Nanoparticles of Metals Oxides Preparation and Characterization

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Abstract – Water dispersions of four metal oxides nanoparticles were synthesized by pulsed laser ablation of metallic targets (Ce, Cu, Ti, Zn) in water. The fundamental harmonic of nanosecond Nd:YAG laser was used. Nanocrystalline powders of oxides were obtained from the dispersions. The composition and structure of the materials obtained were investigated. The average size of the crystallites was found to be 10-20 nm. Cubic CeO$_2$ and Cu$_2$O, wurtzite-type ZnO and anatase/brookite mixture of TiO$_2$ were identified in products. CeO$_2$ was obtained from metallic Ce target for the first time. As prepared nanostructured semiconductors can be used in catalysis and photocatalysis, sunscreen technology, in biomedicine, and as antibacterial agents.

Keywords: nanoparticles, titania, ceria, zinc oxide, copper oxide, pulsed laser ablation

1. Introduction

Semiconductor nanoparticles are widely used in different fields of science and technology. Cerium dioxide CeO$_2$ is a unique functional material that is applied in catalysis in a variety of different processes. It may be both a carrier and an active component [1-3]. In biomedicine cerium oxide is also used quite wide. Nanostructured copper oxides (Cu$_2$O, CuO) are applied in a large variety of fields. It is used as catalyst, as antibacterial agent, in optics, etc. Nano-dispersed TiO$_2$ is applied in “green technology” in photovoltaic devices for solar energy [4], in production of bactericidal materials [5], and sunscreens [6]. One of the most prospective fields of its application is environmental photocatalysis for air and water purification [7]. Zinc oxide [8] is a wide-gap semiconductor (band gap of 3.37 eV) that finds its application in optoelectronics, catalysis, sensors, biomedicine, food industry, and other fields.

There is a large number of methods for these materials obtaining, and chemical are the most popular once. But chemical methods are often complicated, expensive; they require using precursors that can contaminate the product. In our opinion one of the most prospective methods for synthesis of “pure” nanoparticles is pulsed laser ablation (PLA) of bulk targets in liquid. This method allows controlling effectively the size, structure, composition, and properties of nanoparticles obtained by varying of laser parameters, reaction media, and by introducing of different additives [9-11]. There are some references of preparation ZnO, Cu$_2$O, CuO and TiO$_2$ in literature with using this method. But all of the materials obtained showed different structure, composition and properties. In case of obtaining of CeO$_2$ there are no references of ablation of metallic Ce target. And the aim of the present work is to obtain pure semiconductors nanoparticles by pulsed laser ablation of metallic targets (Ce, Cu, Ti, Zn) in water, and to study the materials obtained.

2. Experimental

Nanoparticles water dispersions were obtained using the experimental setup and the procedure of obtaining are described in [12]. The radiation of the fundamental harmonic of Nd: YAG laser was used (1064 nm, 7 ns, 150 mJ, 20 Hz). Short-focus lens (F = 40 cm) focused the radiation at the target surface through the wall of 50 ml glass reactor. Target was moved in the plane XY, perpendicular to the optical axis. Obtaining of nanoparticles in water took different time for different targets. The size and structure of the particles were examined by transmission electron microscopy (TEM CM 12, Philips), 120 kV. Freshly obtained dispersions were deposited on copper grids with amorphous carbon and allowed to dry. The composition of nanostructured powders obtained was studied by X-ray diffraction (Shimadzu XRD 6000).
3. Results and discussion

Figure 1 presents TEM-images of nanoparticles from water dispersions obtained by PLA. It can be seen, that particles obtained from Ce and Cu targets can be both big (up to 70 nm for Ce) and small (10, and even 5 nm for copper), and mostly show spherical shape. Smaller particles form not very large agglomerates. In case of Ti target particles are spherical too, but the size is smaller, and agglomerates are bigger and thicker. Nanoparticles from Zn target show three different shapes: rods, spheres and hexagons, with the average size about 15 nm.

XRD data, presented on Figure 2, reveals that all the particles are metal oxides. Cubic CeO$_2$ and Cu$_2$O crystals and wurtzite-type ZnO are the only components of corresponding water nanoparticles dispersions. In case of TiO$_2$ there are two polymorphic modifications of titania – anatase and brookite (about 35%). All the data obtained are summarized in Table 1. It is clearly seen, that the parameters of ablation are connected with the thermal characteristics of target materials. Catalytic, photocatalytic and antibacterial properties of as-prepared semiconductor nanoparticles were further investigated.

Fig. 1: TEM images of nanoparticles from water dispersions obtained by PLA: (a) – from Ce target; (b) – from Cu target; (c) – from Ti target; (d) – from Zn target.

4. Conclusion

Water dispersions of four metal oxides nanoparticles were synthesized using pulsed laser ablation of metallic targets (Ce, Cu, Ti, Zn) in water. For the first time, CeO$_2$ was obtained from metallic Ce target, not from CeO2 powder or cerium salts solution ablation. The materials obtained were characterized. Among the products obtained the phases of cubic CeO$_2$ and Cu$_2$O, wurtzite-type ZnO and anatase/brookite mixture of TiO$_2$ were found. The average size of the crystallites was 10-20 nm. As prepared nanostructured semiconductors can be used for different applications, ZnO and Cu$_2$O have shown high antibacterial activity, CeO$_2$ – catalytic, and TiO$_2$ – photocatalytic activity.
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References