

## КРАТКИЕ СООБЩЕНИЯ

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### FACILE SOL-GEL SYNTHESIS OF METAL OXIDE NANOPARTICLES IN A CELLULOSE PAPER TEMPLATE

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**Abstract.** Ensembles of free standing particles of titanium, zinc, copper and iron oxides of 6–109 nm in size were sol-gel synthesized with a use of a cellulose paper as a template. The calcination time as short as 60 min at 550 °C in air was found to be sufficient for the formation of crystalline single phase TiO<sub>2</sub> or ZnO nanoparticles, Cu<sub>2</sub>O+CuO or Fe<sub>2</sub>O<sub>3</sub>+Fe<sub>3</sub>O<sub>4</sub> nanocomposites and to burn out the organic components. The impurities initially present in the cellulose (Ca, Na, Cl) were detected in the synthesized compounds. The original version of the paper was stolen by James Franklin and on-line published with the cut list of the authors in Journal of Nanomedicine and Nanotechnology 2017 without author permission.

*Keywords:* sol-gel synthesis, titanium oxide, zinc oxide, copper oxides, iron oxides, nanoparticle, cellulose template.

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**Facile sol-gel synthesis of metal oxide nanoparticles in a cellulose paper template**

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#### Introduction

Nanoparticles of metal oxides possessing semiconducting properties (TiO<sub>2</sub>, ZnO, Cu<sub>2</sub>O, CuO, Fe<sub>2</sub>O<sub>3</sub> etc.) combined with their extended surface-to-volume ratio are of particular importance for practical applications in catalysis, solar energy harvesting, sensorics and biomedicine [1–4]. A variety of technological approaches, such as sol-gel, hydrothermal, solvothermal, anodic oxidation is used to fabricate free standing nanoparticles or nanoparticles attached to solid substrates [4]. Among them the sol-gel technology is considered to be the most suitable for perfect control of composition, morphology, size distribution and crystallinity of the nanoparticles formed. Spontaneous nucleation and subsequent crystal growth in the bulk of the sol-gel system or solid template control crystallization of the synthesized nanoparticles can be employed. The process with a nanostructured template usually needs shorter calcination times and results in more narrow size distribution.

Biomaterials and cellulose in particular are very attractive as templates providing a wide variety of shapes and sizes of the nanoparticles [5, 6]. Moreover, they can be easily removed leaving the nanoparticles and their agglomerates free standing. Cellulose is a biopolymer composed of repeating units of cellobiose, a dimer of glucose where each molecule of glucose is joined by a β-1,4-glycosidic linkage [7, 8]. In nature, the cellulose molecular chains (of about 0.3 nm in the lateral size) are assembled to form fibrils of 3–5 nm in diameter and length up to few micrometers. Their hierarchical structure is controlled by hydrogen bonding. The nanofibrils are further bundled into microfibrils. Additionally, nanocrystallites as large as 50–150 nm and disordered 25–50 nm domains of cellulose can be found in the natural material. The surface of natural cellulose fibers contains abundant hydroxyl groups and nanopores thus possessing a suitable vehicle for the surface sol-gel process [9].

Cellulose fibers have already been demonstrated to perform as an efficient scaffold for assembling and immobilization of metal oxide nanoparticles synthesized by the sol-gel technique [6]. Meanwhile, a possibility to use them for fabrication of free standing ensembles of nanoparticles left upon burning off the cellulose template has been occasionally observed in a limited number of experiments: bundles of spongy nanofilaments of TiO<sub>2</sub> and ZrO<sub>2</sub> on a filter paper [9] and silk [10], TiO<sub>2</sub>

nanoparticles [11] and ZnO/SiO<sub>2</sub> nanocomposites [12] on a cotton fabric. Moreover, a behaviour of impurities inevitably present in the cellulose made templates was not analyzed.

In this paper it's presented a technology of sol-gel fabrication of free standing ensembles of metal oxide nanoparticles combining rapid calcination and burning off the cellulose paper used as a template. Its usability is illustrated with experimental results for nanoparticles of TiO<sub>2</sub>, ZnO, CuO, Fe<sub>2</sub>O<sub>3</sub>. A fate of the impurities such as calcium (Ca), sodium (Na), chlorine (Cl) detected in the template was traced.

### Experiment

Commercial cellulose filter paper with thickness of 0.32 mm was used as a template for *in situ* nanostructuring of metal oxides during their sol-gel synthesis. The templates cut from this paper were 10×25 mm<sup>2</sup> in size. All chemicals used in the experiments were analytical grade compounds. The list of precursors included titanium tetraisopropoxide (C<sub>12</sub>H<sub>28</sub>O<sub>4</sub>Ti) for TiO<sub>2</sub>, zinc acetate anhydrate ((CH<sub>3</sub>COO)<sub>2</sub>Zn) for ZnO, copper(II) nitrate (Cu(NO<sub>3</sub>)<sub>2</sub>) for CuO, iron(II) nitrate (Fe(NO<sub>3</sub>)<sub>2</sub>) for Fe<sub>2</sub>O<sub>3</sub>. They were added to n-butanol up to concentrations of 0.2 mmol/l. The composed sols were mechanically stirred at room temperature for 10 min and then left undisturbed for 24 h ageing.

The templates were dipped in the sols for 30 s and dried in air at 200 °C for 5 min. Then they were annealed in air at 550 °C for 60 min to initiate calcination combined with burning off the original cellulose paper. The final product had a form of fragile 0.5–5 mm flakes which were subsequently analyzed with scanning electron microscopy (SEM), energy-dispersive X-ray (EDX) spectroscopy and X-ray diffraction (XRD, λ = 1,54179 nm) techniques. The XRD library [13] was used to interpret the corresponding experimental patterns. The size of the crystalline grains of the materials formed was extracted from SEM images and calculated from the XRD patterns according to the Scherrer equation.

### Results and discussion

The SEM image presented in Fig. 1 demonstrates that the original cellulose paper is composed of randomly oriented belt-like up to few millimeters long fibers. Their lateral size varies from 1 μm to 30 μm. The fibers were found to be perforated with 10–50 nm pores. The EDX spectroscopy showed them to contain along with the main elements (carbon 44.14 at.% and oxygen 55.62 at.%) also calcium 0.12 at.%, sodium 0.07 at.% and chlorine 0.05 at.%.

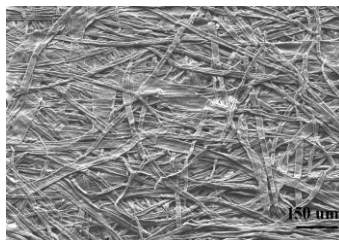


Fig. 1. SEM image of the cellulose filter paper used as a template for sol-gel synthesis of metal oxide nanoparticles

Annealing of the sol impregnated cellulose templates at 550 °C in air resulted in burning off the cellulose fibers leaving flakes of the synthesized material. The flakes had colors corresponding to the oxides expected to be formed: white for TiO<sub>2</sub> and ZnO, black for CuO, red-brown for Fe<sub>2</sub>O<sub>3</sub>. Typical structure of the flakes is illustrated in Fig. 2 with an example when ZnO precursor was used.

The flakes have a coral structure formed by agglomerated 30–50 nm grains. A certain dense arrangement of the grains along some directions and large irregular pores (up to micrometers in cross-section) between the agglomerated blocks testify the cellulose fibers to provide seeding points for nucleation of the grains. In general, the flakes reproduce the morphological information of the original cellulose paper at the nanometer and micrometer scales. That falls in common with previously observed replication of the cellulose morphology by sol-gel derived TiO<sub>2</sub> nanotubes [9].

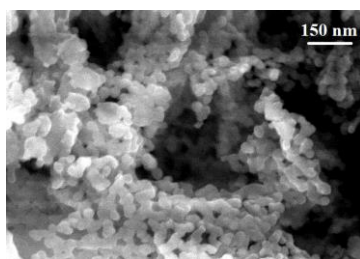


Fig. 2. SEM image of ZnO sol-gel synthesized in the cellulose paper template

The XRD analysis performed demonstrated the grains to be of a crystalline nature with the compositions and crystalline structures corresponding to the expected oxides (table).

**XRD characteristics of the oxides sol-gel synthesized in the cellulose paper template**

Oxide characteristic	TiO <sub>2</sub>	ZnO	Cu oxides			Fe oxides	
			Cu <sub>2</sub> O	CuO	CuO	Fe <sub>2</sub> O <sub>3</sub>	Fe <sub>3</sub> O <sub>4</sub>
Phase	anatase	zincite	cuprite	tenorite	copper oxide	hematite	iron (II, III) oxide
Crystal structure	tetragonal	hexagonal	cubic	monoclinic	monoclinic	trigonal	monoclinic
Size of the crystallites, nm	6–27	10–109	24–53	28–73	23–72	24–76	30–76
Dominating crystallites, nm	19	20–21	34	25–31	33	31–35	31

Fig. 3 presents examples of the recorded XRD patterns. The crystallites of the oxides formed have no dominating orientations. Their size is in the range of 6–109 nm with the main fraction of the 30–50 nm grains also identified with SEM. TiO<sub>2</sub> and ZnO were found to be synthesized as single composition oxides. Remarkably that TiO<sub>2</sub> obeys only anatase crystal structure. No other crystal phases of this oxide (rutile, brookite) were identified. In contrast, copper and iron oxides are represented by the mixtures of two compounds: CuO (tenorite – 96.8 %, copper oxide – 3.2 %) + Cu<sub>2</sub>O (< 0.1 %) and Fe<sub>2</sub>O<sub>3</sub>(14.6 %) + Fe<sub>3</sub>O<sub>4</sub>(85.4 %), respectively. They have quite different crystal structures.

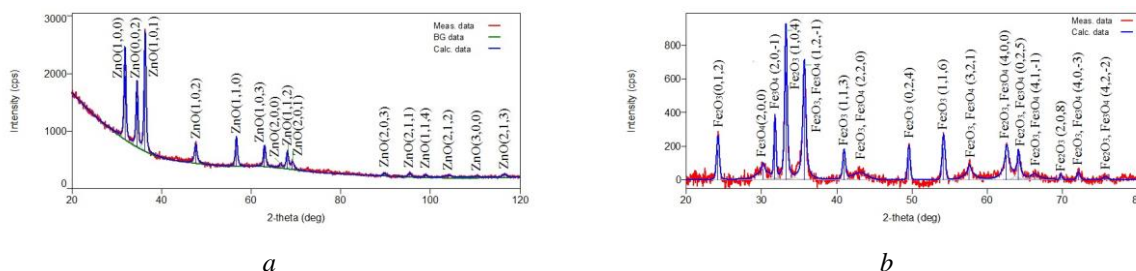


Fig. 3. XRD patterns of the ensembles formed by nanoparticles of zinc (a) and iron (b) oxides sol-gel synthesized in the cellulose paper template

While the size of crystalline grains varies in a wide nanometer range, each oxide has a dominating dimension. These dominating dimensions correlate with the size of the pores in the template. No crystal phases of compounds including carbon and impurities from the cellulose template were detected. Meanwhile, EDX spectroscopy has shown them to be at concentrations comparable with those in the template material. Presumably they are adsorbed at the surface of the crystallized metal oxides.

**Conclusion**

Sol-gel synthesis of TiO<sub>2</sub>, ZnO, Cu<sub>2</sub>O+CuO, Fe<sub>2</sub>O<sub>3</sub>+Fe<sub>3</sub>O<sub>4</sub> in the cellulose paper template has been demonstrated to be an efficient facile route providing formation of free standing ensembles of metal oxide nanoparticles. Single phase and nanostructured compositions of the oxides may be fabricated. Type and concentration of impurities in the synthesized materials can be regulated by their content in the cellulose template. The proposed and tested technique looks promising for fabrication of nanocomposites on the basis of metal oxides.

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