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The effect of Ag(0) colloidal crystals and nanoribbons formation as a result of the redox reaction between Ce(III) and Ag(I) cations occurring on the surface of an aqueous solution of their salts mixture

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ABSTRACT The proposed study shows for the first time that gaseous ammonia treatment of AgNO₃ and Ce(NO₃)₃ salts mixture aqueous solution surface gives rise to formation of a composite layer consisting of Ag(0) faceted colloidal crystals and nanoribbons, as well as CeO₂ nanocrystals. A study of such a composite carried out by FESEM, XRD, EDX, TEM, STEM and HRTEM methods has shown that the nanoribbons are about 50–150 nm wide and up to 2–3 μm long, and that there are 2–3 nm CeO₂ nanocrystals on the surface thereof. Colloidal crystals of about several micrometers consist of separate, almost identical silver nanocrystals about 20 nm in size. The obtained results provided a basis for construction of schemes of chemical reactions taking place during the synthesis, and gave grounds for recommendations on practical application of the obtained compounds.

KEYWORDS silver, colloidal crystals, nanoribbons, CeO₂, composite, interface synthesis.

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1. Introduction

It is known that the crystal lattice sites of the so-called colloidal crystals contain nanoparticles of almost the same size ranging from units to tens of nanometers [1]. These sizes are close to the sizes of colloidal particles contained in appropriate solutions, and this fact in many ways defined the term “colloidal crystals”. A different terminology for such nanosized structures propose the term “colloidal superstructures” [2]. These objects also include the so-called “photonic crystals”, which are formed by amorphous particles of metal oxides or polymers with sizes of tens and hundreds nanometers [3]. One example of such colloidal crystals formed by noble metals would be Au crystals with sizes of several microns consisting of Au nanoparticles about 8 nm in size [4].

These crystals are synthesized using vertical deposition [5], spin-coating [6], microfluidic [7], external-force-driven assembly [8] and other techniques. The main problem of such synthesis reduces to obtaining a large number of nanoscale particles of the same size, from which a colloidal crystal is then formed in the process of “crystallization”. As a rule, metal nanoparticles of the same size are obtained in several stages, which include both the nanoparticles synthesis stage, and the stage of nanoparticles separation by size, while at the stage of synthesis when stirring reagents, even under thorough stirring, it is difficult to obtain monodisperse nanoparticles. In this regard, the synthesis of nanoparticles at the solution-gas interface offers unique opportunities. Treating such an interface with a gaseous reagent allows one to avoid concentration gradient of reactants in the planar direction due to isotropic distribution of concentration of reagents interacting with gas molecules over the surface of the solution.

Another important topic in the preparative chemistry of nanosized noble metals is the synthesis of 1D Ag(0) nanocrystals with the morphology of the so-called nanowires [9] and nanoribbons [10]. As follows from the analysis of the literature sources, the focus on the morphology is mainly caused by the solution of the urgent problem of creating conductive and transparent coatings for optoelectronics [11].

The purpose of the present study was to investigate the conditions needed for formation of nanosized Ag(0) particles during the one-stage crystallization process occurring at the interface of aqueous solution of AgNO₃ and Ce(NO₃)₃ salts mixture with air containing gaseous ammonia or, in other words, under the Gas Solution Interface Technique conditions (GSIT) [12–14]. These reagent compositions were chosen given the known fact that the redox reaction occurs in a

weakly alkaline medium with the participation of Ag(I) and Ce(III) cations, in which Ag(0) and CeO₂ nanoparticles are formed [15]. As is known, such nanosized crystals and the composites based thereon find application, for example, in biomedicine [16–18], catalysis [19] and photocatalysis [20, 21].

2. Experiment

AgNO₃ and Ce(NO₃)₃ · 6H₂O salts (chemically pure) provided by Vekton were used as reagents. Aqueous solutions of the above salts were prepared using high purity Milli-Q water with a resistivity greater than 18 MΩ/cm and under stirring on a magnetic stirrer for at least 30 minutes. The experiments on the synthesis of composites were performed with the use of a series of solutions of the said salt mixtures taken in ratios of 1/4, 1/2, 1/1, 2/1, 4/1. In doing so, 3 series of solutions were prepared with total concentrations equal to 0.1, 0.2 and 0.4 M.

To carry out interfacial synthesis, a flat open container with the working solution (2 mL) was placed into a closed reactor with a volume of 100 cm³. Close to the container with the solution there was an open vessel with 3 % ammonium hydroxide, which served as a source of gaseous ammonia. The exposed surface area of each reagent solution was 2 cm². The reaction proceeded under steady-state conditions for 0.5–15 min. During this time, a semi-transparent films with different thicknesses were formed on the surface of the aqueous solution of salt mixture AgNO₃ and Ce(NO₃)₃ · 6H₂O. After that, the film was next transferred carefully to the surface of pure distilled water in order to remove excess solution. After 10–15 min of exposure, the film was transferred by the Langmuir-Schafer technique to the surface of a single-crystal silicon wafer and then dried at 60°C and analyzed by XRD, FESEM, TEM, STEM, HRTEM and electron microprobe analysis. Before this treatment, the silicon wafers were washed in acetone to remove organic impurities and etched for 10 min in a “piranha” solution (a mixture of H₂O₂ and concentrated H₂SO₄ in a volume ratio of 3:7) with simultaneous ultrasonic cleaning (60 W) to prepare a hydrophilic surface and then rinsed thoroughly in water.

X-ray powder diffraction was performed on a Rigaku Miniflex II diffractometer. The measurement conditions were Cu Kα radiation, 30 kV voltage, and 10 mA current. The sample morphology was determined by Field Emission Scanning Electron Microscopy (FESEM) using Zeiss Merlin and Auriga Laser microscopes. Ion etching of the crystals was performed using an ion column of an Auriga Laser microscope using a gallium ion beam with the accelerating voltage of 30 keV, and the current of 20 pA.

3. Results and discussions

The first results of the synthesis of the aforesaid series of samples showed that the layers obtained on the surface of a salts mixture solution can be transferred to the surface of distilled water, and thus be washed from excess reagents. A preliminary study of their morphology by the FESEM method showed that the layer thickness and density significantly depend on the concentration of reagents and the time of contact of ammonia with the solution surface. In particular, at a contact time of less than 0.5 minutes, a discontinuous layer of nanoparticles is formed on the solution surface, while at a contact time of more than 5 minutes the formed layer is relatively dense, and is about 0.3 μm thick. The layer thickness increases up to 1 μm in case the sample was obtained under the 15 minutes treatment time. Morphological analysis of nanoparticles of this dense layer meets significant problems caused by relatively dense packing of individual nanocrystals in the layer, and therefore, for further study the samples with the least packing density of nanocrystals were selected, namely, those obtained using the salts mixture solution with individual salts concentrations equal to 0.1 M, and the ammonia gas treatment time equal to 5 minutes.

The study of the samples by the XRD method (Fig. 1a) showed that the obtained layer contains silver crystals with the *fcc* cubic structure, and the cerium (IV) oxide with fluorite structure [22]. Fig. 1b presents the EDX microanalysis data, which confirm that the composition includes Ce, O and Ag atoms.

A more detailed study of such samples using the FESEM method (Fig. 2) makes it possible to see whether they contain nano- and microparticles with different morphologies (Fig. 2). In particular, the general micrograph presented in Fig. 2a shows both individual nanoribbons 50–150 nm in width, up to 2–3 μm in length, and densely packed agglomerate thereof of irregular shape measuring up to 2 μm in width and up to 10–12 μm in length. It is also notable that there are faceted crystals 1–2 microns in size. EDX analysis of these objects allowed us to conclude that the nanoribbons contain both Ag and Ce atoms (Fig. 1b), and that the crystals actually contain only silver atoms, since the Ce content in them does not exceed several percent (the figure does not show the results of the crystals analysis). We did not evaluate the oxygen atoms concentration in these experiments, as oxygen can be present in the sample also as part of adsorbed water molecules.

As follows from the micrographs shown in Fig. 2b-d, the surface of such crystals is formed by silver nanoparticles of almost equal size of about 20 nm. Ion etching of these crystals with a gallium ions beam showed that their interior is also formed by nanoparticles of similar sizes (Fig. 3). Moreover, the crystals contain cavities, and thus the Ag(0) nanoparticles on the outer surface form the walls of a sort of boxes. In other words, the results of the study of such crystals indicate that they can be classified as colloidal crystals, but that these crystals have a certain feature associated precisely with the presence of a denser and stronger outer wall.

An important piece of information was derived from studying the obtained nanoribbons using EDX (Fig. 1b), STEM, TEM and HRTEM techniques (Fig. 4). Thus, according to the microphotograph shown in Fig. 4a, the nanoribbons surface

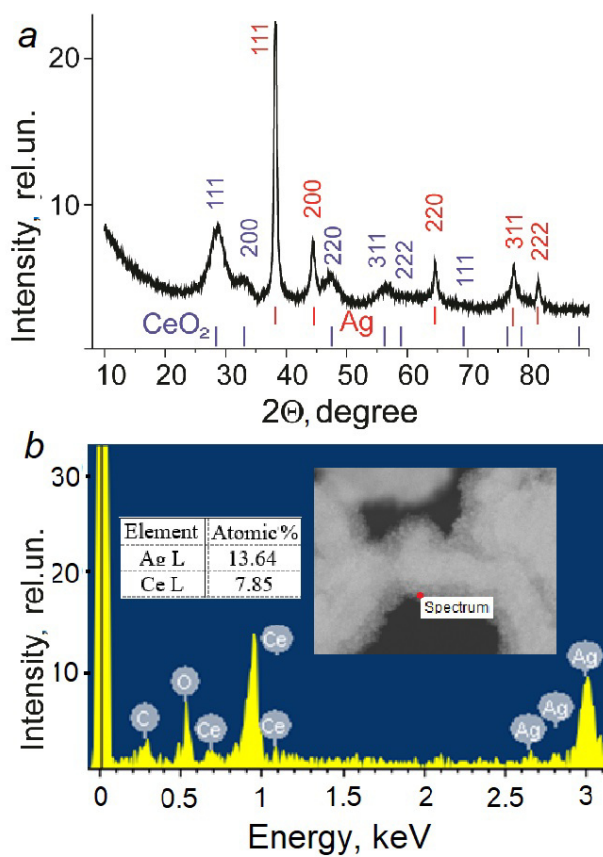


FIG. 1. XRD diffractogram (a) and EDX spectrum (b) of the layer obtained on the surface of the solution of AgNO_3 and $\text{Ce}(\text{NO}_3)_3$ salts mixture after contact with gaseous NH_3

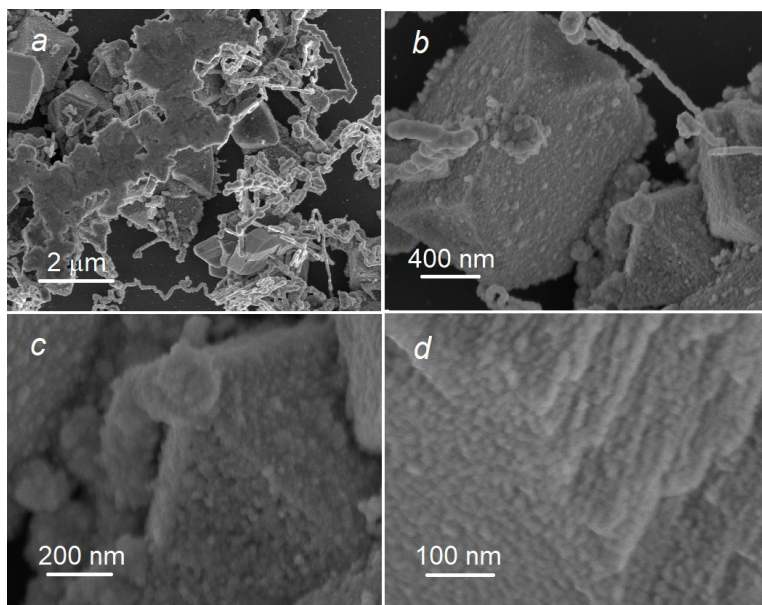


FIG. 2. FESEM images of $\text{Ag}(0)_x\text{CeO}_2$ composite, obtained with different magnifications

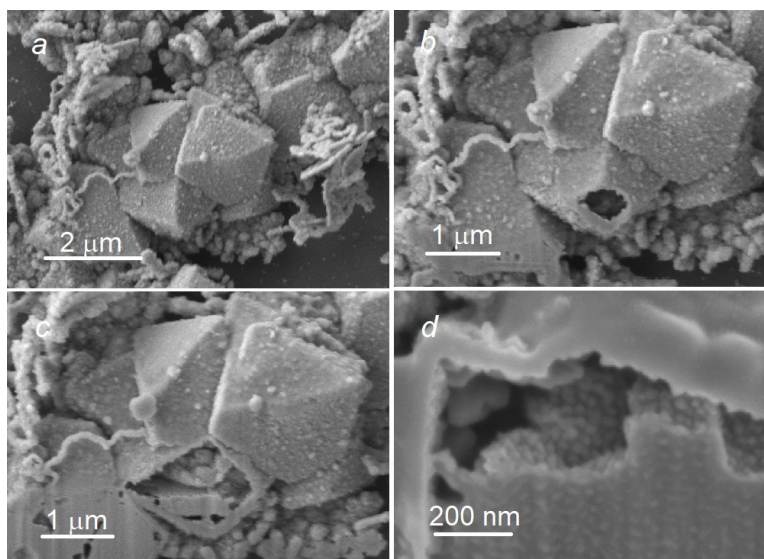


FIG. 3. FESEM images of Ag(0) colloidal crystals during etching thereof with a beam of gallium ions

is not atomically smooth, and individual 2–3 nm nanoparticles can be identified on it. These nanoparticles, however, practically do not exist in the terminal section of this nanoribbon. Moreover, the ribbon terminal fragment has an implicit faceting with a peculiar circular point in the center (Fig. 4b). As follows, for example, from the study [23], such a contour is characteristic of the growth of the $\langle 111 \rangle$ face of a cubic Ag(0) crystal. A local study of the nanoribbons surface performed by the EDX method showed that the ratio of Ag and Ce atoms concentrations over their surface is not uniform: the maximum amount of Ag (up to 90%) is observed in the central part of the nanoribbon, while in the areas along its edges the Ag content decreases to approximately 50% (the figures do not show EDX spectra of these areas). Analysis of HRTEM images, including the one shown in Fig. 4c indicates that, e.g., one of the interplanar distances in nanoparticles on the nanoribbon outer surface equals to 0.31 nm, and this value is close to the interplanar distance characteristic of the $\langle 111 \rangle$ direction in the CeO₂ fluorite structure [22].

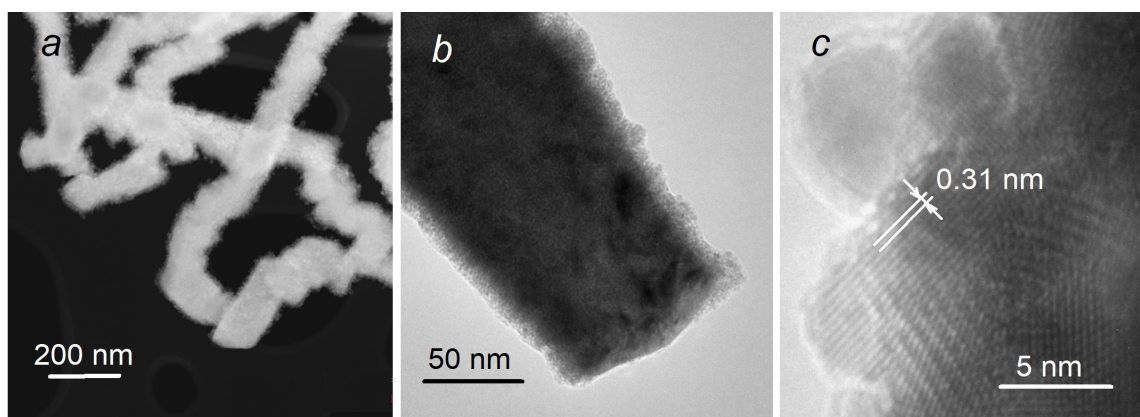


FIG. 4. STEM image of the nanoribbon array (a), TEM image of the terminal fragment of one of the nanoribbons (b) and HRTEM image of the nanoribbon edge fragment (c)

When discussing the full set of the presented results, the first thing to note is that the redox reaction involves the transfer of one electron between Ag(I) and Ce(III) cations in a weak alkaline medium; that is on the one hand, Ag(0) atoms are generated, and on the other hand, Ce(IV) cations are formed; the cations hydrolyze and then form the CeO₂ nanoparticles. At the same time, the EDX study results indicate that the number of Ag atoms in the composite is approximately one and a half times greater than that of Ce atoms. In our opinion, this effect can be observed due to the fact that a certain amount of the formed CeO₂ nanoparticles goes into solution in the form of colloidal particles.

A part of Ag(0) atoms form planar nanoribbons on the surface of a salt mixture solution, and CeO₂ nanoparticles are adsorbed on them. At a certain stage, these nanoparticles form a relatively dense layer that prevents the growth of Ag(0) crystals in a given direction. As follows from Fig. 4b, it is precisely this layer that is not presented in the terminal section of the nanoribbon, and in fact that's why the growth of a planar crystal in this direction can be observed. In other

words, the selective adsorption determines the nanoribbon longitudinal growth. Also noteworthy is the fact that some of the ribbons form closed geometric shapes in the course of such growth; as it may be observed for example, in Figures 3a and 3b that show rings with a diameter of several hundred nm.

As for the other part of the Ag(0) atoms, they form nanoparticles about 20 nm in size during the synthesis process, and these nanoparticles are practically equal in size. This effect is caused by the fact that the nanoparticles formation process occurs in the near-surface film of the solution at the phase interface, which at the first time point is characterized by isotropic concentration of reagents in the direction along the solution surface. It can be assumed that these nanoparticles are selectively adsorbed on the surface of the ribbons that form geometric patterns of regular shape, and this is the way in which a specific faceting of the growing colloidal crystal is set. Next, layer-by-layer growth of the faces of such crystals is observed, and the crystal acquires a characteristic crystal faceting as a whole. It is obvious that the density of Ag(0) nanoparticles in the surface layers of faceted crystals exceeds their density inside the crystals due to a longer time of interaction between the surface Ag(0) nanoparticles and the mother solution; therefore, after drying the samples in air and evacuating them in the electron microscope chamber the inner part of the crystals is compacted, and the cavities free from nanoparticles are formed therein.

Thus, the unique conditions that are created during the synthesis according the GSIT method make it possible to obtain, in fact at room temperature and with simple equipment, a nanocomposite consisting of Ag(0) colloidal crystals, as well as Ag(0) nanoribbons with CeO₂ nanocrystals located on the surface thereof. There is no doubt that the obtained nanocomposites can find application, in particular, as part of bactericidal materials, substrates for signal amplification in SERS, etc.

4. Conclusion

Gaseous ammonia interaction with aqueous solution of AgNO₃ and Ce(NO₃)₃ salt mixture, results in the increase of the pH value in the solution surface layer, and Ag(I) and Ce(III) cations enter into a redox reaction. As a result of the interaction, a hydrophobic layer of the Ag(0)_x-CeO₂ composite is formed on the solution surface. The composite components are characterized by crystalline structure and unique morphology. In particular, a part of Ag(0) atoms forms nanoribbons about 50–150 nm in width, and up to 2–3 μm in length on the surface of which there are CeO₂ nanoparticles 2–3 nm in size, while the other part of the Ag(0) atoms forms colloidal faceted crystals several μm in size, consisting of a collection of Ag(0) nanoparticles of equal size measuring about 20 nm. Based on the results of experimental studies a model-based approach was substantiated regarding the processes occurring on the surface of the mentioned salts mixture solution, and a forecast is made about possible areas of the synthesized compounds practical application.

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