Plasma assisted fabrication of zinc oxide based nanostructures

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ZnO/Ag nanocomposite structures were prepared by using a discharge with an atmospheric-pressure microplasma cathode and a solid metal anode immersed in an electrolyte solution and their properties were studied. The effect of Ag on the microstructure and optical properties of ZnO has been discussed.

Keywords: plasma in contact with liquid, ZnO nanostuctures, optical properties

1 INTRODUCTION

Zinc oxide (ZnO) nanostructures have received a great interest in recent years due to potential applications in transparent electrodes, solar cells, blue/UV light emitting diodes, gas sensors, etc. [1]. Stimulated by these applications significant attempts have been made to design ZnO-based composite nanostructures, such as doped and heterostructure nanocrystals. The composite nanostructures exhibit new optical and electronic properties due to the different functionality of their components. For example, the metal/semiconductor nanojunctions are being extensively studied for these purposes. Interaction between ZnO and Ag can be also of interest for realization of p-type ZnO.

In this work, a method based on a discharge with an atmospheric pressure microplasma cathode and a solid metal anode immersed in an electrolyte solution was used for preparation of ZnO/Ag nanocomposite structures. The effect of Ag on the microstructure and optical properties of ZnO were studied.

2 EXPERIMENTAL

Our experiments were focused on the anodic dissolution of metallic (Ag or/and Zn) electrodes followed by reduction of aqueous metal cations with charged energetic species directed from a microplasma. The principle of synthetic process is clear from the Fig.1, where the laboratory model of the experimental reactor is presented. Metal electrode (Ag or Zn) was placed inside an electrolyte consisting of 1 mM HNO_3 with 10 mM fructose or without fructose. The acid is necessary to make the solution conductive; the fructose is a stabilizer that prevents uncontrolled particle growth and agglomeration. A stainless steel capillary tube served as a cathode (500 µm inside diameter, 5 cm length) was located 3 cm away from the metal electrode with a distance of 1 mm between the tube end and the liquid surface. Argon gas flow (approximately 15 sccm) was directed through the capillary tube. The discharge was ignited by applying of a high voltage of 3.6 kV using a dc power supply. The discharge current was kept constant at 4 mA during the experiments.

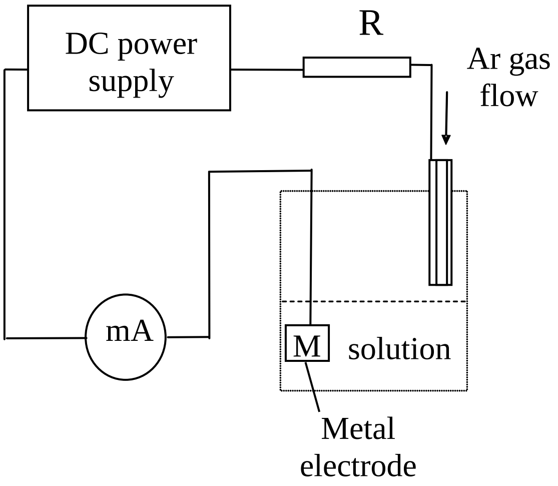

Fig.1: Schematic diagram of the experimental setup

ZnO/Ag nanoparticles were prepared by two different ways. First, current passed through Ag electrode followed by the Zn electrode immersed in the same solution. In the other case, ZnO nanoparticles were synthesized at first.

For comparison purposes, the Ag and ZnO nanoparticles were also prepared separately under the similar conditions.

Particle generation was monitored by UV-vis absorbance spectroscopy using the Cary-500 spectrometer. Absorbance spectra were analyzed after the subtraction of the background spectra from the initial electrolyte solution. The formed nanoparticles were characterized by TEM, SEM and X-ray diffraction (XRD) in order to determine the powder composition, its crystalline structure, lattice parameters and grain size. Nanopowders for XRD measurements were obtained after drying of the colloidal solutions. It should be noted that the growth kinetics is intimately coupled to the process parameters including current density, acid and stabilizer concentration. In a standard electrochemical cell, redox reactions occur by flowing current between solid electrodes and the electrolyte. As a source of electrons and ions, plasma discharge can be coupled to electrochemical systems to initiate redox reactions based on plasma-liquid interactions. The reduction of metal cations by gas-phase electrons supplied by the microplasma provides an approach for nanoparticle synthesis from either bulk metals or metal salt solutions [2, 3]. In a typical experiment, igniting the microplasma above the solution caused a color change as a result of particle formation. The particles were observed to nucleate at the plasma-liquid interface and diffuse into the solution volume.

3 RESULTS AND DISCUSSION

Figure 2 shows the TEM photographs of the prepared pure Ag and composite ZnO/Ag nanostructures synthesized under similar conditions. TEM analysis of pure Ag nanoparticles indicates the size of about 4 – 6 nm. TEM analysis of as-grown nanoparticles confirms that particles are nonagglomerated, spherical and uniform. The higher size obtained from the XRD pattern was indicative of agglomeration of nanoparticles while forming a powder suitable for analysis. The size of synthesized ZnO/Ag nanocrystals increased to about 40 nm.

We found that varying of the process time did not significantly alter the particle size distribution, but increased the particle density and led to particle agglomeration. While further experiments may be necessary to fully understand the mechanism of particle nucleation and growth, we believe that the particle size is controlled by the reaction volume, which can be defined as a small region near the microplasma-liquid interface. Our experimental observations suggest that particle nucleation is driven by the electromigration of metallic cations to this region and subsequent electrochemical reduction by the microplasma. Growth then occurs until particles are carried out of the reaction volume by convective or diffusive flow back into the solution.

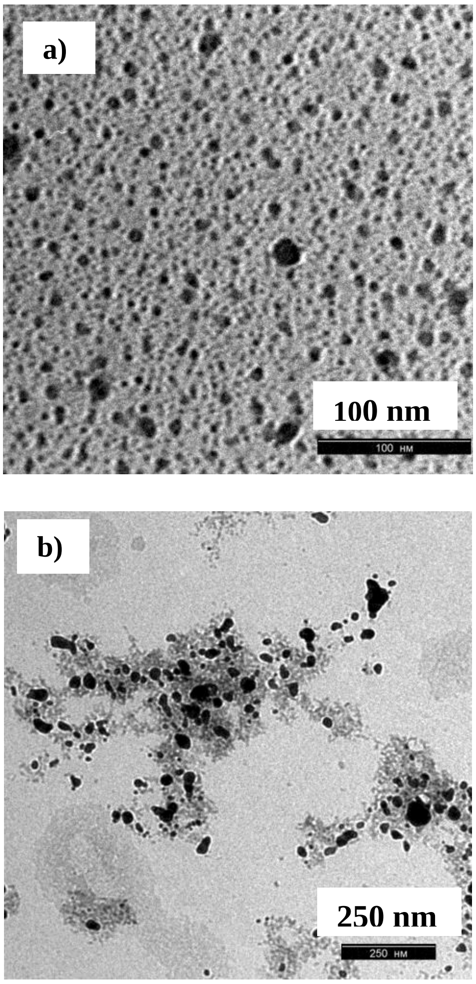

Fig.2: TEM images of Ag (a), and ZnO/Ag (b) nanoparticles

Typical absorption spectra of colloidal solutions prepared by gas–liquid interfacial discharge with silver and zinc electrodes are shown in Fig 3. For silver nanoparticles the spectrum exhibited the characteristic plasmon absorption band with a peak located at 400 – 417 nm. This band characteristic for spherical Ag nanoparticles appeared and grew in intensity with increasing reaction times. The spectral features of the colloid prepared using zinc electrode are characterized by a sharp absorption increasing with steep cut-off characteristics which can indicate a semiconducting nature of the formed nanoparticles in this case. The optical band-gap estimated from the absorption spectrum indicated the formation of ZnO (E_g = 3.36 eV) nanoparticles.

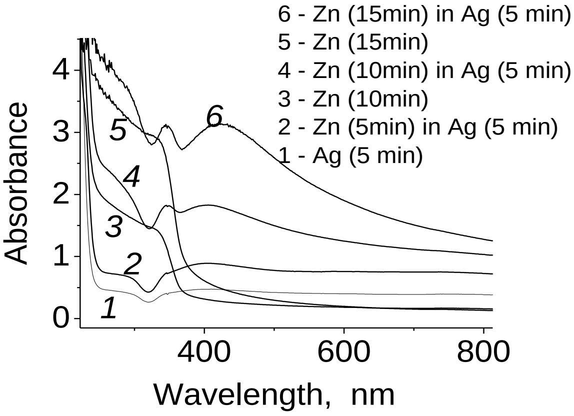

Fig.3: UV-vis absorption spectra of Ag, ZnO and ZnO/Ag nanoparticles synthesized by discharge with liquid electrode

In the case of discharge with a zinc electrode immersed in the cell with colloid previously prepared with silver electrode, the spectra of the solutions do not exhibit the pronounced features attributable to the Ag or ZnO particles. Optical absorption spectra indicate presence of well-defined and red-shifted Ag surface plasmon band only at longer reaction times (curve 6, Fig.3). Most probably, composite ZnO-Ag structures are formed in this case. The composite formation primarily affects the surface plasmon band of metal depending on the dielectric constant of the oxide semiconductor as well as on the electron density in the metal particle.

4 CONCLUSION

In summary, coupled ZnO/Ag nanostructures were prepared using a discharge in contact with an electrolyte solution. Their structure and optical properties were studied based on TEM, XRD and optical absorption measurements. The observed peculiarities of the optical properties of the synthesized structures can be connected with the interfacial charge transfer between metal Ag and ZnO nanocrystals.

Igniting the microplasma resulted in current flow through the electrolyte and reactions were observed at the anode and cathode. At the anode, oxidation reactions led to dissolution of the solid metal into metal cations which were then reduced at the cathode by the microplasma to nucleate metal NPs. These observations suggest that gas-phase electrons can react with a solution at the plasma–liquid boundary to drive electrochemistry. Microplasma–liquid interactions have therefore initiated new synthetic and functionalization approaches that are different from both standard liquid electrochemistry as well as from the submerged discharge method. In comparison to conventional wet chemical methods, plasma-assisted synthesis of colloidal metal NPs has been found to be simple, rapid, and clean since the particles are grown without any chemical reducing agents. This is particularly attractive because NPs are produced at ambient conditions (atmospheric pressure and room temperature), making the approach safe and biocompatible. In addition the approach is low cost, scalable and should allow a wide range of nanoparticle materials to be synthesized. NPs have been grown with and without stabilizer molecules which allows the particles to be selectively functionalized.

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