



Tuning surface properties of amino-functionalized silica for metal nanoparticle loading: The vital role of an annealing process



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ABSTRACT

Metal nanoparticles (NPs) loaded on oxides have been widely used as multifunctional nanomaterials in various fields such as optical imaging, sensors, and heterogeneous catalysis. However, the deposition of metal NPs on oxide supports with high efficiency and homogeneous dispersion still remains elusive, especially when silica is used as the support. Amino-functionalization of silica can improve loading efficiency, but metal NPs often aggregate on the surface. Herein, we report that a facial annealing of amino-functionalized silica can significantly improve the dispersion and enhance the loading efficiency of various metal NPs, such as Pt, Rh, and Ru, on the silica surface. A series of characterization techniques, such as diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), Zeta potential analysis, UV–Vis spectroscopy, thermogravimetric analysis coupled with infrared analysis (TGA–IR), and nitrogen physisorption, were employed to study the changes of surface properties of the amino-functionalized silica before and after annealing. We found that the annealed amino-functionalized silica surface has more cross-linked silanol groups and relatively lesser amount of amino groups, and less positively charges, which could be the key to the uniform deposition of metal NPs during the loading process. These results could contribute to the preparation of metal/oxide hybrid NPs for the applications that require uniform dispersion.

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1. Introduction

Hybrid NPs, endowed with two or more unique properties, have been the focus of growing attention as advanced nanoarchitectures in a wide spectrum of applications, such as optical and magnetic imaging, drug delivery, energy harvesting, and heterogeneous catalysis [1–8]. Of specific interest are inorganic hybrid NPs that metal NPs (Au, Ru, Pt, Pd etc.) decorated on well-designed metal oxides (SiO₂, Al₂O₃ and Fe₃O₄) [9–16]. For example, Au/SiO₂ with tunable sizes is effectively utilized in surface-enhanced Raman spectroscopy (SERS) and surface plasmon resonance (SPR) [17]. Replacing the SiO₂ support with magnetic Fe₃O₄, the obtained hybrid Au/Fe₃O₄ NPs have been considered as promising candidates for in-vivo diagnostic tests that include both optical detection and targeting capabilities under an external magnetic field [18,19]. Using Rh, Pt, and Pd NPs, the versatile design of heterogeneous oxide-supported metal hybrid NPs can also be achieved, such as Rh/SiO₂, Pd/Al₂O₃ and Pt/CeO₂ [20–22]. The assembly of metal NPs on oxides possesses exceptional advantages ranging from the size control of metal NPs, enhanced thermal stabilities provided by oxide supports, and the utilization of metal–oxide interactions. These evince the metal/oxide hybrid NPs as multifunctional catalysts for a number of reactions.

The dispersion homogeneity and size uniformity of these hybrid NPs are highly desirable, due to the size and shape-dependent properties in practical applications. For catalytic purposes, the aggregation of NPs would significantly deactivate catalysts, due to the decreased surface area. Well-dispersed and separated metal NPs on oxide supports are thus beneficial to relieve the aggregation tendency of NPs during thermal pretreatment and harsh catalytic reaction conditions [5]. Monodispersity and size homogeneity of hybrid NPs are also regarded as important criteria in the fabrication of efficient light harvesting materials and solar cell films [23]. Surface smoothness, interparticle spacing and uniformity of the self-assembled NPs are also highly demanded for high quality optical detection and magnetic resonance imaging [24].

Several conventional strategies have been studied to obtain various metal/oxide hybrid NPs [25–29]: i) growth of metal components on oxides or reversed approach, such as reduction of metal ions on preformed oxides NPs [30–37], decomposition of one metal precursor on other preformed metal NPs followed by oxidation [38], and chemically-triggered phase segregation of alloy NPs [39]; and ii) direct deposition of preformed metal NPs on oxides via colloidal method [9,11,40]. Strategy i) is challenging to accomplish the uniform growth of metal NPs on other surfaces. Strategy ii) provides a more advantageous platform to prepare metal/oxide hybrid NPs with precise controls in size and geometry by isolating the synthesis of metal NPs and oxide substrates in advance of the colloidal deposition. Among the direct deposition, charged metal NPs can be well dispersed on various substrates due to

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the electrostatic repulsion between metal NPs [9]. Hydrophobic/hydrophilic interactions also play important roles in instances that involve loading ligand-protected neutral metal NPs onto substrates [15]. Nevertheless, the direct assembly of metal NPs on bare oxides with uniform dispersion and high loading efficiency is still challenging due to the complicated surface compatibility of metal/oxide interfaces derived from diverse synthetic methods. Chemical functionalization of the oxides is an alternative strategy to enhance metal NP–oxide interactions utilizing the chemical bonding. Amino-, thiol- and carboxylic-terminated alkyl groups are commonly functionalized on the surface of silica to anchor various ligand-capped precious metal NPs through strong coordinating interactions, such as Au, Pt, Rh and Pd [41]. However, the general mechanism of assembly remains unsolved leading to the empirical endeavors in the fabrication of metal/oxide hybrid NPs.

Recent studies have revealed that the pretreatment steps on oxide substrates, such as heating and drying, can tune the surface characteristics [42] and thus likely improve the uniformity of the coating material on such substrate. For example, a mild thermal treatment of SiO₂ was found to be advantageous to obtain conformal CeO₂ coatings in the synthesis of SiO₂–CeO₂ NPs [43]. In this article, we have used amino-functionalized silica spheres (NH₂–SiO₂) as a model system to study the loading of metal NPs on them. We demonstrate herein that the annealing process performed on NH₂–SiO₂ can largely improve both the dispersion and loading efficiency of diverse precious metal NPs. We explored the surface variance of NH₂–SiO₂ pertaining to this annealing process, zeroing in on the most important factors that affect the loading of metal NPs. This annealing process can be easily executed, thus broadening its technical applications for the efficient manufacture of various metal/oxide nanostructures.

2. Experimental section

2.1. Chemicals

Methanol, ethanol, isopropanol, ammonium hydroxide (28%), ethylene glycol (EG), and cyclohexane were purchased from Fisher Scientific. 3-aminopropyltriethoxysilane (APTS, 99%), and RhCl₃·xH₂O were obtained from Alfa Aesar. K₂PtCl₄ and K₂PdCl₄ were obtained from Acros Organics. RuCl₃·xH₂O, tetraethyl orthosilicate (TEOS, 98%), L-arginine, polyvinylpyrrolidone (PVP, K30), and myristyltrimethylammonium bromide (C₁₄TAB) were obtained from Sigma-Aldrich.

2.2. The synthesis of 200 nm SiO₂ spheres with uniform particle size (deviation <5%)

200 nm SiO₂ spheres were synthesized by a four-step seeded growth approach [44].

24 nm SiO₂ seeds: 18.2 mg L-arginine and 13.9 mL of ultrapure water were mixed thoroughly. Then 0.9 mL of cyclohexane was added gently to the water–arginine solution without disturbing the two-layer solution. The solution was heated to 60.0 ± 0.2 °C for 30 min at ~300 rpm. 1.10 mL of TEOS was added to the mixture. The reaction was kept for 20 h at 60 °C. After reaction, the bottom layer was taken out and kept in the refrigerator (Sample A).

45 nm SiO₂ seeds: 4 mL of the 24 nm seeds (Sample A) was taken and diluted with 14.4 mL ultrapure water after which 2 mL cyclohexane was added. The mixture was brought to 60 °C for 30 min at ~300 rpm. Then 1.408 mL TEOS was added to the top layer immediately, and the mixture was kept at 60 °C for 30 h. After reaction, the bottom layer was taken out and kept in refrigerator (Sample B).

82 nm SiO₂ seeds using Stöber method: 1 mL of the 45 nm seeds (Sample B) was taken and diluted with 2.6 mL deionized water and 18 mL ethanol. Subsequently, 1.7 mL NH₃·H₂O (~28%) was added. The solution was mixed at ~500 rpm for 1 h at room temperature. A total of 0.8 mL TEOS was added to the solution dropwise, three times at

intervals of 30 min. The solution was stirred for 6 h and later kept in the refrigerator (Sample C).

200 nm SiO₂ spheres using Stöber method: 1 mL of the 82 nm seeds (Sample C) was taken and diluted with 2.6 mL deionized water and 18 mL ethanol. 1.7 mL NH₃·H₂O (~28%) was added. The solution was mixed at ~500 rpm for 1 h. A total volume of 0.44 mL TEOS was added to the solution dropwise twice at intervals of 30 min. After 6 h, 200 nm SiO₂ spheres (Sample D) were obtained and kept in the refrigerator for further use. This step could be easily scaled up. In our group, >10 g silica spheres could be obtained in one batch. The size deviation is typically within ±10 nm.

The purification of SiO₂ spheres was conducted by washing them 5 times with an ethanol/water solution (50/50 v/v). The purified SiO₂ spheres were stored in ethanol.

2.3. The synthesis of 5 nm Pt, 4 nm Rh, and 1.8 nm Ru NPs

All metal NPs were synthesized according to previously reported literature with modifications [45].

5 nm Pt NPs: 20.8 mg K₂PtCl₄, 505 mg C₁₄TAB and 222 mg PVP (K30) were mixed in 20 mL EG with sonication. Under argon protection, the mixed solution was heated to 140 °C for 2 h. After reaction, Pt NPs were precipitated by adding excessive acetone (acetone:EG = 8:1). The precipitate was further washed 5 times with an ethanol/hexane mixture (1/4 v/v). Purified 5 nm Pt NPs were dispersed in 20 mL ethanol.

4 nm Rh NPs and 1.8 nm Ru NPs: The synthetic conditions and purification procedure are the same as 5 nm Pt NPs except for using 20.7 mg RhCl₃·xH₂O and 20.7 mg RuCl₃·xH₂O respectively as starting materials.

2.4. The synthesis of NH₂–SiO₂ [5,40]

1.0 g SiO₂ spheres were centrifuged from the original ethanol solution and re-dispersed in 175 mL isopropanol. 200 μL APTS was dissolved in 25 mL isopropanol and mixed with the above SiO₂–isopropanol solution. A round-bottom flask containing the mixed solution was heated to 80 °C. The reaction was stopped after 2 h. NH₂–SiO₂ spheres were separated, washed with ethanol 3 times and stored in 20 mL ethanol.

2.5. The annealing process of NH₂–SiO₂

As-synthesized NH₂–SiO₂ spheres were taken out from their ethanol solution and dried in vacuum at room temperature. The dried solids were annealed in an oven in air at 100 °C for 5 h, and then cooled down to room temperature naturally.

2.6. The preparation of metal NPs (M) loaded on NH₂–SiO₂ (M/NH₂–SiO₂)

Typically, 200 mg NH₂–SiO₂ (fresh or annealed) spheres were taken out and dispersed in 60 mL ethanol. The appropriate amount of the metal NPs solution was taken out according to the desired metal loading and diluted to a final volume of 110 mL with ethanol. The 110 mL diluted metal NPs solution was added to 60 mL NH₂–SiO₂ solution dropwise with vigorous magnetic stirring. After addition, the resulting M/NH₂–SiO₂ solution was further sonicated for 30 min. After separation, the M/NH₂–SiO₂ precipitate was washed with ethanol 5 times and stored in ethanol.

2.7. Characterization details

The morphology of NH₂–SiO₂ spheres and M/NH₂–SiO₂ were investigated using transmission electron microscopy (TEM) recorded on a Tecnai G2 F20 electron microscope operated at 200 kV. Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) measurements were performed using an Agilent Cary 670 FTIR equipped with a

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