C, the oxide absorption band edge can be seen only in the UV region. When the calcination temperature reached

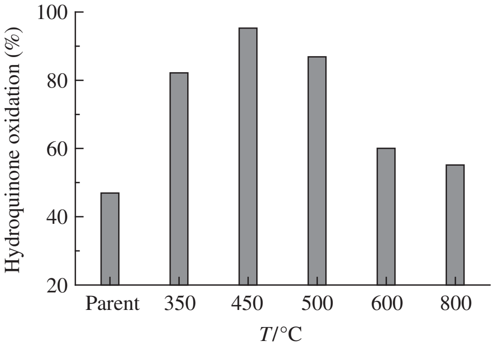

Figure 3 Effect of the $ZnO_{1-x}C_x$: nC annealing temperature on the rate of hydroquinone oxidation under UV irradiation after 8 h.

450 °C, according to Raman spectra and DTA data, all carbon (C_{carbon} ~ 0.2 wt%) became bound and the spectra exhibited a red shift of the absorption band edge to the visible region. For a wide-gap oxide semiconductor, the red shift of the optical absorption edge leads to extending photoresponse of ZnO from the UV to the visible spectral region. The EPR spectra of $ZnO_{1-x}C_x$ solid solutions obtained after calcination at 450 °C and the $ZnO_{1-x}C_x$: nC source composites exhibited a narrow symmetrical line with the Lorentzian shape and a *g*-factor of 2.001. According to published data,[12,13] the EPR signal with *g*-factor close to the spin-only value is attributed to singly charged oxygen vacancies in ZnO. Samples calcined at 300 °C exhibited a maximum EPR signal. The presence of single defect points with a considerable oxidation potential and red shift of the absorption band edge to the visible region determine the increased catalytic activity of $ZnO_{1-x}C_x$.[12] The maximal photocatalytic activity can be expected for $ZnO_{1-x}C_x$ solid solutions obtained at 450 °C. The rise of the calcination temperature up to 600–700 °C led to a decrease in the concentrations of both bound carbon and point defects, as indicated by the absorption band edge shift to the UV region (Figure 2). The photocatalytic activity of $ZnO_{1-x}C_x$: nC and $ZnO_{1-x}C_x$ was studied in the oxidation reaction of hydroquinone (HQ) carried out in aqueous solutions irradiated at λ_{max} = 253 (UV) or 460 nm (blue light). The maximal rate of HQ photooxidation was observed with the samples of $ZnO_{1-x}C_x$ obtained at 450 °C.

Thus, the thermolysis of a $Zn(HCOO)(HOCH_2CH_2O)_{1/2}$ precursor allowed us to obtain 1-D nanomaterials with high concentrations of singly charged oxygen vacancies: $ZnO_{1-x}C_x$: nC composite and $ZnO_{1-x}C_x$ solid solutions. The introduction of carbon into ZnO causes a red shift of the absorption band edge to the visible region and improves the photocatalytic characteristics of $ZnO_{1-x}C_x$ solid solutions for the oxidation of toxic organic substances.

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