Electroless nickel metallization to prepare SiO₂–Ni composite particles via polyelectrolytes route

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Abstract

Metallization of submicrometer silica (SiO₂) particles was carried out by an aqueous electroless nickel (Ni) plating to which polyelectrolytes of polydiallyldimethylammonium chloride and poly(sodium styrene sulfonate) were used to modify the SiO₂ surface through sequential electrostatic adsorption prior to the deposition process. The adsorbed polyelectrolytes gave rise to a negative surface charge (−80 mV) so that anchoring of Ni²⁺ ions on the particle surface was facilitated in the precursor solution. This resulted in formation of a continuous Ni layer deposited preferentially on the SiO₂ surface upon subjected to chemical reduction in the metallization bath with dimethylamine borane as the reducing agent. Surface characteristics and microstructure of the SiO₂–Ni composite particles were examined by zeta-potential measurement, electron microscopy, and X-ray photoelectron spectroscopy.

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1. Introduction

Ceramic–metal composite particles featuring specifically core–shell [1–4], “rattle-in-ball” [5–7], and anisotropic Janus [8] structures have received increasing attention over the last decade due mainly to their unique functionalities that are suitable to a wide range of advanced applications [9–12]. Routes to synthesize the composite particles with tailored hierarchical structures include, for example, preferential surface precipitation, seeded growth, Pickering emulsion, electroless (autocatalytic) plating, sonochemistry, and electrostatic layer-by-layer (LbL) assembly [9,10,13–19]. Among them, the electroless plating involves use of chemical reducing agent to facilitate reduction of metallic ions in solution so that metallic nuclei can deposit preferentially on the core surface of various chemical compositions, forming either a uniform metal shell or a raspberry core–shell structure so long as a continuous electron transfer between the reacting species can occur selectively at specific activation sites on the core surface [3,9,10,20–31]. The process is facile with a good throwing power, and is also flexible and cost-effective. Nonetheless, suitable surface roughening, sensitization, and noble-metal activation are critically important to the success of the plating process, in addition to repeated washing and cleaning required at the end of each process step for successful preparation of the core surface ready for the electroless plating. In view of the literature, electroless metallization of dielectric particle to form core–shell composite of various chemistries has been examined [3,4,20–25]. For the electroless nickel (Ni) plating specifically, Guo et al. [28] prepared Ni coated poly(methyl methacrylate) (PMMA) core–shell beads; to which, surface of the PMMA beads was first sensitized in SnCl₂ solution and then activated in PdCl₂ solution with an aim that the core surface with suitable catalytic sites is readily available for the nucleation and growth of Ni nuclei on the bead surface. When the Pd-modified PMMA particles were mixed with Ni precursor solution containing sodium hyrophosphate hydrate (Na₃H₂PO₄·H₂O) as the reducing agent, magnetic PMMA-Ni core–shell composite formed in the metallization bath. Similarly, Ma et al. [30] used polystyrene
(PS) beads in replace of the PMMA beads for the synthesis of PS–Ni particles with a shell thickness ranging from 100 to 250 nm.

On the other hand, the electrostatic LbL assembly has been used for the metallization of dielectric particles as well. Liang et al. [2] first prepared PS-gold (PS-Au) composite particles by utilizing electrostatic forces to attract Au nanoparticles on surface of the PS beads. Polyelectrolytes of poly(allylamine hydrochloride) (PAH) and poly(acrylic acid) (PAA) were used to modify the core surface sequentially in order to adsorb the Au hydrochloride (PAH) and poly(acrylic acid) (PAA) were used to modify the core surface sequentially in order to adsorb the Au nanoparticles through the LbL assembly. The polyelectrolytes-modified PS beads bearing a negative surface charge were able to attract positively charged, 4-dimethylaminopyridine-coated Au nanoparticles through the LbL assembly. The polyelectrolytes-modified PS beads were slowly added into the mixture solution drop-by-drop. The solutions were stirred vigorously at room temperature for 3 h, followed by repeated centrifugation at 6000 rpm (Universal 300, Hettich Zentrifugen, Germany) and washing by D. I. water for 3 times. The as-prepared SiO2 particles showed an average particle diameter of 400 nm determined by a dynamic light-scattering technique (Zetasizer Nano ZS, Malvern Instrument, U.K.) in dilute solids concentration.

2.2. Polyelectrolytes adsorption on the SiO2 surface

The SiO2 particles of 0.1 g were added into D. I. water of 9.9 ml with the solution pH being kept at 7 by addition of hydrochloric acid (HCl, 37%, Aldrich, U.S.A.). Cationic PDDA polyelectrolyte ((C8H16NCl)n), 35 wt% in H2O, molecular weight < 100,000, Aldrich, U.S.A.) of 0.001 g was then added into the colloidal solution with continuous vigorous stirring at room temperature for 10 min. The solution was then subjected to centrifugation and the sediment was washed by D. I. water repeatedly. The washed particles were re-dispersed in 10 ml D. I. water at pH 7, followed then by addition of 0.001 g anionic PSS polyelectrolyte ((C8H17NaOS)n), 30 wt% in H2O, molecular weight ca. 70,000, Aldrich, U.S.A.). The solution was agitated vigorously for 10 min, followed then by repeated centrifugation and water-rinsing for the polyelectrolytes-modified SiO2 particles.

2.3. Electroless Ni plating

The polyelectrolytes-modified SiO2 particles of 0.1 g were added in 30 ml aqueous NiCl2 solution (98%, Sigma Aldrich, U.S.A.) of various concentrations ranging from 0.0255 to 0.255 M. DMAB ((CH3)2NH·BH3, Aldrich, U.S.A.) of 0.170 M was then added as the reducing agent. The solutions were stirred vigorously at 85 °C for 1 h followed then by repeated centrifugation and water-rinsing for 4 times to obtain the colloidal SiO2–Ni composite particles. For comparison purposes, SiO2–Ni “composite” particles were also prepared by the same electroless Ni plating but used the as-prepared SiO2 particles without the polyelectrolytes adsorption.

2.4. Characterizations

Zeta (ζ) potential of the as-prepared and the polyelectrolytes-modified SiO2 particles was measured by the laser Doppler electrophoresis (Zetasizer Nano ZS, Malvern Instrument, U.K.) in water over a pH range from 2 to 12 using. A 0.1 M sodium chloride was used as the buffer solution for the measurement, while the solution pH was adjusted with HCl and sodium hydroxide (NaOH, 95%, Shimakyu, Japan). Crystalline structure of the SiO2–Ni composite particles was determined by X-ray diffraactometry (XRD, MXP III, MAC, Japan) using Cu Kα radiation (λ=1.5406 Å) with accelerating voltage and current of 40 kV and 30 mA, respectively. The measured 2θ varied from...
10° to 90° with a scan rate of 2°/min. Morphological microstructure of the particles was examined by field-emission scanning electron microscopy (FE-SEM, JSM-6700F, JEOL, Japan) equipped with energy-dispersive X-ray spectroscopy (EDS, Oxford Inca Energy 400, U.K.). Surface composition of the SiO2–Ni particles was examined by X-ray photoelectron spectroscopy (XPS, PHI-5000, Ulvac-PHI, Japan).

3. Results and discussion

Fig. 1 shows that the isoelectric point (IEP) of the as-prepared SiO2 particles is at pH~3.5. This indicates that surface of the SiO2 particles is negatively charged over a broad pH range, and the ζ potential remains steadily unchanged at ca. −80 mV over a pH range from 9 to 12. After adsorption of the cationic PDDA polyelectrolyte, the ζ potential of the PDDA-modified SiO2 particles reverses markedly from negative to positive over the entire pH range examined. This reveals that the NH3⁺ functional group of the PDDA molecules protonated easily and anchored preferentially on the negatively charged SiO2 surface so that a positively charged surface was resulted in a broad pH range from 2 to 12. When the anionic PSS molecules were adsorbed on the PDDA-modified SiO2 particles, the ζ potential changes from positive to negative again over the pH range examined. This indicates that the SO3⁻ functional group of the PSS polyelectrolyte was able to dissociate in water and strongly attached with the NH3⁺ functional group of the PDDA polyelectrolyte available on the SiO2 particles. According to Lin et al. [3], the polyelectrolytes layer formed on the SiO2 particles provides a uniformly distributed negative charge on the surface to facilitate attraction of the Ni2⁺ ions in solution through the electrostatic interaction. In addition, the “soft” polyelectrolytes layer formed on the hard SiO2 core particles would provide a “harbor” space, allowing hence the anchoring of Ni2⁺ “seeds” within the porous polyelectrolytes layer for the subsequent chemical reduction to take place, leading to a uniform formation of Ni layer on the core surface when a suitable reducing agent is used in the metallization solution.

In Fig. 2, a broad peak is obtained for the as-prepared SiO2 particles, revealing the amorphous structure of the particles prepared from the sol–gel route. After the electroless Ni plating, a diffraction peak belonging to Ni{1 1 1} becomes pronouncedly apparent at 2θ=45° as the NiCl2 concentration exceeded 0.0255 M. The Ni2⁺ ions were reduced from the solution to their metallic state because of the presence of reducing DMAB molecules. Ni embryos were formed and grown on the SiO2 surface selectively. Since the Ni2⁺ ions could not be reduced to their metallic counterpart spontaneously without the presence of chemical catalyst as an external driving force for the reaction to occur, the electrons were therefore provided by the reducing DMAB molecules through a series of hydrolysis reactions as follows [32]:

\[(\text{CH}_3)_2\text{NH} \cdot \text{BH}_3 + \text{OH}^- \rightarrow \text{BH}_3\text{OH}^- + (\text{CH}_3)_2\text{NH} \]

\[\text{BH}_3\text{OH}^- + \text{OH}^- \rightarrow \text{BH}_2(\text{OH})_2^- + 1/2\text{H}_2 + e^-\]

\[\text{BH}_2(\text{OH})_2^- + \text{OH}^- \rightarrow \text{BH}(\text{OH})_3^- + 1/2\text{H}_2 + e^-\]

\[\text{BH}(\text{OH})_3^- + \text{OH}^- \rightarrow \text{B}(\text{OH})_4^- + 1/2\text{H}_2 + e^-\]

From the reactions, the reducing capability of Ni2⁺ depends critically on the hydrolysis rate of the DMAB molecules in solution. In this study, the initial DMAB concentration was held at a fixed concentration of 0.170 M for the broad NiCl2 precursor concentrations used; therefore, one would suspect that the increase of NiCl2 concentration would provide more Ni2⁺ ions to react with the hydrolyzed DMAB molecules. This formed embryos on the existing nucleus sites on the particle surface and facilitated the growth of Ni(0) embryos so that a uniform Ni shell around the polyelectrolytes-modified SiO2 particles resulted. An increased diffraction intensity from the crystalline Ni was found in Fig. 2 as the NiCl2 concentration was increased. Crystallite size of the Ni shell was calculated from the Scherrer equation using the Ni{1 1 1} peak. The crystallite size falls in a range from 0.79 to 0.99 nm for the NiCl2 concentrations examined; to which, the calculated size appears not increased much with the NiCl2 concentration employed. This suggests that the concentration of DMAB used in the study might have been over-supplied so that an abundant amount of the Ni nuclei was quickly formed in the metallization bath as the DMAB was added, and thus the grain coarsening on the SiO2 surface was prohibited to a
Fig. 3. FE-SEM images of (a) the as-prepared SiO₂ particles, (b) the SiO₂ particles with surface modified by 0.5% PDDA and PSS polyelectrolytes adsorption, and the SiO₂–Ni composite particles that were prepared (c) without and (d) with the polyelectrolytes adsorption on the SiO₂ particles. For (c) and (d), the electroless Ni plating was conducted by using NiCl₂ of 0.1275 M and DMAB of 0.17 M with a continuous agitation at 85 °C for 1 h. Discrete Ni particles with a particle size of about 1 μm were found in (c).

Fig. 4. The SiO₂–Ni core–shell particles prepared from using NiCl₂ of (a) 0.0255 M, (b) 0.0637 M, and (c) 0.255 M with 0.5% PDDA and PSS polyelectrolytes adsorption on the SiO₂ particles prior the electroless plating. The electroless Ni plating was conducted by using 0.17 M DMAB with a continuous agitation at 85 °C for 1 h.
significant extent. The abundant presence of the reducing DMAB molecules in the metallization bath might favor formation of Ni-B hydrates instead of pure Ni in the prepared SiO₂–Ni composite particles. However, only Ni crystals were found from the XRD result in Fig. 2.

Fig. 3 shows morphology of the as-prepared SiO₂, polyelectrolytes-modified SiO₂, and SiO₂–Ni composite particles prepared without and with the polyelectrolytes adsorption. Surface of the as-prepared SiO₂ particles is smooth and featureless in Fig. 3a. This featureless morphology is also found in the polyelectrolytes-modified SiO₂ particles (Fig. 3b). In comparison, the SiO₂–Ni particles show mixtures of the submicrometer-sized SiO₂ particles and micrometer-sized Ni particles in Fig. 3c, confirmed by EDS, when the composites were synthesized from the as-prepared SiO₂ particles without the polyelectrolytes adsorption. As shown in the inset of Fig. 3c, surface morphology of the SiO₂ particles resembles to that of Fig. 3a and b except some few nanometer-sized particulates were found randomly on the SiO₂ surface. On the contrary, a continuous Ni layer was formed on the polyelectrolytes-modified SiO₂ particles (Fig. 3d). Two main mechanisms were involved in the process. First, the strong electrostatic force chelates the Ni²⁺ ions on the polyelectrolytes-modified SiO₂ surface in the metallization solution and facilitates the metal coating. Second, preferential formation of the metallic Ni(0) nuclei on the SiO₂ surface results when the reducing DMAB was added in the metallization bath. This triggers a chain reaction so that a continuous deposition of Ni(0) layer was built up on the SiO₂ surface selectively. In Fig. 3d, the SiO₂–Ni core–shell particles show a rough surface with an average particle size of about 450 nm, which is substantially greater than that of the as-prepared SiO₂ particles (400 nm).

When the NiCl₂ concentration was altered, morphology of the SiO₂–Ni composites changed accordingly. As shown in Fig. 4, particle size and surface roughness of the composite particles appear to increase with the NiCl₂ concentration. A relatively smooth and continuous Ni shell results when the NiCl₂ concentration was kept under 0.0637 M, as shown in the inset of Fig. 4a and b, with a slightly cockled surface. The Ni morphology then becomes mesh-like as the NiCl₂ concentration was raised above 0.1275 M (Fig. 3d and Fig. 4c). Fig. 5a illustrates XPS wide scan of the SiO₂–Ni particles prepared from the NiCl₂ concentration of 0.255 M (Fig. 4c). In Fig. 5a, elements such as O, Ni, Si, C, and B have been found, which are in good agreement with the SiO₂–Ni composition prepared. The minor B 1s peak stems from the reducing DMAB used in the plating process. Fig. 5b shows the deconvoluted Ni 2p peaks from the SiO₂–Ni particles prepared from the NiCl₂ concentration of 0.255 and 0.0255 M, respectively. Both of the high-resolution scans show a pronounced presence of NiO with strong Ni 2p peaks attributable to the NiO at binding energies of 855.4 (2p₃/₂), 861.5 (2p₃/₂ sat), 873.5 (2p₁/₂), and 879.4 (2p₁/₂ sat) eV, respectively. This compares favorably with relatively weak peaks belonging to the metallic Ni, i.e., 2p₃/₂ and 2p₁/₂ at binding energies of 852.2 and 868.4 eV, respectively. In addition, the presence of NiO on the surface of SiO₂–Ni particles is also verified in Fig. 5c; in which, the deconvoluted O1s peak shows existence of the NiO in addition to the SiO₂ phase. The relative intensity from peaks of NiO-related peaks to those of Ni (Fig. 5b) and SiO₂ (Fig. 5c) reveals that the NiO concentration increases with the DMAB concentration on the composite surface. These findings suggest that the morphological change of the composite particles in Fig. 4 is likely resulted from oxidation of the Ni coating layer during the electroless deposition. The morphology is hence sensitive to process variables used in
the metallization reaction; to which, surface composition of the Ni layer differs as the NiCl₂ concentration was varied.

4. Conclusion

Metallization of inorganic SiO₂ particles to form SiO₂–Ni core–shell composite structure with a uniform Ni shell on the SiO₂ core has been carried out by an aqueous electroless plating on polyelectrolytes-modified SiO₂ beads. Use of the PDDA and PSS molecules modified the SiO₂ surface effectively through the electrostatic adsorption. This gave rise to a uniform negative surface charge so that a preferential anchoring of Ni²⁺ ions on the particle surface was formed in the precursor solution. The polyelectrolytes-modified surface led to a formation of continuous Ni layer deposited on the SiO₂ core surface subsequently when DMAB was used as the reducing agent in the metallization bath. The concentration of NiCl₂ precursor solution was found to influence morphology and surface composition of the Ni coating layer; to which, a mesh-like morphology with a predominately NiO phase was observed when the NiCl₂ concentration was raised above 0.1275 M. Formation of the NiO surface was likely resulted from the oxidation during the aqueous metallization deposition, and was critically dependent on the NiCl₂ concentration used. This metallization process on the dielectric SiO₂ particles is expected to be extendable to the synthesis of metal-oxide core–shell particles of a wide range of chemical compositions.

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