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The Controlled Single-Step Synthesis of Ag/TiO_2 and Au/TiO_2 by Ultrasonic Spray Pyrolysis (USP)

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This article reports the synthesis of Ag/TiO_2 and Au/TiO_2 nanoparticles by single-step ultrasonic spray pyrolysis (USP) conducted by an investigation of the process parameters and the morphological characteristics of the obtained nanostructures. The influence of the ratio in the precursor solution, physical characteristics of used components, and temperature had a large influence on the formation of different nanoparticle morphologies. The experimental investigations were performed using classic USP equipment, with variations of the process parameters. Scanning electron microscopy, transmission electron microscopy, and focused ion beam analyses were used to characterize the complex nanostructures. Based on the obtained results, the optimal process window for the formation of the different morphologies for the Ag/TiO_2 and Au/TiO_2 nanoparticles is determined and the possibility of synthesis of the core–shell structures in one step by USP is confirmed.

INTRODUCTION

In recent decades, the development in nanotechnology has been going in several directions: developing new nanomaterial's, testing their characteristics, searching for their new implementation, and testing of the various synthesis methods to achieve the target quality, characteristics, and quantity of the nanomaterial. By exceeding the complexity of nanoparticles, it is possible to improve their characteristics and, in this way, expand their application. The introduction of binary systems is among the easiest ways to achieve this. Coating the nanomaterial's surface with another functional material can produce new properties or improve existing ones.[1] Recently, the core–shell nanostructures (the core is made of one material which is surrounded by a shell of another material) are gaining more and more interest because of their high functionality. The coupling mechanism between core and shell leads to advanced particle properties and has economic interest when a precious material is coated over an inexpensive material. Catalysis, sensors, biomaterials, and electronics are some of the common applications of composite materials. Multicomponent nanoparticles can be composed of a variety of materials, such as metals, oxides, semiconductors, polymers, organic, etc.[2–4] Their properties can be modified by changing the constituent elements, the ratio of those elements (especially of core and shell materials), the particle size, and the morphology.[5,6] Various complex structured nanomaterials were studied in the last decade. Haugen et al.[7] studied the synthesis of TiO_2/Ag and TiO_2/Au nanoparticles prepared by spray pyrolysis of aqueous solutions of titanium citrate complex and titanium oxalate precursors mixed with gold chloride trihydrate or silver acetate.[7] The produced nanoparticles had, after different production and calcination conditions, a large variety of crystallite sizes (12–120 nm), different phase compositions (10–100% rutile), and metal loading up to 10.6% Ag and 3% Au). In this one-step synthesis process, metal particles were dispersed inside the TiO_2 volume and not only in the surface area. Zhao et al.[8] used the ultrasonic spray pyrolysis (USP) method to produce mesoporous Ag/TiO_2 composite particles using TiO_2 nanoparticle suspension (Degussa P25) and $AgNO_3$ as the precursors. The suspension of TiO_2 nanoparticles was homogenized first and afterward $AgNO_3$ was added in various amounts so that the wt.% of Ag could be influenced in the end particle. The starting P25 nanopowder was a mixture of anatase and rutile (80% anatase and 20% rutile), and the end particle had a similar composition. The Ag percentage was changed from 2% to 8%. Flame spray pyrolysis was also used for the simultaneous deposition of Au nanoparticles on TiO_2 and SiO_2 support.[9] Gold nanoparticles were crystalline, well dispersed, size dependent on precursor concentration, and independent of oxides‘ support, which indicates that their formation is independent of support formation. The Au wt.% was changed between 1% and 4%, and the corresponding Au particle sizes were 3–15 nm. The metal/oxide nanoparticles, produced and tested in the presented research, have been made for photocatalytic application. The demands for optimal catalytic properties are, among other things, small noble metal nanoparticle size and low content of noble metal in the shell (up to maximum 10%). For this reason, in the previous research[7–9], it was not tested the maximum share of noble metal in those complex structures and how particle size is related to content dependence in the scope of the presented research.

In this work, USP was used for the synthesis of the complex Ag/TiO_2 and Au/TiO_2 nanoparticles. USP is a continuous method based on the droplet-to-particle (D-T-P) principle.[10] The particle formation occurs through the thermal decomposition of the aerosol of the precursor solution (droplets 1–15 μm) and runs over the following intermedia steps: evaporation, precipitation, reaction/decomposition, drying, and final particle formation.[11] Some of the advantages of this method are its simplicity, good process control, high flexibility, and good scale-up potential. The synthesis of those nanoparticles will provide development of a novel method for the improvement of the tribological and electrical properties and extension of the lifetime of the galvanic gold layers by the incorporation of the nanoparticles.[12]

MATERIALS AND METHODS

The precursor solution preparation is generally the first step in all conducted experiments. The selection of the concentration of the precursor solution is one the most important points in this step because there is a direct connection between the nanoparticle size and the precursor solution concentration.[13] All the chemicals in this study were used as purchased: tetra-*n*-butylorthotitanate $C_{16}H_{36}O_4Ti$ (Merck, Darmstadt, Germany); hydrogen tetrachloroaurate $HAuCl_4$ (A Johnson Matthey Company, Germany); and silver nitrate $AgNO_3$ and hydrochloric acid HCl, nitric acid HNO_3 (Applichem GmbH, Germany). The precursor solutions used in the experiments were prepared in different concentrations. The solvent for all experiments was distillate water. Preparations of the precursor solutions for TiO_2 nanoparticle synthesis were done in two steps: A defined mass of $C_{16}H_{36}O_4Ti$ was first stabilized with hydrochloric acid because $C_{16}H_{36}O_4Ti$ is unstable in contact with water and hydrolyses very quickly to butanol and reactive titan hydroxide ($Ti(OH)_4$) or titan dioxide ($TiO_2\downarrow$). It is possible to stabilize it with very low values of pH ($pH < 2$) and, in this way, to achieve a high concentration of stabile $Ti(OH)_2^{2+}$ complexes in the water solution. After preparation of this stabilized solution, it can be diluted with water to obtain the chosen concentration. The preparation of the precursor solutions for nano Ag and nano Au synthesis was done by direct dissolution of a defined mass of $AgNO_3$ or $HAuCl_4$ in distillate water. Because both solutions were used for synthesis of metal/oxide nanoparticles, a prepared noble metal precursor solution was mixed in a defined ratio with the above explained prepared $C_{16}H_{36}O_4Ti$ solution. Here, it is important to notice that in the case of the $AgNO_3/C_{16}H_{36}O_4Ti$ mixture, the titan solution was stabilized with HNO_3 instead of HCl. This was done because Ag^+ ions are highly unstable in the presence of any Cl^-. The synthesis was done on the laboratory scale and the technical-scale single-step USP equipment, which represents classic equipment used for USP and is described in previous work.[14] The main equipment parts are carrier and/or reaction gas connected over the flow regulator (with the possibility to mix the carrier and reaction gas), the ultrasonic aerosol generator (2.5 MHz; Gapusol, RBI, France), the horizontal or vertical furnace with a quartz tube reactor, and the collection of produced nanoparticles in the collection bottles or electrofilter. The process steps occurring in this equipment are the same as the ones known from the general USP theory: aerosol formation, particle formation (evaporation, precipitation, thermal decomposition, and drying) and particle collection.

After the successful preparation of the precursor solution, the selection of the experimental conditions had to be made. This is related to the variation of the following process parameters: temperature profile (combination of the two process parameters—the temperature and the flow rate), carrier and/or reaction gas. The optimal temperature and flow-rate conditions for the oxide nanoparticle formation were determined from the previous investigation for the TiO_2 nanoparticle synthesis by the USP method.[15] This process window was tested with complex precursor system presented here, from its minimum to its maximum value: The reaction temperature was changed in the range 550–1000°C, the carrier gas flow rate was in the range from 1 to 5 L/min, and different reaction atmospheres were tested (reducing or inert). The weight content of the noble metal (Ag or Au) in the conducted experiments was changed from 20 wt.% to 40 wt.% (the target end content was 20 wt.%, demanded by the special application of this complex system).

RESULTS AND DISCUSSION

Single-Step Synthesis of Ag/TiO_2 Nanoparticles

The synthesis of the Ag/TiO_2 complex nanoparticles was conducted with two different precursor

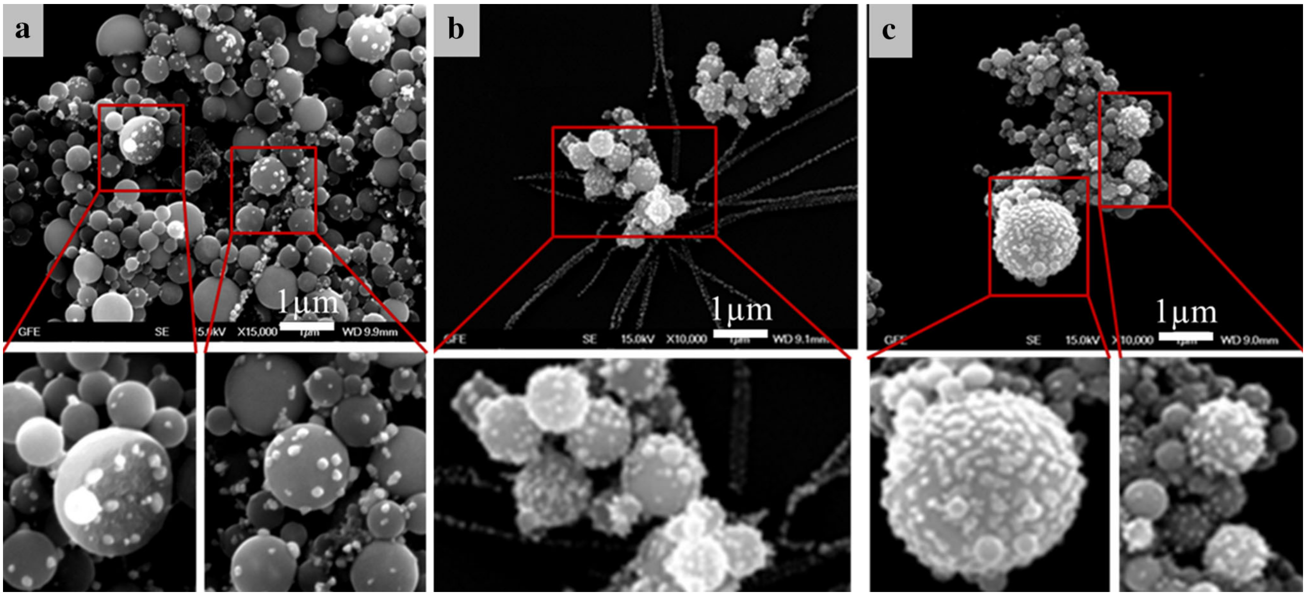

Fig. 1. SEM micrographs of Ag/TiO_2 nanoparticles obtained in the one-step USP process by the various experimental conditions with the characteristic particle morphology close-up. (a) Ag content in the precursor solution 20 wt.% and the temperature in the furnace 800°C, (b) Ag content in the precursor solution 40 wt.% and the temperature in the furnace 800°C, and (c) Ag content in the precursor solution 40 wt.% and the temperature in the furnace 1000°C.

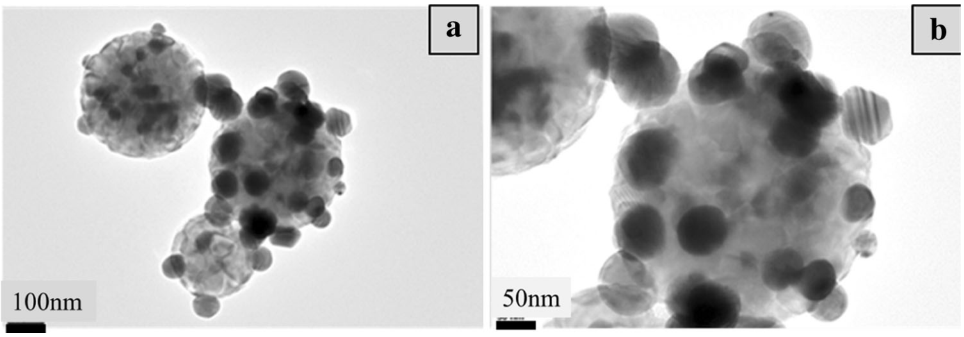

Fig. 2. TEM micrographs of Ag/TiO_2 nanoparticles obtained in one step by USP synthesis: (a) spherical TiO_2 nanoparticles with the distributed Ag nanoparticles and (b) TiO_2 nanoparticles with partly defined primary nanoparticles and clearly visible Ag nanoparticles.

compositions (Ag content 20 wt.% and 40 wt.%) and by temperature from 800°C to 1000°C. The characterization of the obtained nanoparticles was done with scanning electron microscopy (SEM) and transmission electron microscopy (TEM) to determine the structural characteristics of the obtained nanoparticles. The SEM micrographs presented in Fig. 1 show examples of the Ag/TiO_2 nanoparticles obtained in the described experiments. From the presented results, it is possible to see that some of the oxide nanoparticles, such as those presented in Fig. 1a, show the irregularities in the morphology. Besides that, most of the oxide surface is covered with the silver nanoparticles. The distribution of the Ag nanoparticles on the surface areas of the oxide is not homogeneous. This distribution is present in the case of the lower concentration of the Ag in the precursor solution. By comparing the results presented in Fig. 1b and c, it is possible to see that the oxide nanoparticles have a similar form and morphology in both the experiments and that the coverage of Ag is better than in Fig. 1a, which must be the result of the higher content of Ag in the precursor solution. The silver coverage was observed to be better in the case of the higher temperature (1000°C). It is assumed that the increase in the temperature has a positive influence on the particle formation kinetic (especially diffusion) because it seems that it has favored the silver distribution on the oxide surface. Here, it is also possible to see that the silver nanoparticles obtained in the experiment presented in Fig. 1c have not only spherical form, which was the case in the other presented experiments, but also irregular shape, which is drawn in length form. The reason for this could be the synthesis at the temperature near and above the melting temperature of the silver (961.78°C). In the experiment presented in Fig. 1b, the slightly lower

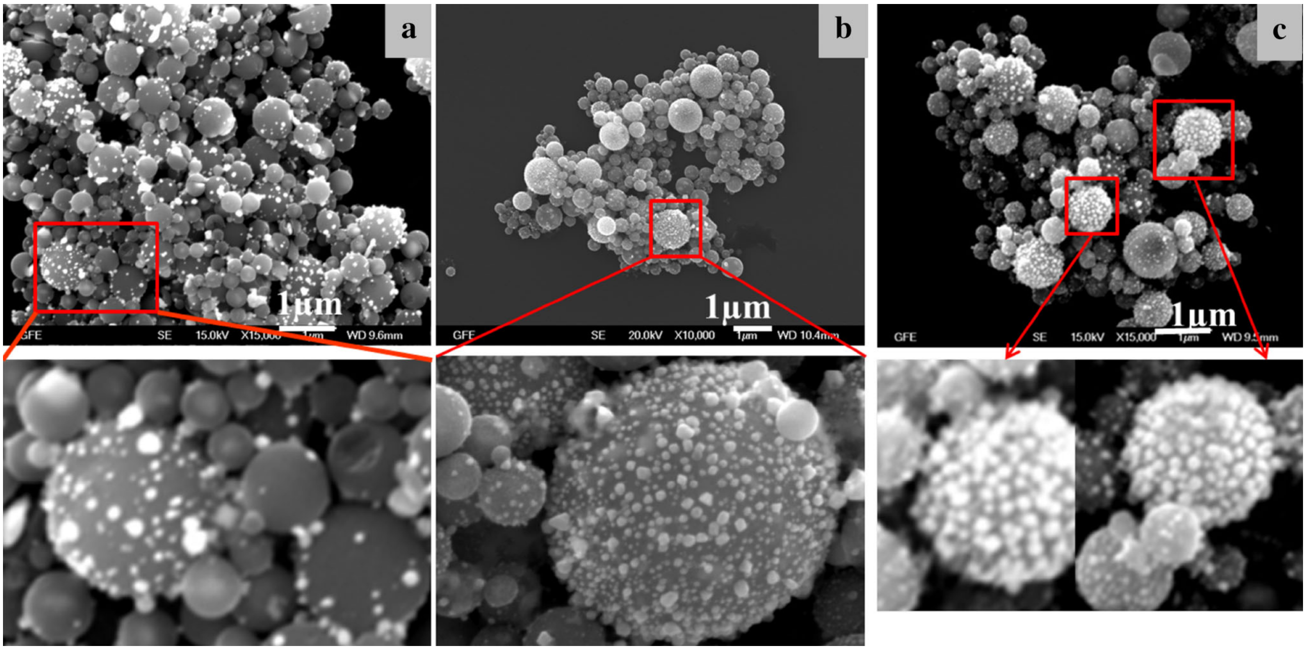

Fig. 3. SEM micrographs of Au/TiO$_2$ nanoparticles obtained in the one-step USP process by the various experimental conditions with the characteristic particle morphology close-up: (a) temperature in the furnace 550°C, (b) temperature in the furnace 800°C, and (c) temperature in the furnace 1000°C.

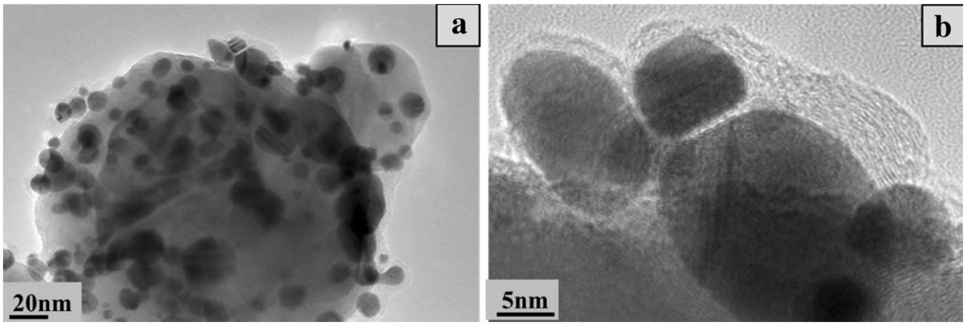

Fig. 4. TEM micrographs of Au/TiO$_2$ nanoparticles obtained in one step by USP synthesis: (a) spherical TiO$_2$ nanoparticles with the distributed Au nanoparticles and (b) TiO$_2$ nanoparticles with partly defined primary nanoparticles and clearly visible spherical, polygonal and elliptic Au nanoparticles.

coverage rate is determined, whereas the silver nanoparticles have maintained their spherical form.

The experiments with a higher content of Ag in the precursor solution were marked as the ones with the more optimal results in terms of the particle morphology and the coverage rate. For this reason, the method of repetition of them was done on the vertical USP equipment at the temperature of 900°C (a little below the melting temperature of the silver).

From the results presented in Fig. 2, it can be observed that the TiO$_2$ nanoparticles have spherical form with particle sizes in the range 200–300 nm. Primer particles are partly visible (size below 50 nm), with their structure and grain boundaries. The oxide nanoparticle seems to have a filled morphology because no concentration gradient can be observed. The silver nanoparticles are easy to spot and differentiate from the oxide primer particle by their color on the TEM micrograph. The silver nanoparticles are darker than the oxide, which is a consequence of sufficient density difference for silver and titanium dioxide (10.49 g/cm^3 for silver, 4.23 g/cm^3 for rutile, and 3.78 g/cm^3 for anatase). The Ag nanoparticles are mostly spherical and partly hexagonal or polygonal in form with the average particle size of 50 nm. The presence of structural defects can be observed in the structure of some particles.

Single-Step Synthesis of Au/TiO$_2$ Nanoparticles

The synthesis of the Au/TiO$_2$ nanoparticles was done with a precursor solution with a constant

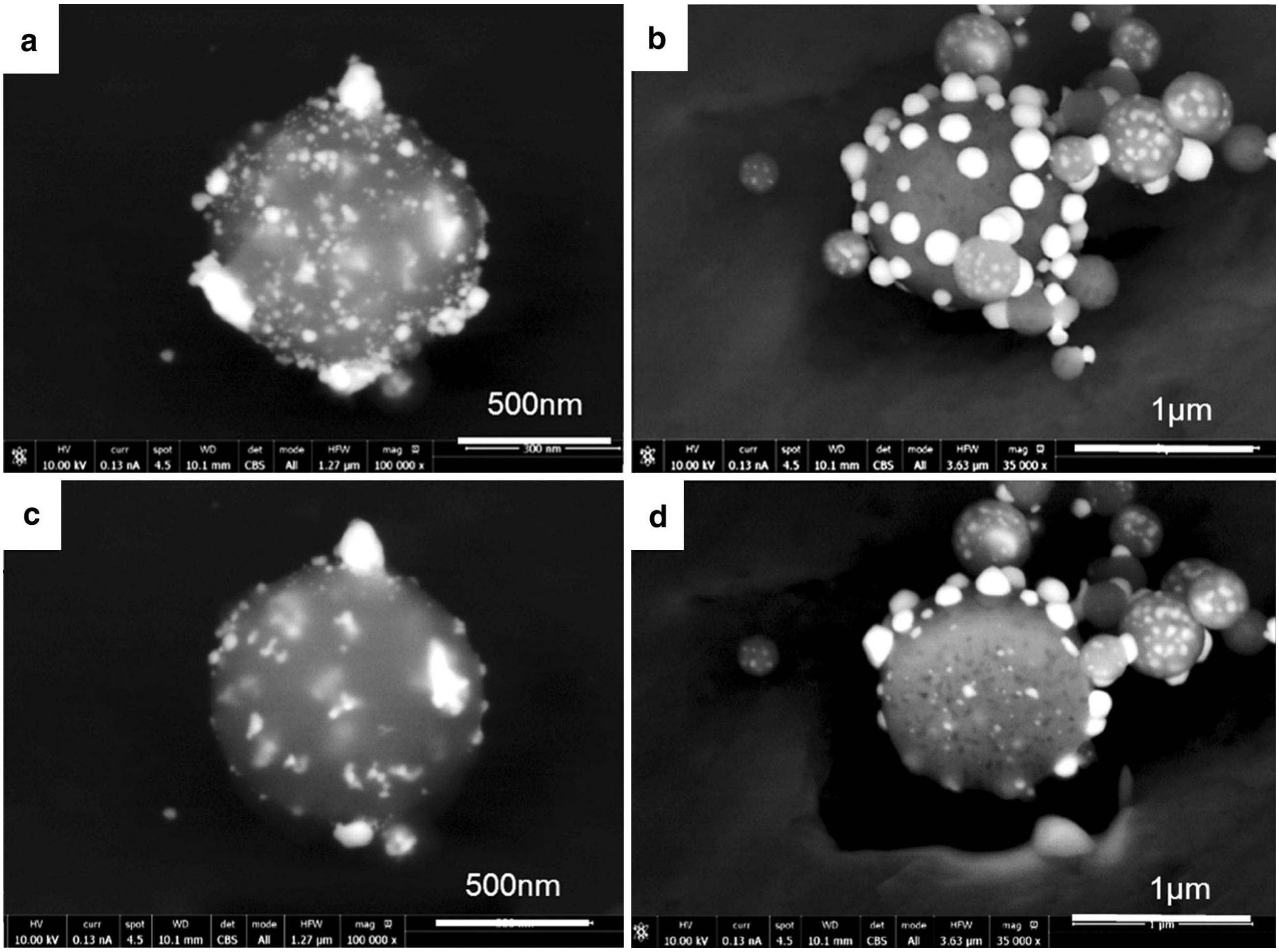

Fig. 5. Examples of the FIB analysis of the obtained Ag/TiO_2 and Au/TiO_2 nanoparticles in the one- step USP process: (a) Au/TiO_2 before FIB milling; (b) Au/TiO_2 after FIB milling; (c) Ag/TiO_2 before FIB milling; (d) Ag/TiO_2 after FIB milling.

content of Au in it (20 wt.%) and at a temperature in the range 550–100°C. The characterization of the obtained nanoparticles was done with SEM and TEM to determine the structural characteristics of the obtained nanoparticles. The SEM micrographs presented in Fig. 4 show examples of the Au/TiO_2 nanoparticles obtained in the described experiments.

From the obtained SEM micrographs presented in Fig. 3 it is possible to see that the TiO_2 nanoparticles' size distribution is similar in all experiments, whereas the main difference is in the covering rate and homogeneity of the gold nanoparticles on the TiO_2 surface. The formed gold nanoparticles are heterogenic in their form: spherical, triangular, cubic, and hexagonal, and with particle size distribution in the range of 25–75 nm. For more details about the morphology, the TEM analysis was done. The TEM micrograph for the experiment conducted at the 1000°C is presented in Fig. 4.

From the presented results, it is easy to see that the TiO_2 sphere is polycrystalline. Individual gold nanoparticles are distributed homogenously on the oxide surface. The gold nanoparticles are sized between 7 nm and 50 nm in spherical, hexagonal, or polygonal form. Most of the particles are approximately 10 nm in size. The lattice fringes can be observed nicely on the high-resolution TEM, as well as the various defects and the growth of individual particles in the contact surface. In addition, many defects can be found in the Au and TiO_2 structure. The reason for this could be the high temperature.

Comparison Between the Ag/TiO_2 and Au/TiO_2 Nanoparticle Morphology

The last important question to be answered was whether the Ag and Au nanoparticles are distributed only on the TiO_2 surface or if the Ag and Au nanoparticles can also be found in the TiO_2 nanoparticle volume. Focus ion beam (FIB) milling was done to determine this. The SEM micrographs of the FIB-milled sample are presented in Fig. 5.

The results of the FIB milling analysis gave important information about the three-dimensional structure of these complex nanoparticles. By looking at the presented results, it is obvious that most of the Ag nanoparticles are formed on the surface of the TiO_2. In the case of Au/TiO_2 nanoparticles, some Au nanoparticles are trapped in the volume of titanium dioxide. They are not concentrated in the particle center but are distributed randomly in the particle volume. Nevertheless, the amount of Au nanoparticles formed in the TiO_2 volume is smaller than the amount of Au nanoparticles formed on the TiO_2 surface.

CONCLUSION AND OUTLOOK

Based on the presented results, it can be concluded that it is possible to synthesize the Ag/TiO_2 and Au/TiO_2 nanoparticles by the single-step UPS process and to control their morphology (size and distribution of Ag/Au nanoparticles on the oxide surface) by the right choice of the process parameters. There exists a certain similarity in morphology between both systems. Nevertheless, a few differences are noticeable:

- The size of the Au nanoparticles is much smaller than the size of the Ag nanoparticles (the Au nanoparticles were in the size range 7–50 nm, where most of the particles were around 10 nm in size, whereas the average size of the Ag nanoparticles ranged from around 20 nm to 80 nm).
- The Ag nanoparticles are mostly ideally spherical in shape (hexagonal in the case of the defect formation, twinning, etc.), whereas the Au nanoparticles had various forms from spherical and cylindrical to an irregular shape.
- On the FIB analysis results, it is clear to see that in the case of Ag/TiO_2 nanoparticles, almost all the Ag nanoparticles are formed on the oxide surface ($>90\%$), whereas in the case of Au/TiO_2 nanoparticles, some of the Au nanoparticles are formed in the volume of the TiO_2 nanoparticles ($\sim30\%$) and distributed randomly in the oxide matrix.

These results of the successful synthesis are going to be the platform for further analysis and the proposal of the model that describes the Ag/TiO_2 and Au/TiO_2 nanoparticle formation.

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