New approaches of soft chemistry for preparation of nanostructured multifunctional composite coatings.

Alexandr V. Vinogradov, Vladimir V. Vinogradov, Alexandr V. Agafonov

Institute of Solution Chemistry RAS, vav@isc-ras.ru

ABSTRACT

In this work we consider a new approach to synthesize the composite phase crystallites of CuO/TiO_2, Ag/TiO_2, psevdobrookite and ilmenite (Co) possessing high photoactivity and magnetic properties based on the sol-gel transformations and interaction components of the multiphase colloidal system which yields hydroxylated crystallites of the material at close to room temperature without calcination. The effect of stoichiometric ratios of initial components on forming during low-temperature sol-gel synthesis products is investigated. The formation of geterooxide system with ilmenite type structure in the process of interaction between the phases of the hydrolysis products of titanium isopropoxide and hydrated forms of Co(OH)2 nanocrystals is investigated. The study of the phase composition of the samples was carried out using X-ray diffraction analysis. Possible ways of chemical interaction are represented. The morphology of thin films of diluted magnetic semiconductors attached to the surface of the thermally unstable materials was investigated with using atomic force microscopy. Comparison of the spectral characteristics of the nanocomposite consisting of titania (anatase) and magnetite, CuO, Ag or ilmenite (Co) in the visible and UV spectral regions showed a significant visible-region shift of the nanocomposite absorption bands compared to pure components.

Keywords: Low-temperature sol-gel synthesis, titania-based composite, thin films, hetero-oxide systems.

1 INTRODUCTION

At present time polyoxide titania-based materials, structural type of TiO_2-Fe_3O_4, TiO_2-CuO, TiO_2-CoO and Ag/TiO_2 lead to find of unique properties inherent of both individual components and composites based on them are, which is increasing a great interest in various fields of science and technology. Polymetallic systems are widely used in optics, electronics, spintronics, catalysis, and also to create a variety of functional and structural nanocomposites systems. Traditional methods for the synthesis of such materials (pseudobrookite, ilmenite, Ag-TiO_2 and CuO-TiO2) base on the stage of separation of solids from solutions and formation of amorphous structure, which does not exhibit photocatalytic and catalytic activity as previously shown [1,2].Annealing at temperatures above 400°C leads to an increase in photoactivity, but implies a considerable change in the formed structure due to burning out the organic phases and a decrease in adsorption capacity. An essential drawback of the traditional approach is that there is no possibility of coating layered heterostructures and dilute magnetic semiconductors in the form of thin coatings onto the surface of heat-unstable materials (polymers), as the formation of titania crystal phases traditionally occurs at temperatures above 350°C, as previously shown [2]. A solution to the problem is developing conditions under which crystal phases are formed directly during the synthesis as shown by [3], describes a sol-gel method of generating the TiO_2 anatase-brookite crystal form in an aqueous solution using peptizing agent, and [4,5] reports high photoactivity of nanocomposites obtained using this method without annealing. The combination of these approaches will obviously make it possible to realize a simple way to synthesize a nanocomposite on the basis of titania and magnetite that forms pseudobrookite crystal form during the synthesis. Hereby the combination of these approaches will allow to obtain a simple way for preparation of titania-based nanocomposites, which form spinel-type crystal modification at low-temperature sol-gel synthesis.

The goal of the present work is developing an approach to producing pseudobrookite crystallites which is based on sol-gel transformations and interaction of the multiphase colloidal system components and does not include annealing stage.

2 EXPERIMENTAL

General data

In this work the chemical reagents produced by the “Aldrich” international company have been used.

Wide-range X-ray powder diffraction data have been processed using Bruker D8 Advance equipment with molybdenum anode MoKα ($\lambda = 0.071073$ nm).

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

Spectral analysis of films has been carried out using PG Instruments T70+ UV/VIS spectrophotometer in the wavelength range from 300 to 850 nm.

Synthesis of pseudobrookite

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Synthesis of crystalline pseudobrookite was carried out in a single stage by mixing two solutions. The first one was obtained in the process of magnetite peptization in a highly acidic aqueous medium (HNO_3:Fe_3O_4 = 1:2) upon stirring and heating to 70°C, while the second was prepared by mixing isopropyl alcohol and titanium isopropylate (C = 0.05 M). As a result, the formation of a dark-brown prepicitate was observed. Upon intensive stirring for 4 h and maintaining temperature this precipitate developed into the state of a stable sol.

Synthesis of copper (II) oxide nanoparticles

Synthesis of copper nanoparticles was carried out 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 instilled drop by drop upon intensive stirring. The formation of a brown solution of colloid copper simultaneously took place. Addition of P-123 polymer made it possible to avoid the aggregation of nanoparticles during reduction. The NPs were then washed in alcohol and aqueous medium at 70°C with gradual oxidation of the latter to the state of oxide.

Synthesis of heterostructural TiO_2-CuO coatings.

Synthesis of TiO_2-CuO crystalline coatings was carried out by staged coating the titania and copper oxide films onto the surface of preliminarily dried and washed Plexiglas by spin-coating method. After coating every layer the film surface was exposed to vacuum drying at 70°C.

Then films were exposed to vacuum drying at 70°C for 1 h. This route uses a cheap and non-toxic solvent (water) and gives crystalline films with potential applications for coating low thermal stability substrates (polymers).

Synthesis of ilmenite

Synthesis of crystalline $CoTiO_3$ was carried out in a single stage by mixing two solutions. The first one was obtained by pyrochroite peptization in a strong acidic water environment, at stirring and heating to 70°C, while the second was prepared by mixing isopropyl alcohol and titanium isopropylate (C = 0.05 M). The resulting solution was stirred for 4 hours at 80°C. Then the effect of stoichiometric ratios of components on the structure of formed products was studied.

3 RESULTS AND DISCUSSION

Equations must be placed flush-left with the text margin X-ray diffraction data analysis of all samples is presented in Fig. 1. Titania-based powders obtained without calcination stage are characterized by the presence of reflexes corresponding to the anatase-brookite form, see Fig. 1b. The broadening of diffraction pattern peaks indicates the presence of nanosized crystals. Average value of parameter d calculated using Scherer equation was 6.4 and 7.2 nm for brookite and anatase, respectively. According to X-ray diffraction data analysis, synthesis of CuO in aqueous media leads to formation of well-crystallized tenorite phase, Fig. 1a, and metallic copper phase, with the 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 every component, with the anatase : tenorite : brookite ratio of 5 : 5 : 1. The absence of metallic copper characteristic peaks in the composite is apparently due to oxidation of residual nanoparticles in air, in the presence of titania phases. And synthesis of Fe_3O_4 in an aqueous medium leads to the formation of well-crystallized magnetite phase, Fig. 1d, and amorphous hematite phase, with the ratio of 1:2:1. A sample obtained by interphase interaction of titanium isopropylate hydrolysis products and magnetite phase peptization products is characterized by the presence of pseudobrookite, Fig.1 e, anatase, and magnetite phases with the ratio of 5:5:1. As a result of such interaction, according to XRD analysis data, see (Fig. 1 (f, g)), the hydrated crystallites whose structure is similar to that of ilmenite, are formed.

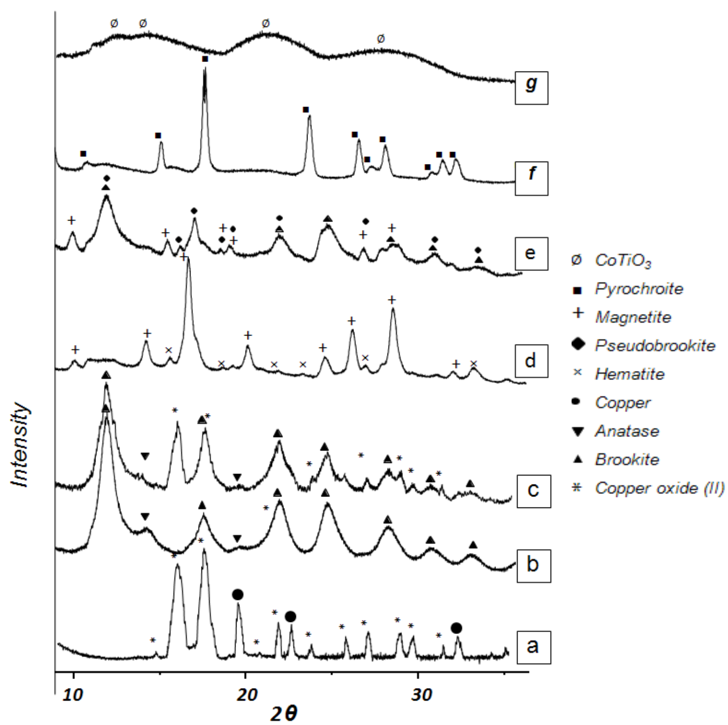

Figure. 1. An XRD analysis of powders: a) magnetite; b) titania; c) pseudobrookite, d) magnetite, e) pseudobrookite, f) pyrochroite, g) ilmenite.

It was find that synthesis of crystalline phase frequently leads to an increase in the average size of formed particles, which complicates further dispersion of functional solid phase on the surface of such materials. The structuredness of nanosized particles in meso- and microregions, as shown by [6], is considered to be optimal for preserving high activity of titania-based preparations. In the present work the particle size distribution was assessed according to a statistical analysis by scanning probe microscopy (silicon probe Ø = 5 nm), Fig.2, and also by dynamic light scattering data of Fig. 3. The histogram of particle distribution on the TiO_2 film surface (Fig. 2c) indicates the formation of crystalline nanoparticles with narrow size distribution of about 10 nm, which corresponds to a dimensional state promoting preservation of photoactivity and highly developed structure, as previously shown [7].

In case of formation of cobalt ilmenite, the obtained data indicate the formation of structurally homogeneous reaction products in the form of spherical nanoparticles, Fig. 2d. These results are confirmed by a characteristic profile of the histogram demonstrating a narrow particle distribution with a single maximum at Δh = 9 nm. At the same time, the presence of titania and $Co(OH)_2$ phases as the reaction products leads to separation of phases in film structure, which prevents the formation of the ordered surface, Fig. 2e. These data are confirmed by the presence of a few characteristic maxima on the histogram indicating the presence of a multi-component system.

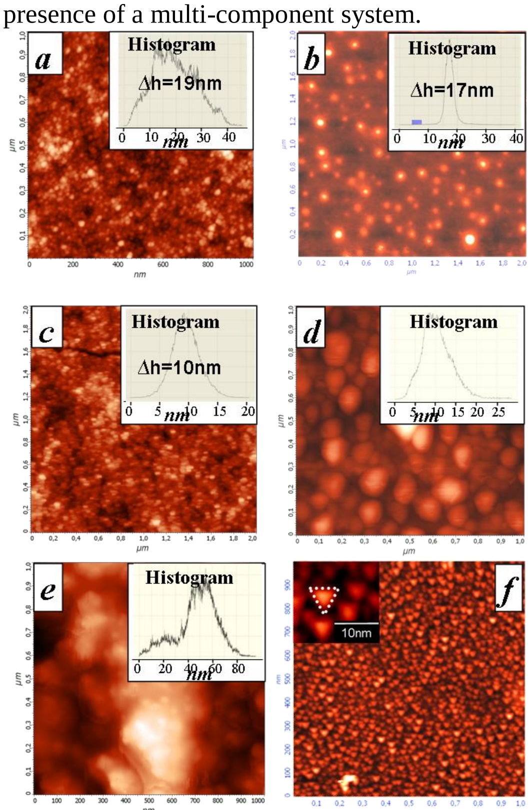

Figure. 2. Morphology of films generated from titania, copper oxide, silver or pyrochroite nanoparticles and histogram of surface relief distribution for samples: a) CuO/TiO_2; b) CuO; c) TiO_2; d) ilmenite Co; e) unreacted TiO_2-Fe_2O_3 phases; f) Ag/TiO_2.

The maximum of titania particles distribution is at r_{av} = 16 nm, Fig. 3a, i.e. corresponds to a state promoting the preservation of photoactivity and highly developed structure. The nanosized magnetite crystallites obtained in the co-precipitation process consist of particles with distribution maximum at r_{av} = 19 nm, Fig. 3b. Spinel-type materials synthesized by interphase interaction between solid phases of titanium isopropylate primary hydrolysis products and magnetite Fe_3O_4 peptization products in an aqueous medium should obviously possess a larger average particle size compared to initial components, which is confirmed by dynamic light scattering r_{av} value of 51 nm, Fig. 3c. This conclusion is also supported by the presence of a small peak in the 15 nm region, Fig. 3c, that belongs to partially unreacted components.

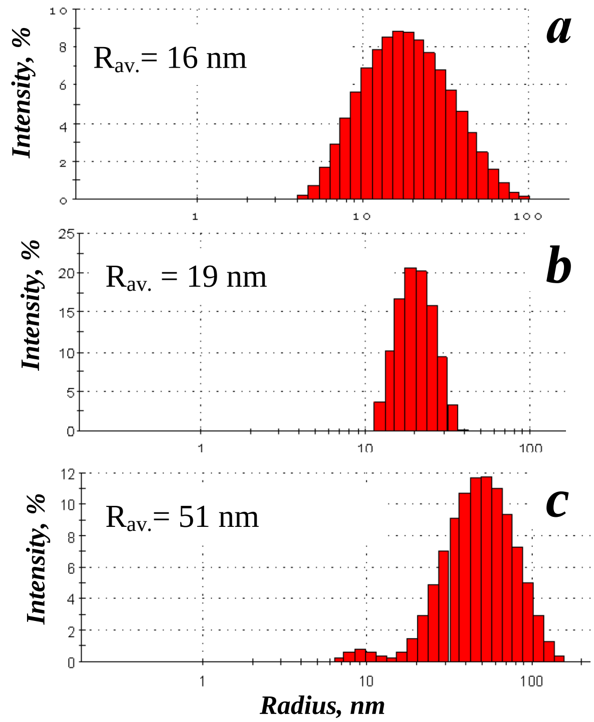

Figure. 3. Particle size distribution in aqueous powder suspensions: a) titania; b) magnetite; c) pseudobrookite.

The majority of modern approaches to synthesizing pseudobrookite-type, CuO/TiO_2 and ilmenite (Co)-type composite materials are based on the formation of crystal phases using high-temperature processing (at more than 400°C), as shown by [8], as this allows to fix the structure generated during the synthesis stage and to develop magnetic and semiconductor properties due to transforming the amorphous phase into the crystal one. An increase in crystallinity promotes a sharp increase in photoactivity properties due to a visible-region shift of spectral activity for a material. The approaches to synthesizing pseudobrookite-type, CuO/TiO_2 and ilmenite(Co) crystalline phases directly from a solution without annealing stage used in this work have led to formation of materials that are highly active in visible region of the spectrum. Results on spectral activity of preparations are presented in Fig. 4. An analysis shows that comparison of spectra for pure TiO_2 and pseudobrookite or CuO/TiO_2 clearly indicates the absorption band red shift. And the characteristic spectrum for pure Fe_3O_4 or CuO involves only intermediate values. Apparently, in this case an increase in spectral activity is caused by the action of synergetic factor between constituents of a multicomponent system with highly active phases.

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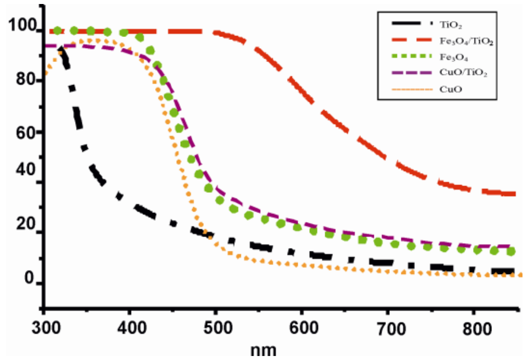

Figure 4. UV and visible absorption spectra of samples.

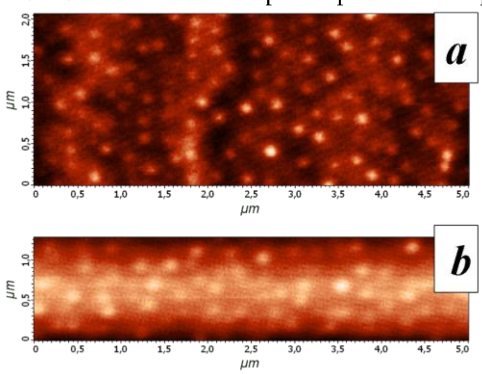

Figure 5. Topography of the CuO/TiO_2 film surface in: a) semicontact mode; b) contactless mode using ferromagnetic probe.

Magnetic microscopy technique allows to study magnetic field distribution over the surface of a sample. The basis of topography for the presented surface is formed by a long-range interaction of a magnetic probe (Ø = 18 nm) with local magnetic field of the CuO/TiO_2 film. Investigating the distribution of magnetic particles is performed using a two-pass technique. The first pass surface topography, in semicontact mode, is presented in Fig. 5(a). In the second, Fig. 5(b), pass the cantilever fluctuates and additionally rises above the surface to the height ΔZ of 80 nm, so that van der Waals forces can be neglected and the cantilever is affected only by long-range magnetic forces. The data obtained indicate the formation of CuO/TiO_2 particles possessing magnetic properties. The structure of a film surface thus looks similar to that presented in Fig. 2, however, an exhibition of magnetic properties appears to be characteristic only for a certain part of a material. Apparently, the origin of magnetic forces in a film is provided by the presence of copper oxide particles possessing antiferromagnetic properties, as previously shown [9], which leads to generation of the ordered domain structures.

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4 CONCLUSIONS

The results obtained demonstrate a simple and ecologically safe approach to producing the crystalline composite materials directly in the synthesis process without annealing stage.

Such an approach, in our opinion, has doubtless advantages due to a possibility of exact stoichiometry control, low temperature of synthesis, high purity of materials. This makes it possible to carry out the processes of forming the nanocomposites in a polymer matrix both using polymer solutions as the reaction medium and performing polymerization of monomers in the presence of the formed sol system, for achieving the homogeneous particle distribution. On its basis obtaining dilute magnetic semiconductors (DMS) in the form of thin coatings on the surface of heat-unstable materials (polymers) as well as DMS-based nanocomposites in a polymer matrix becomes possible.

The effect of generated prestructure of the materials formed in the course of interphase interaction of a colloidal system, on the growth and stoichiometric ratio of crystalline phases structured as a result of heat treatment is studied. XRD analysis data confirm the structure of obtained preparations. Using statistical analysis of the film surface structure the morphology of the formed materials possessing the organized structure and narrow particle size distribution has been studied. A comparative analysis of absorption spectra has revealed an exhibition of synergetic effect for the composite film absorption band shift to visible region of the spectrum.

Obtaining highly visible-region-active CuO/TiO_2 and Ag/TiO_2 coatings is achieved due to a deep interphase interaction, due to formation of crystalline titania and copper oxide nanoparticles with complementary diameters. It is shown that the CuO nanoparticles formed on a film surface promote generation of magnetic fields in the samples.

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REFERENCES

1. A.V.Agafonov, A.V. Vinogradov, High Energy Chemistry, 42(7), 578, 2008.
2. A.V.Vinogradov, V.V.Vinogradov, A.V.Agafonov, J. Sol-Gel Sci Technol. 49, 180, 2009.
3. P. Alphonse, A.Varghese, C. Tendero, J. Sol-Gel Sci. Technol., 56, 250, 2010.
4. A.V.Vinogradov, A.V. Agafonov, V.V. Vinogradov, Journal of Alloys and Comp., 515,1, 2012.
5. A.V.Vinogradov, A.V. Agafonov, V.V.Vinogradov, Mendeleev Commun, 22, 1, 2012.
6. A.V. Agafonov, A.V. Vinogradov, V.V. Vinogradov, Nova Science Publishers, (2011) 201-248
7. Castro, M. Nunes, M. Carvalho, L. Ferreira, J. Solid State Sci. 182, 1838, 2009.
8. H.C.Pedro etc. J. Braz. Chem. Soc., 19(8), 1501, 2008.
9. V. Bisht, K. Rajeev, S. Banerjee, J. Solid State Communications, 150,884, 2010.