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Examination of Ostwald ripening in the photocatalytic growth of silver nanoparticles on titanium dioxide coatings

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ABSTRACT

Silver nanoparticles (AgNPs) were grown on the surface of titanium dioxide coating (TiO_2) using a photochemical method. The size and number of AgNPs were monitored using scanning electron microscopy (SEM) after 20, 30, 180 and 300 s of UV illumination. It was found that for short illumination times (20 s) a significant number of small nanoparticles were grown. However, after an additional 10 s of illumination, small nanoparticles were subject to decomposition and the released Ag^+ ions were utilized for the growth of the existing larger nanoparticles, causing an increase in their dimensions. The observed results indicate that the nucleation and further growth of AgNPs proceed according to Ostwald ripening. For longer illumination times (180, 300 s) a coalescence of closely located particles was observed.

1. Introduction

Composites of silver nanoparticles with titanium dioxide (AgNPs/TiO_2) have received much attention owing to the broad applications of such metal-semiconductor systems in photocatalysis [1,2], solar energy harvesting [3] and in surface enhanced Raman scattering (SERS) sensors [4]. The combination of TiO_2 with AgNPs enable a decrease in the recombination rate of the photogenerated electron-hole pairs by transferring the excited electrons from TiO_2 to AgNPs and broadening the light absorption of the photocatalyst to the region covering the visible range of the solar spectrum [5,6]. Moreover, AgNPs exhibiting appropriate morphology and size can be used in advanced sensor applications, due to their localized surface plasmon resonance (LSPR) phenomenon [7–10]. The growth of AgNPs on the TiO_2 surface can be created by a photocatalytic reduction of Ag^+ ions using electrons trapped on the TiO_2 surface as photocatalytic reducing centers, leading to the formation of AgNPs/TiO_2 nanocomposites.

However, the jury is still out regarding the dynamics of the photocatalytic growth and the mechanism of the formation of AgNPs, and is still the center of interest for many research groups. This is also important from the point of view of the precise control of the size and shape of particles, since these parameters can strongly affect many physicochemical properties of nanocomposites. For example, the kinetics and the mechanism of the reduction of Ag^+ ions by stored electrons on TiO_2 nanoparticles as well as the further growth of AgNPs on TiO_2 surfaces were studied using a stopped flow technique [11]. Three steps of AgNPs formation were proposed: (I) the reduction of silver ions to form silver atoms, which, subsequently, formed the nuclei for the metal particles, (II) the growth of the silver nuclei to form silver particles and (III) the coalescence of the formed silver. It was also found that after the reduction of all Ag^+ ions, the remaining excess of electrons were then transferred to the deposited AgNPs, resulting in a slight blue shift of the surface plasmon band. Subsequently, the stored electrons on the AgNPs were used to produce H_2 from the adsorbed H^+ ions.

In another study, the plasmonic properties of the AgNPs/TiO_2 coatings were studied in terms of extinction, surface enhanced Raman scattering and fluorescence enhancement [4]. It was found that the growth of AgNPs can be isotropic or anisotropic depending on the $AgNO_3$ solution concentration and the reduction ability of TiO_2 coatings. Additionally, the dependence of average size d after the coalescence phenomenon *vs.* time was found as $d^3 \sim t$. Such a relationship is considered an indication of diffusion-limited growth typical for Ostwald ripening.

A similar mechanism of AgNPs growth on TiO_2 nanorods was proposed by Lu et al. [12]. The first step of the AgNPs synthesis was typical. Photoexcitation of TiO_2 nanorods under UV illumination

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produced electrons that were used to reduce Ag^+ ions and deposit multiple small AgNPs on the surface of the TiO_2 nanorods. However, after prolonged UV illumination, a ripening process was induced. In this process, smaller nanoparticles were dissolved by the photogenerated oxidative species and then redeposited onto larger and more stable Ag particles attached to TiO_2 nanorod.

It appears that while knowledge about the Ostwald ripening process is not new, its importance in the synthesis and formation of objects in nanoscale increases all the time. Recently, the aging and ripening of various colloidal silver salts in the presence of stabilizers were used in the examination of Ostwald ripening in detail [13]. The experiments, focused mainly on the elucidation of the role of stabilizers, indicated that the steric length rather than the adsorption strength of a stabilizer molecule was the most important parameter in the hindrance of Ostwald ripening.

A further study, reporting the role of ammonia in the chemical synthesis of colloidal AgNPs conducted in ethanol, observed that during the reaction, as the particles were growing, the residual small particles were disappearing, whereas larger particles were growing, which is evidence of the Ostwald ripening process [14].

Finally, it has also been powerfully highlighted recently that Ostwald ripening theory needs to be modified by taking into account morphology and structural defects in addition to size factor, if the size and shape evolution of metallic nanoparticles in solutions are to be predicted more accurately [15]. It was demonstrated that such parameters as morphology, structural defects and facet surface energy significantly influence the size and shape evolution of nanoparticles in Ostwald ripening processes. They also strongly affect the electrochemical oxidation potentials of metallic nanoparticles.

In our study we provide the results of experiments showing that the Ostwald ripening process also occurs during the photocatalytic growth of AgNPs on TiO_2 coatings. To our knowledge, examination of Ostwald ripening in such systems is rarely described in the literature and therefore can still be considered a novelty in the field of photocatalytic growth of metallic particles on the TiO_2 surface.

2. Experimental

2.1. Materials

Single-side polished silicon Si (1 0 0) wafers were purchased from ITME (Institute of Electronic Materials Technology, Warsaw, Poland).

Silver nitrate (99.85%) was obtained from POCH (currently Avantor Performance Materials, Poland). Silver nitrate ($AgNO_3$) solutions at concentrations of 5 mM and 10 mM were prepared in ethanol (POCH, pure, min. 99.7%).

Hydrochloric acid (2 M) was prepared from concentrated hydrochloric acid (Chempur, 11 M, pure for analysis), using water purified by Millipore simplicity UV system 18.2 MΩ cm at 25 °C.

Other chemicals were purchased from commercial sources as guaranteed-grade reagents and used without further purification: isopropanol (POCH, pure, min. 99.7%), titanium tetraisopropoxide (Aldrich, 99.7%).

2.2. Preparation and examination of AgNPs/TiO_2 composites

Titanium dioxide coatings were prepared by the sol–gel dip-coating method on silicon wafers according to the procedure reported in our previous studies [16,17]. Photocatalytic growth of AgNPs on the TiO_2 coatings was performed in polymethacrylate (PMMA) cuvettes, with a width of 1 cm, using a 2 × 15 W UV-lamp (UV-Consulting Peschl, wavelength $\lambda = 365$ nm). The power density measured on the sample level was 5 mW cm^{-2}.

A Field Emission Scanning Electron Microscope (FEI NovaNano SEM 450) equipped with Schottky gun, operated in immersion mode using a through lens detector (TLD), was used in the imaging of the AgNPs supported on TiO_2. Images were acquired at magnifications of 250,000×.

3. Results and discussion

In order to examine the kinetics of the growth of AgNPs, the TiO_2 coatings immersed in the solution containing Ag^+ ions were illuminated for 20 and 30 s. These time intervals were chosen on the basis of our preliminary experiments showing that illumination periods shorter than 20 s were giving very small nanoparticles, which were difficult to image using the SEM technique. It was also found that during the first 20–30 s of illumination, AgNP growth is particularly dynamic in terms of nucleation, the disappearance of small nanoparticles and the enlargement of larger ones. In turn, longer illumination periods, exceeding 150 s, appeared to be suitable for observation of the joining process of closely situated particles leading to their coalescence.

Keeping the same parameters during the experiments on AgNPs growth (*i.e.* the constant power and wavelength of the UV lamp, the distance from the UV source and finally the same type of substrate and solvent), it can be assumed that all changes in size and number of the generated AgNPs depend solely on the duration of UV illumination and the concentration of Ag^+ ions.

SEM images showing AgNPs, typically visible as white round-shaped objects, photochemically grown on the surface of TiO_2 coating after 20 and 30 s of illumination are presented in Figs. 1a and c and 2a and c. It is easy to identify two populations of AgNPs, exhibiting small and large diameters. This topography is typical for AgNPs synthesized by the photocatalytic reduction of Ag^+ ions, since the nucleation of AgNPs may start at various moments of illumination, giving larger “older” and smaller “younger” nanoparticles. It is also clearly visible that the number of larger AgNPs increases after a further 10 s of illumination at the expense of small AgNPs—Figs. 1c and 2c. This behavior is common for both applied concentrations of Ag^+ ions.

Acquired SEM images were also used to calculate such parameters as the diameter and number of AgNPs as well as their surface coverage (the surface area occupied by nanoparticles related to 1 μm^2).

The histograms of average particle size distribution were obtained from the diameter measurements of at least 100–150 AgNPs, assuming that they have a regular, round shape—Figs. 1b and d and 2b and d. The number of AgNPs was obtained directly from calculating the number of particles related to one μm^2—Fig. 3. Changes in the diameter of large AgNPs exhibiting maximal size (*i.e.* above 10 nm) were observed and analyzed with great attention—Fig. 4. In order to estimate the AgNPs' surface coverage, the surface area occupied by each individual particle was calculated and multiplied by the number of nanoparticles in 1 μm^2—Fig. 5.

It was found that for experiments carried out for both applied concentrations of Ag^+ ions ($c = 5$ mM and $c = 10$ mM), the prolongation of illumination time from 20 s to 30 s caused a significant reduction in the number of small AgNPs, with a simultaneous growth of large particles. These changes can be observed in the SEM images gathered in Figs. 1a and c and 2a and c as well as in accompanying histograms—Figs. 1b and d and 2b and d. These histograms clearly show a decrease of particle numbers in the areas marked as small AgNPs and the appearance and/or growth of particles in areas marked as large AgNPs. Analyzing the above mentioned parameters, it was also found that the number of AgNPs fell roughly three fold during the additional 10 s of illumination—Fig. 3. Moreover, it was revealed that this longer illumination caused an increase of the

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