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Low-temperature sol-gel synthesis, spectroscopic properties and conductivity of the thin films of TiO_2–CuO nanoparticles

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The highly photoactive conductive coatings of nanosized titania and a titania/copper(II) oxide nanocomposite were prepared based on the low-temperature sol-gel transformations and interactions of multiphase colloidal system components.

The TiO_2-based coatings possessing a highly developed surface area with a narrow pore size distribution find wide application in solar energy conversion,[1,2] multifunctional coating,[3] photocatalysis,[4,5] photoelectrochromic coatings,[6] materials for biochemical or medical purposes, *etc*.

The CuO–TiO_2 materials, which are highly active photocatalysts[5] and possess electric and electromagnetic properties[7] are of special interest. Moreover, copper oxide exhibits weak magnetism and its introduction into a semiconductor matrix of titania can be used for obtaining dynamic mechanical properties.[7]

Layered CuO–TiO_2 heterostructures are of importance because they can be used for the organization of PN transitions comparable with the work of multijunction cells[8] as TiO_2 is an n-type semiconductor, and copper oxide is a p-type one. However, the charge transfer mechanism in such nanosized materials remains poorly understood. The aim of this work was to obtain the conductive CuO–TiO_2 crystalline coatings† that are highly active in the visible region of the spectrum based on the sol-gel transformations and interactions of multiphase colloidal system components without a heat treatment stage.

Figure 1 shows the X-ray diffraction data.‡ Titania-based powders obtained without calcination are characterized by the presence of reflections corresponding to anatase (ICDD 21-1272) and brookite (ICDD 291360) [Figure 1(*b*)]. The broadening of diffraction pattern peaks indicates the presence of nanosized crystals. The average parameter *d* calculated from the Scherer equation was 6.4 or 7.2 nm for brookite or anatase, respectively. The synthesis of CuO in aqueous solution leads to the formation of a well-crystallized tenorite phase (ICDD 481548) [Figure 1(*a*)] and a copper metal phase in a ratio of 4 : 1. A sample obtained by interphase interaction of titania and copper oxide nanoparticles is characterized by the presence of separate phases for each component, with the anatase : tenorite : brookite ratio of 5 : 5 : 1. The absence of the characteristic peaks of metallic copper in the composite is apparently due to the oxidation of residual nanoparticles in air in the presence of titania.

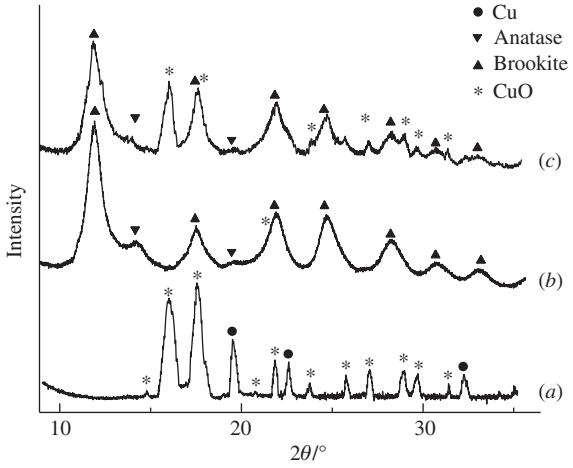

Figure 1 XRD analysis of powders: (*a*) Cu (CuO); (*b*) TiO_2; and (*c*) TiO_2–CuO.

The structure of nanosized particles in meso- and microregions[4] is optimal for preserving the high activity of titania-based species. We determined the particle size distribution by scanning probe microscopy (a silicon probe of 5 nm) (Figure 2). The profilogram of particle distribution on the TiO_2 film surface [Figure 2(*c*)] indicates the formation of crystalline nanoparticles with narrow size distribution of about 10 nm, which corresponds

† *Synthesis of titania nanoparticles.* Nanostructured titania was synthesized in a single stage using a solution prepared by mixing 12 ml of isopropanol (Aldrich) and 16 ml of titanium isopropoxide $Ti(OPr^i)_4$ (98%) and a peptizing solution heated to 70 °C and consisting of 100 ml of twice-distilled H_2O and 0.7 ml of concentrated HNO_3 was added to it dropwise after stirring for 2 h. As a result, the aggregated amorphous precipitate upon peptization and long-term heat exposure (at 70 °C for 8 h) dissolved in a colloidal solution of the TiO_2 sol, which was used for coating the films onto the surface of a preliminarily washed and dried coverslip.

Synthesis of copper(II) oxide nanoparticles. Copper nanoparticles were prepared by reducing Cu^{2+} from a solution containing 0.35 g of $CuSO_4 \cdot 5H_2O$ (99%, Aldrich), 7 ml of H_2O and 0.5 g of Pluronic P-123 (Aldrich, M_r = = 5 800) with a solution of 0.022 g $NaBH_4$ in 2 ml of H_2O. The formation of a brown solution of colloid copper simultaneously took place. The addition of P-123 polymer made it possible to avoid the aggregation of nanoparticles during reduction. The nanoparticles were then washed in alcohol and aqueous medium at 70 °C with gradual oxidation to the oxide state.

Synthesis of heterostructural TiO_2–CuO coatings. The crystalline coatings of TiO_2–CuO were synthesized by the coating of titania and copper oxide films onto the surface of preliminarily dried and washed Plexiglas using a spin-coating method. The films were vacuum dryed at 70 °C for 1 h.

‡ The X-ray powder diffraction data were processed using a Bruker Nanostar instrument using MoKα radiation (λ = 0.071073 nm).

The analysis of film surfaces was carried out using an SPM Solver P47H-PRO scanning probe microscope. Magnetic force microscopy employed a silicon probe with magnetic coating subjected to preliminary activation.

The spectral analysis of films was performed using a PG Instruments T70 + UV-VIS spectrophotometer in a wavelength range from 300 to 850 nm.

The conductivity measurements were carried out at room temperature on an MNIPI E7-20 LCR-meter (Belarus) using a two-electrode cell with a spring-type film holder and silver paste for making electrical contact.

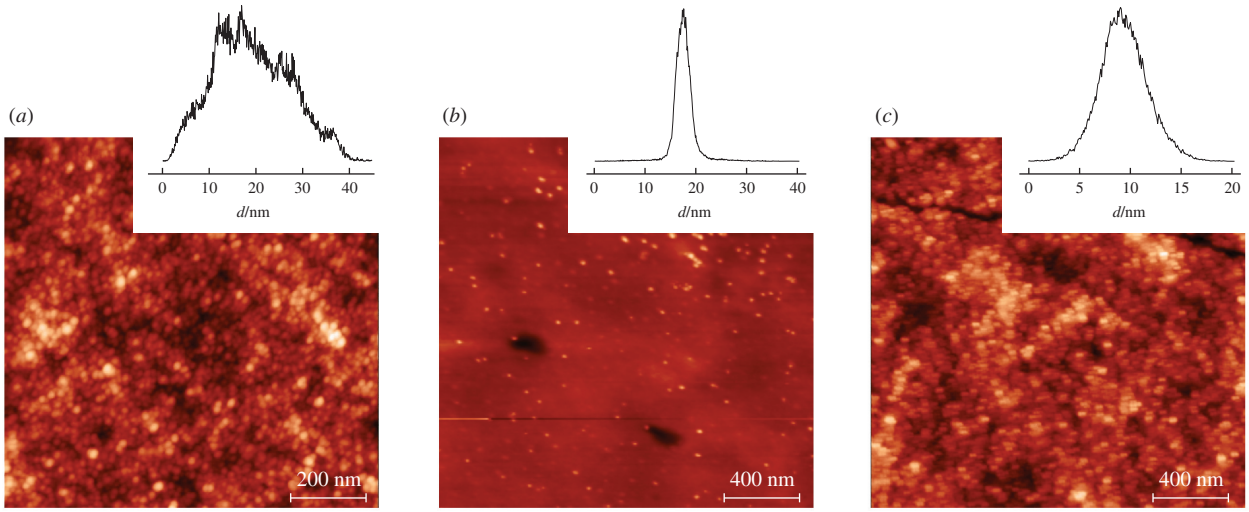

Figure 2 Morphology of films generated from titania and copper oxide nanoparticles and the profilograms of surface relief distribution for samples: (*a*) CuO–TiO_2; (*b*) CuO and (*c*) TiO_2.

to a dimensional state promoting preservation of photoactivity and highly developed structure.[5]

Tenorite nanosized crystals obtained by the oxidation of colloid copper form particles with distribution maximum at r_{av} = 17 nm [Figure 2(*b*)]. It is evident that the films obtained upon the sedimentation of TiO_2 and CuO nanoparticles have an average size of crystal formations larger than that of the initial components as a result of the partial aggregation and interphase interaction of disperse phases,[9] which is confirmed by the statistical analysis [Figure 2(*a*)]. This conclusion is also supported by the presence of characteristic bicomponent wide distribution in the profilogram.

The majority of modern approaches to obtaining titania-based composite materials are based on the formation of crystal phases using high-temperature processing (at 350 °C or higher),[5] as this allows one to fix the structure generated during the synthesis stage and to develop conductive and semiconductor properties due to the transformation of an amorphous phase into a crystal one.[10] Using Cu–CuO nanoparticles as a modifying additive promotes a sharp increase in photoactivity properties due to a spectral activity shift to the visible region. The synthesis of CuO–TiO_2 crystalline phases directly from a solution without calcination led to the formation of materials, which are highly active in the visible region of the spectrum (Figure 3).‡

Comparative analysis shows that the spectral activity of CuO and TiO_2 is characterized by different absorption regions. For a titania-based film an UV region overlap is observed, whereas a Cu–CuO coating is in the beginning of visible region (300–480 nm). At the same time, the combination of both oxides leads to a red shift of spectral activity. At frequencies lower than 10 kHz, the conductivity of the composite does not depend on frequency, as for copper dioxide, and then changes like the conductivity of a titania film. At low frequencies, the conductivity of the film is determined by charge carrier transfer to delocalized copper oxide states. According to published data,[11] copper oxide has a much higher electrical conductivity than titania, and dielectric permeability of titania is a few times higher than that of copper oxide. Moreover, the conductivity of titania linearly depends on the logarithm of frequency in the entire range, and conductivity of copper oxide does not depend on frequency below 1 MHz, and then the conductivity mechanism changes. A decrease in the frequency of transition of conductivity from direct current to alternating current below 10 kHz in case of the nanocomposite as compared to copper oxide can be related to an increase in the effective dielectric permeability of a material and interphase polarization processes in the nanocomposite. The given explanation corresponds to a published model,[12] according to which critical frequency depends on conductivity at direct current and dielectric properties: $\omega = \sigma_{DC}/\varepsilon_0\varepsilon_S$, where σ_{DC} is the conductivity at direct current, and ε_S is the static dielectric permeability of a material.

Comparison of data on the photoactivity and electrical conductivity of films reveals that the introduction of copper oxide into titania leads to a synergetic effect in the shift of an absorption band of a composite material, while for electrical conductivity this does not occur. We believe that it is related to the structure of copper-containing nanoparticles. During synthesis, at first copper nanoparticles are produced, which are then oxidized by oxygen to the oxide. The oxide layer formed on the surface of copper nanoparticles prevents their further fast oxidation. The core-shell structure Cu–CuO is thus formed. Such structures lead to a substantial shift of an absorption band upon their introduction

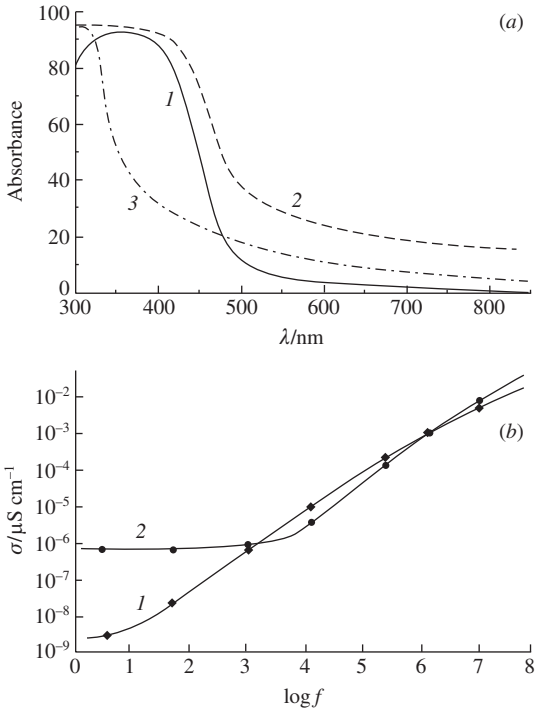

Figure 3 (*a*) UV-VIS absorption spectra of films generated from colloidal aqueous solutions of the corresponding nanoparticles: (*1*) CuO, (*2*) CuO–TiO_2, (*3*) TiO_2, and (*b*) dependences of conductivity on the frequency of the AC for (*1*) a pure TiO_2 film and (*b*) a composite film CuO (20%)–TiO_2.

into titania whose film protects the particles against full oxidation.[13] Apparently, in this case, an increase in spectral activity is caused by the action of a synergetic factor between the constituents of a multicomponent system with highly active phases (Figure 3). Upon generating electrical conductivity of a composite, such particles exhibit a contribution comparable to the conductivity of copper oxide.

The obtained result is in accordance with data on the effect of metal-oxide nanoparticles introduced into polymeric matrices on the shift of an absorption band of the material.[13]

In conclusion, a simple and ecologically safe approach (without calcination stage) for producing the CuO/TiO_2 crystalline conductive coatings possessing visible region photoactive properties has been elaborated.

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References

1 A. V. Agafonov and A. V. Vinogradov, *Khim. Vys. Energ*., 2008, **42**, 79 [*High Energy Chem.* (*Engl. Transl.*), 2008, **42**, 578].
2 A. V. Vinogradov, V. V. Vinogradov, A. V. Agafonov, A. V. Balmasov and L. M. Inasaridze, *Electromotive Forces in Solar Energy and Photocatalysis (Photo Electromotive Forces)*, Intech Publishers, Croatia, 2011, p. 21.
3 A. V. Vinogradov, A. V. Agafonov and V. V. Vinogradov, *J. Sol-Gel Sci. Technol.*, 2010, **53**, 312.
4 A. V. Agafonov, A. V. Vinogradov and V. V. Vinogradov, *Sol-Gel Synthesis of Mesoporous Ordered Nanomaterials on the Basis of Alumina and Titania*, Nova Science Publishers, USA, 2011, p. 201.
5 A. V. Vinogradov, V. V. Vinogradov and A. V. Agafonov, *J. Sol-Gel Sci. Technol.*, 2009, **49**, 180.
6 A. V. Vinogradov, V. V. Vinogradov, T. V. Gerasimova and A. V. Agafonov, *J. Alloys Compd.*, 2012, **535**, 102.
7 Y. Shin, B. W. Arey, C. Wang, X. S. Li, M. H. Engelhard and G. E. Fryxell, *Inorg. Chem. Commun*., 2007, **10**, 642.
8 G. I. Koleilat, X. Wang and E. H. Sargent, *Nano Lett.*, 2007, **12**, 3043.
9 D. Vorkapi and T. Matsoukas, *J. Colloid Interface Sci.*, 1999, **214**, 283.
10 S. Kim and S. H. Ehrman, *J. Colloid Interface Sci.*, 2009, **338**, 304.
11 *Fiziko-khimicheskie svoistva oksidov (Physico-chemical Properties of Oxides)*, ed. G. V. Samsonov, Metallurgiya, Moscow, 1978, p. 472 (in Russian).
12 K.-M. Jager, D. H. McQueen, I. A. Tchmutin, N. G. Ryvkina and M. Kluppel, *J. Phys. D: Appl. Phys.*, 2001, **34**, 2699.
13 A. L. Stepanov, *Prikl. Fiz.*, 2004, **74**, 1 (*Russ. J. Appl. Phys.*, 2004, **74**, 1).

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