Metal Nanoparticle Coating of Oxide Nanospheres for Core-Shell Structures

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(Received: 7 March 2002; in revised form: 24 April 2002; accepted: 16 May 2002)

Abstract

A low-temperature route for coating oxide nanospheres with metal nanoparticles to achieve core-shell structures is introduced. First results indicating a dense coverage of silica nanospheres of about 300 nm size with regularly arranged Ag and Au nanoparticles deposited by a modified incipient wetness impregnation procedure are presented. This synthesis works completely without external reducing agents or media,

adhesive aids or functionalizing agents. Metal particles of only a few nanometers in size may serve as seeds for continuous metal coating of the oxide spheres by complementary processes. Structural characterization of the materials by transmission electron microscopy reveals a nearly spherical shape of the metal particles, the structure of which ranges from single crystalline to single twinned and multiply twinned configurations.

Keywords: coating characteristics, electron microscopy, incipient wetness impregnation, metal nanoparticles, oxide nanospheres

1 Introduction

Novel optical effects are expected by appropriately arranging metal particles on the surface of insulating cores of spherical shape, so as to compose, on a nanometer scale, core-shell structures [1–3]. Optical resonances from near-infrared to the visible range may then be tuned by adjusting the core size, shell thickness and type of metal and/or core material [4–7]. Core-shell structures have been intensively studied very recently, in particular since such structures exhibit peculiar properties which make them attractive for applications in optical and biological sensors and in optoelectronics [7–10]. To this purpose, oxide nanospheres of nearly equal size, offering great flexibility of composition, are well suited [11–13].

While on planar substrates a number of vacuum-based deposition methods may be utilized, including physical and chemical vapor deposition, laser ablation and cluster beam deposition, and also spin-coating techniques, the

situation is different with non-planar substrates because of their peculiar geometry. This requires access of the deposit species not only from one, but from all directions which may be achieved in a gas stream or in solution. For practical reasons, solution methods, such as the deposition of nanoparticles from a colloidal route of synthesis or particle formation directly on the surface by appropriate processes, are preferred. The first route includes electrostatic deposition of colloidal particles by means of adhesives such as polyelectrolytes covering the oxide surface [2] and ligand-mediated immobilization of metal colloids on functionalized oxide surfaces [3, 5]. The second route includes controlled chemical reduction, photochemical or radiation-chemical, photocatalytic and sonochemical reduction [14–16]. The controlled reduction of precursor molecules on the oxide surface [17–20] has two main advantages: (i) it avoids uncontrolled surface chemical interaction of the metal particles with functionalizing agents which may seriously influence the surface plasmon resonances [21, 22]; (ii) it allows control of the precursor decomposition kinetics and therefore the particle size at moderate temperatures [23, 24]. By varying the coating conditions (pH, concentration, temperature and duration of exposure of the metal complex solution), the coverage of the oxide nanospheres and size of metal nanoparticles may be controlled [19].

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As a synthesis route meeting the requirements of producing spectroscopically clear (no adhesives!) and photochemically stable (no ligands!) metal nanoparticle coatings of silver and gold on monodisperse Stöber silica nanospheres, we employed incipient wetness impregnation using water-soluble metal complexes. Apart from temperature and the initial concentration of the metal precursor, there is not much scope for controlling nucleation and growth processes in the practical execution of this route. The aim of producing core-shell structures requires one to achieve a high nucleation but low growth rate, so as to obtain a high number density of metal nanoparticles without the formation of aggregates. Therefore, we decided first to form a seeding layer of metal particles on the silica nanosphere surface by applying low precursor concentrations. Further nanoparticle coating from complementary processes to form continuous metal nanoshells may utilize the previously formed particles serving as seeds which catalyze metal deposition without nucleation of new particles [25–27]. Such multi-step processing includes some prospects of fabricating bimetallic structures by varying the metal precursor employed.

2 Experimental

Silica nanospheres were fabricated according to the well-known Stöber method by hydrolysis and condensation of tetraethoxysilane (TEOS) in a mixture of ethanol with water, using ammonia as catalyst to initiate the reaction [28]. The silica nanosphere size is controlled by the molar ratio of TEOS, water and ammonia. The synthesis starts with mixing and stirring of the components, requires a reaction time of about 2 h and is finished by centrifugation and about 3 h of drying at temperatures up to 100 °C. For metal nanoparticle coating, typically silica nanospheres of 100–300 nm size range with about 10–20 nm full width at half-height of the size distribution were employed.

The incipient wetness impregnation, widely used for the preparation of heterogeneous catalysts, consists of wetting the surface of a powder substrate with a metal salt solution of certain concentration so as to cover it in a defined manner. In contrast to catalyst preparation, where after drying the impregnated powder usually calcination and subsequent reduction treatment at elevated temperatures follow [29], we achieved metal particle formation by simply drying the impregnated silica nanospheres at temperatures below 100 °C. As metal precursors the water-soluble complexes hydrogentetrachloroaurate (HAuCl_4) and silver acetate (AgOOCCH_3) from Fluka were employed. Silica nanospheres and metal complexes were used without further

pretreatment. According to the mass of silica employed, the amount of metal salt required to achieve a certain metal concentration was dissolved in a defined volume of distilled water to fit incipient wetness. The solution was then added to the oxide and stirred until a uniform color was observed. For thermal decomposition of the metal complexes the samples were filled into quartz boats and placed in a quartz tube inside a cylindrical oven.

Structural characterization of the prepared materials was done by transmission electron microscopy (TEM) using a JEM 1010 (conventional TEM at 100 kV) and a JEM 4010 (high-resolution TEM at 400 kV) instruments. For electron microscopy examination, the metal-coated oxide nanospheres were dispersed in 2-propanol and spread dropwise on thin holey carbon films mounted on copper microgrids. Image processing was applied to digitized high-resolution images by using the NIH Image [30] and Gatan Digital Micrograph programs.

Optical properties in the visible range of the prepared materials were investigated by a thin-film optical analysis system from Theiss equipped with a halogen light source and two grating spectrometers for transmittance and reflectance measurements. To obtain homogeneous samples, the powders were embedded in transparent liquid resin, deposited on plane glass slides and solidified by exposure to UV radiation.

3 Results and Discussion

3.1 Metal Particle Formation and General Characteristics

This is the first time that metal particle formation at such low temperatures on oxide support without applying external reducing agents or media has been reported. The applied metal deposition process is considered to be sensitive to the configuration of terminating groups on the silica surface, since such surface groups obviously provide the capability required for the reduction of metal ions. Terminating OH groups usually formed on the oxide surface by dissociative adsorption of water molecules can acquire such properties, depending on their coordination symmetry [31, 32]. Accordingly, nanoparticles may form by auto-reduction of noble metal ions with oxide surfaces [33] via reactions such as

where the H^+ ions become incorporated into the silica network. The creation of $\equiv\text{Si}-\text{O}\cdot$ non-bridging oxygen hole centres, accompanying noble metal particle formation, was confirmed by their distinct electron paramagnetic resonance [34]. The efficiency of these surface-

Fig. 1: HREM image (a) of Au nanoparticles (1% precursor) on silica after 2 h of drying at 70 °C. The areas marked in (a) by boxes are shown at higher magnification in (b) and (c).

mediated reduction processes may decrease with consumption of hydroxyl groups and generation of surface charging.

Generally, the deposition method applied results in a dense coverage of uniformly arranged very small particles of rather narrow size variation for both metals. Figure 1(a) shows a characteristic HREM image of Au particles formed upon 2 h drying at 70 °C from a 1% precursor sample. This image is accompanied by higher magnified lattice plane images of the regions marked in (a) by boxes which are given in Figure 1(b) and (c). The tendency to form particles of nearly spherical shape without truncations at the interface is well established owing to the weak interaction between the metal deposit and silica substrate. Actually, the particles exhibit a cuboctahedral shape rather than that of ideal spheres. The smaller particles, i.e. those below about 5 nm in size, mostly are single crystalline, as can be seen in Figure 1(b). The larger particles frequently exhibit planar defects such as twin boundaries; an example is shown in Figure 1(c). Fringe spacings and angular relationships of the lattice planes measured in real space images and also in diffractograms (Fourier transformation) agree fairly well with those of the fcc lattice of the bulk metals.

3.2 Optical Characteristics

The optical properties of these materials correspond to their overall structure of nanoparticulate composites having a very low filling factor of the metal phase.

Fig. 2: Extinction spectra of Au (1% precursor) on silica as dried (a) and upon additional drying: 4 h at 100 °C (b), 4 h at 200 °C (c), and 2 h at 300 °C (d).

Therefore, the optical spectra are dominated by light scattering contributions of silica nanospheres peaking at about 425 nm. The latter completely cover the surface plasmon resonance of Ag nanoparticles and partly that of Au. A nominal metal loading factor (or filling factor) can be estimated from the silica core radius and the mean particle diameter (used as shell thickness) with consideration of the incompleteness of the metal shell by the respective coverage. This metal loading amounts to about 0.0065 for the sample illustrated in Figure 1. With higher metal loadings and increasing particle size, diminishing the effect of resonance damping, the optical absorption reveals the signature of resonances due to metal particles. The spectrum of a 1% Au sample, as shown in Figure 2 (as dried), only exhibits a rather broad extinction dominated by scattering contributions of silica nanospheres. Different from the case of silver, the maximum of the surface plasmon resonance of small gold particles is situated around 550 nm such that it is not completely covered by the extinction of silica nanospheres. Hence, with the occurrence of a sufficient number of particles larger than about 10 nm in size, the resonance damping is less effective and the evolution of metal particle resonances is observed. This behavior is demonstrated by the extinction spectra shown in Figure 2 for samples subjected to additional drying at

elevated temperatures. The apparent blue shift of the resonance position from about 565 to 540 nm, seen in these spectra, is not indicative of certain size effects, but is most probably due to superposition with the predominating extinction of silica nanospheres. The more the metal plasmon resonance evolves out of the background, the more the maximum of the corresponding shoulder moves towards the true resonance position. However, as long as the coating of oxide nanospheres by metal nanoparticles remains incomplete, this behavior in principle is not expected essentially to change.

3.3 Coating Characteristics

The coating of oxide nanospheres with metal nanoparticles can be characterized by two parameters, the mean particle size and the coverage, i.e. the portion of the nanosphere surface covered by metal particles. To control the size and size evolution of the metal nanoparticles deposited by incipient wetness impregnation on silica nanospheres, the influence of precursor concentration, drying temperature and repetition of deposition steps was investigated in a certain range. From series of experiments with varying silver precursor concentrations ranging from 1 to 10%, Figure 3 shows TEM images of the 5% and 10% samples after 2 h of drying in vacuum at 70 °C and Table 1 gives the coating characteristics of the whole series. An increase in coverage of the silica surface by Ag particles from 13 to 48% is achieved by both particle growth and nucleation of new particles. The metal loading increases linearly from 0.0039 to 0.0233 in the concentration range studied. It is remarkable, that there was no change in the uniform arrangement of metal particles on the silica surface and no aggregates were formed. Also, the size distribution remains narrow and monomodal, indicating rather uniform particle growth and the absence of coalescence and enhanced particle mobility. Even for a 10% precursor concentration, a dense population of Ag particles of only 3.6 nm mean size was obtained. These are very promising characteristics, making the chosen conditions of synthesis well suited for fabrication of core-shell structures of extremely small shell thickness. However, on applying higher

Fig. 3: TEM image of Ag nanoparticles on silica after 2 h of drying at 70 °C with (a) 5% and (b) 10% precursor concentration; (c) size distributions of both samples.

precursor concentrations, no further improvement could be achieved since the particle distribution and arrangement started to become non-uniform.

The coating characteristics of both metals are influenced in the same way by variations of the drying temperature. The more this temperature is increased, the more the particle size distribution broadens and becomes bimodal. Simultaneously, the coverage of the silica surface distinctly decreases, indicating that at higher drying temperatures the growth proceeds via consumption of a certain proportion of particles. Hence the uniformity of size and arrangement observed for lower temperatures is disturbed. Since the shape of individual particles remains nearly spherical, this behavior is assumed to be caused by

Table 1: Coating characteristics of Ag nanoparticles on silica nanospheres upon 2 h drying at 70 °C for various metal precursor concentrations.

Concentration [%]	Mean size [nm]	σ (std.dev.) [nm]	Coverage [%]	Filling factor
1	2.2	0.2	13	0.0039
2	2.2	0.2	14	0.0042
4	2.7	0.3	30	0.0110
5	2.8	0.2	32	0.0122
10	3.6	0.2	48	0.0233

Fig. 4: TEM image of Au nanoparticles (1% precursor) on silica after 2 h of drying at 70 °C: (a) first coating and (b) repeated coating; (c) size distributions of both samples.

increased particle-particle interaction and coalescence processes. It does not enable the metal loading to be increased essentially, but worsens the shell-like properties of the coating. Consequently, an increased drying temperature is not suited for our purpose.

Repetition of the incipient wetness impregnation was utilized for the Au precursor 1% sample using 2 h of drying at 70 °C. TEM images and the corresponding size distributions of the first and repeated deposition are shown in Figure 4. The particle size changes from a 2.4 ± 0.3 nm mean value for a monomodal distribution to 2.1 ± 0.3 and 4.7 ± 1.3 nm for a bimodal distribution in a remarkably uniform way. The coverage increase from 17% to 52% is by far above that obtained in a one-step procedure employing an equivalent concentration of the precursor complex. This behavior points to simultaneously proceeding nucleation and growth processes. Obviously, the nucleation rate and the growth rate are well adjusted to each other so as to keep the uniformity of the nanoparticle coating while increasing the metal loading. It can be assumed that the nucleation rate is governed by the availability of reducing radicals on the silica surface, being approximately a function of free

space on the nanosphere surface, and the growth rate is governed by both, the concentration of metal atoms and small clusters on the surface, and their mobility. Therefore, low precursor concentration and low temperature approaches are more successful in producing core-shell-like structures. The observed behavior indicates that repeated coating cannot be understood in terms of a so-called ‘seeding’ treatment, where an enlargement of metal particles is achieved by surface-catalyzed reduction of metal ions based on the presence of preformed particles. This would require that no new particle nucleation occurs, but instead a uniform growth of the seeds [25–27]. The incipient wetness impregnation, however, is mediated by terminating groups of the silica surface which are available also when the procedure is repeated. The accommodation of freshly formed metal atoms on pre-existing particles occurs in competition with nucleation processes as long as there is enough free surface present, leaving behind a bimodal distribution of particle sizes.

4 Summary

Metal coating experiments using incipient wetness impregnation with Ag and Au metal precursors resulted in a uniform and reasonably dense nanoparticulate coverage of monodisperse silica nanospheres. The oxide surface-mediated process, only slightly above room temperature, is well suited for preparing metal nanoparticle coatings on monodisperse silica nanospheres without the chemical aids usually applied to achieve particulate coatings. The general structure of the particles of both metals is the same. Single crystalline particles of nearly cuboctahedral shape grow on the silica surface without indications of substrate-deposit interaction. With particle sizes increasing above about 5 nm, planar lattice defects and shape deviations occur, indicating some changes in the growth mode. Despite the uniform arrangement of particles and relatively dense coverage of the oxide surface, the overall metal filling factor remains rather low. Consequently, the optical spectra mainly reflect the light scattering properties of silica nanospheres. Only upon higher metal loading and particularly for Au the signature of metal particle resonances is observed. Core-shell resonances of the nanospheres studied are expected to occur only upon formation of closed shells. This aim has not yet been achieved, but improvements of the coating characteristics were achieved by adjusting appropriately the metal precursor concentration and repetition of the coating procedure. With Ag nanoparticles the coverage could be enhanced by a concentration increase up to nearly 50%, preserving a remarkably uniform particle size and

arrangement. Repeated impregnation with Au produced a coverage increase distinctly above that obtained by employing an equivalent concentration in a one-step procedure.

5 References

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