

Preparation of Au/Ag Multilayers *via* Layer-by-Layer Self-assembly in Spherical Polyelectrolyte Brushes and Their Catalytic Activity^{*}

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Abstract Spherical polyelectrolyte brushes (SPBs) consisting of polystyrene (PS) core and poly(2-aminoethyl methacrylate hydrochloride) (PAEMH) shell were prepared by photo-emulsion polymerization. Au nanoparticles (Au-NPs) with controlled size and size distribution were synthesized *in situ* using SPBs as nanoreactors. *Via* layer-by-layer deposition technique on the surface of SPBs, nano-composite particles with Au/Ag-NPs bilayer and Au/Ag/Au-NPs trilayer were prepared. The structures of the as-prepared Au/Ag multilayer SPBs were characterized by UV-Vis spectroscopy, TEM, ICP-AES and DLS. The charge reversal of the nano-composite particles observed by zeta potential confirmed the success of layer-by-layer assembly. The Au/Ag-NPs bilayer nano-composite particles showed high catalytic efficiency with an apparent activation energy of about 41.2 kJ/mol in the reduction reaction of 4-nitrophenol to 4-aminophenol in the existence of sodium borohydride monitored. The catalytic activity of Au/Ag-NPs multilayer SPBs close to that of Au-NPs SPBs and much higher than that of Ag-NPs SPBs reveals its potential applications in cost-effective catalysts with high-performance.

Keywords: Layer-by-layer self-assembly; Spherical polyelectrolyte brushes; Catalytic activity.

INTRODUCTION

Layer-by-layer self-assembly technique is an alternative process of fabricating multilayer structure by adsorption of polycations and polyanions alternately which was first proposed by Decher^[1–3]. The layer-by-layer adsorption process is normally driven by charge transfer interactions^[4]. Nowadays, layer-by-layer self-assembly is largely applied to prepare microcapsules^[5, 6] and multilayer membranes^[7–10] which can be used in the field of multilayer catalysts^[11–13], drug release^[14–16], and optical apparatus^[17]. More interesting structure is the functional core/shell nanoparticles synthesized *via* layer-by-layer technology where the core can be dissolved resulting in hollow nanospheres^[18].

Spherical polyelectrolyte brushes (SPBs) are structures that polymer chains were attached to a solid spherical core through an anchor group. The stretch of polymer chains can be tuned by external stimuli such as temperature, pH value and ionic strength. Due to the Donnan effect, SPBs can keep the concentration of counter-

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ion constant within the brush layer which should be ideal nano-reactors to prepare metal nano-particles^[19–23]. Nanoparticles of noble metals show much higher catalytic activity than their bulk materials due to larger surface-to-volume ratio^[24–27]. Therefore noble metal nanoparticles have been used as catalyst widely in oxidation reaction^[28–31], hydrogenation reduction^[32–36], cross-coupling reaction^[37–39] and electron transfer reaction^[40, 41]. SPBs have been employed to prepare metal nanoparticles below 10 nm such as Ag^[42, 43], Au^[44, 45], Pd^[46], Ni^[47], Au-Pt nanorods^[48, 49], which could prevent aggregation of metal nanoparticles without adding additional stabilizing agent.

In this work, SPBs with Au/Ag multilayers were prepared. Cationic SPBs were used as nanoreactors to prepare Au nanoparticles (Au-NPs) with the size around 1.4 nm by *in situ* reduction reaction. Then, silver nanoparticles (Ag-NPs) immobilized on anionic poly(L-aspartic acid) (PAsp) were deposited onto cationic SPBs. Finally, Au-NPs binding on cationic poly(allylamine hydrochloride) (PAH) were loaded *via* layer-by-layer to form Au/Ag/Au multilayer composite nanoparticles (Fig. 1). Moreover, the reduction reaction of 4-nitrophenol to 4-aminophenol by sodium borohydride (NaBH_4) was employed to study catalytic activities of the obtained Ag/Au multilayer nanoparticles which was monitored by UV-Vis spectroscopy.

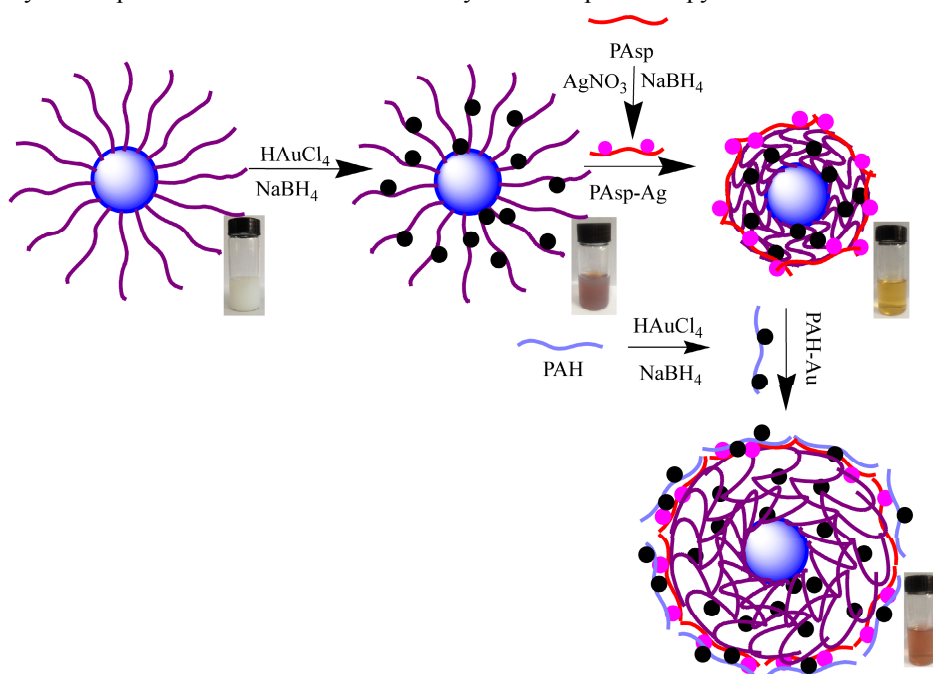


Fig. 1 Schematic description of preparation of Au/Ag multilayer *via* layer-by-layer assembly in SPBs

EXPERIMENTAL

Materials and Measurements

Styrene and acrylic acid were purchased from Shanghai Reagent Company (SRC), distilled under a reduced pressure and stored in refrigerator at $\sim 4^\circ\text{C}$. Sodium dodecyl sulfate (SDS) and potassium persulfate (KPS) were purchased from SRC and used without further purification. Photo-initiator 2-[*p*-(2-hydroxy-2-methylpropiophenone)]-ethyleneglycol-methacrylate (HMEM) was synthesized as reported previously^[19]. 2-Aminoethyl methacrylate hydrochloride (AEMH) was purchased from Sigma-Aldrich Co., Ltd. Silver nitrate (AgNO_3) and hydrogen tetrachloroaurate hydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$) were obtained from Sinopharm Chemical Reagent Co. Ltd and used as received. NaBH_4 was purchased from Lingfeng Chemical Reagent Co., Ltd. Poly(allylamine hydrochloride) (PAH) ($M_w \sim 12000 \text{ g}\cdot\text{mol}^{-1}$) was supplied from Aldrich, Hannover, Germany. Poly(L-aspartic acid) (PAsp) ($M_w \sim 10000 \text{ g}\cdot\text{mol}^{-1}$) was purchased from Aike Reagent. The water used in all experiments was purified by reverse osmosis (Shanghai RO Micro Q).

The size and size distribution of SPB and Au/Ag multilayer SPB were measured by dynamic light scattering (DLS) (PSS, NICOMPTM380ZLS). Morphology of SPB-Au, Au/Ag bilayer SPB (SPB-Au-PAsp-Ag) and Au/Ag/Au trilayer SPB (SPB-Au-PAsp-Ag-PAH-Au) were observed by TEM (JEM-1400). Zeta potentials were determined by Zetasizer Nano (Zetasizer3000HS). The amounts of Au-NPs and Ag-NPs in all steps of preparation were determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) (IRIS 1000).

Synthesis of Au-NPs in SPB (SPB-Au)

Cationic SPBs with polystyrene core and the poly(2-aminoethyl methacrylate hydrochloride) (PAEMH) shell were prepared by photo-emulsion polymerization^[44]. In a typical run, 30 g of SPBs (0.76 wt%) was diluted with 60 g of water in a three-necked flask at the stirring rate of 300 r·min⁻¹. The whole reactor was fulfilled with nitrogen. 0.02 g HAuCl₄·3H₂O dissolved in 10 g water was added to SPB latex and stirred for 3 h. Then 5 mL of 1 mol·L⁻¹ NaBH₄ solution was added slowly under the atmosphere of nitrogen followed by stirring for another 1 h. As a result, AuCl₄⁻ ions were reduced to Au-NPs along with the color change. The obtained SPB with Au-NPs were purified by dialysis against water until the conductance of the eluate did not change anymore (Membrane: cellulose nitrate with molecular weight cut off 15000 supplied by Shanghai Yuanye Bio-Technology Co., Ltd).

Synthesis of Au/Ag Multilayers by Layer-by-Layer Deposition

To prepare Au/Ag multilayers on the surface of SPB *via* layer-by-layer deposition, Ag-NPs binding on PAsp (PAsp-Ag) and Au-NPs binding on PAH (PAH-Au) were prepared firstly. In a typical run, polyanions PAsp were dissolved in 100 mL of water. A 10 mL AgNO₃ (2×10^{-3} mol·L⁻¹) was added to a 100 mL PAsp solution (0.2 g·L⁻¹) under the atmosphere of nitrogen with stirring for 3 h. 5 mL NaBH₄ (0.4 mol·L⁻¹) was added slowly into above solution, and Ag⁺ ions were reduced into Ag-NPs. Similarly, 10 mL HAuCl₄ with the concentration of 8×10^{-4} mol·L⁻¹ was added into 100 mL PAH solution of 0.2 g·L⁻¹, and AuCl₄⁻ ions were reduced into Au-NPs by adding 5 mL NaBH₄ (0.18 mol·L⁻¹). The pH values of PAsp-Ag and PAH-Au were adjusted to 6.8 with 0.01 mol·L⁻¹ aqueous NaOH and 0.01 mol·L⁻¹ aqueous HCl. 100 mL PAsp-Ag (0.2 g·L⁻¹) was charged into the three-necked flask, then 15.38 g of SPB-Au latex (0.13 wt%) diluted with 100 mL of water was dropped slowly under vigorous stirring in 1 h. The obtained aqueous dispersion of Au/Ag bilayer SPB (SPB-Au-PAsp-Ag) was purified by ultrafiltration against water. Finally, SPB-Au-PAsp-Ag solution concentrated to 100 mL with pH 6.8 was dropped slowly into 100 mL PAH-Au (0.2 g·L⁻¹) under vigorous stirring for 1 h. The prepared dispersion of Au/Ag/Au trilayer SPB (APB-Au-PAsp-Ag-PAH-Au) was purified by ultrafiltration (Fig. 1)^[50, 51].

Evaluation of Catalytic Activity

The reduction of 4-nitrophenol to 4-aminophenol by NaBH₄ was employed to evaluate the catalytic activity of the composite nanoparticles^[52]. The pH value of 4-nitrophenol (0.1 mmol·L⁻¹) was adjusted to 10 with 0.01 mol·L⁻¹ aqueous NaOH. Then 1.2 mg solid NaBH₄ was mixed with 3 mL of 4-nitrophenol (0.1 mmol·L⁻¹) in the quartz cuvette. A given content of composite nanoparticles was added to the above solution and the reduction reaction was monitored using UV-Vis spectrum (UV-2550 spectrophotometer) by measuring the absorbance at a fixed wavelength of 400 nm.

RESULTS AND DISCUSSION

Synthesis and Characterization of SPB with Au/Ag Multilayers

The diameter in all stages of preparation of Au/Ag multilayers could be monitored by DLS^[53]. As seen in Fig. 2, the PS core was around 45 nm in radius, the thickness (*L*) of SPB layer could be determined as 79 nm. After Au-NPs were generated in PAEMH brush layer, the thickness of SPB decreased to 52 nm due to the reduction of counterion (AuCl₄⁻) concentration and osmotic pressure in SPB. After deposition of polyanions PAsp-Ag, the brush thickness dropped significantly to 11 nm. It reflects the fact that the PAsp may diffuse into SPB and neutralized the positive charges of SPB which leads to the clasp of brush layer.

However, after another layer of PAH-Au was deposited onto SPB-Au-PAsp-Ag, the thickness increased from 11 nm to 44 nm, and the size distribution became broad. The reason is probably due to the recovery of positive charge of PAEMH chains in SPB, which implies that the PAsp may move to the outer layer of brush to interact with PAH. But extra amount of PAH can form a bridge among SPB which leads to aggregation among SPB and thus increases the size distribution as observed by DLS.

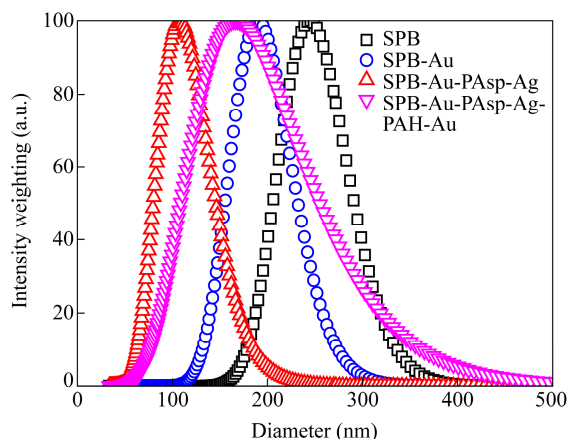


Fig. 2 Size and size distribution of SPB (quadrangle), SPB-Au (circle), SPB-Au-PAsp-Ag (triangle) and SPB-Au-PAsp-Ag-PAH-Au (inverted triangle) (pH = 5.6)

Morphology of SPB-Au, SPB-Au-PAsp-Ag and SPB-Au-PAsp-Ag-PAH-Au was observed by TEM (Fig. 3). In Fig. 3, SPB showed well-defined spherical structure and narrow size distribution. Au-NPs synthesized *via* the reduction of HAuCl_4 by NaBH_4 in SPB showed an average diameter of 1.4 nm (Fig. 3d). After adsorption of polyanions PAsp-Ag, the amount of metal nanoparticles increased as displayed in Fig. 3(b). The size distribution of both Au and Ag-NPs was shown in Fig. 3(e). The masses of Au-NPs and Ag-NPs were determined from ICP-AES of SPB-Au and SPB-Au-PAsp-Ag. Obviously, the size of Ag is larger than that of Au. Unfortunately, the brush layer and deposited polyelectrolyte layers were invisible by TEM^[54]. Further deposition of PAH-Au layer led to increased amount of metal particles (Fig. 3c).

As shown in Fig. 4, UV-Vis spectra of SPB and SPB-Au-PAsp-Ag demonstrated the specific peak of Ag-NPs at 427 nm and a probably hidden peak at around 540 nm which belongs to Au-NPs^[55, 56]. Cationic polyelectrolyte brushes had no adsorption peak around these two wavelengths. Due to the relatively small amount of Au-NPs as well as the overlap of peaks, the adsorption peak of Au-NPs was not obvious.

The amounts of Au and Ag nanoparticles in SPB were determined by ICP-AES after using nitric acid to eliminate organics. When Au-NPs were generated in cationic SPBs, the color of latex changed to dark amaranth (Fig. 1) and the content of Au-NPs was $46.9 \text{ mg} \cdot \text{g}^{-1}$. Coated with PAsp-Ag, the color changed to yellow (Fig. 1) and the contents of Au-NPs and Ag-NPs were 12.5 and $43.0 \text{ mg} \cdot \text{g}^{-1}$, respectively. During ultrafiltration, part of Au-NPs were deposited on the membrane which resulted in the loss of Au-NPs. Deposited with PAH-Au, the solution was changed from yellow to amaranth again (Fig. 1). The obtained nanocomposite SPB-Au-PAsp-Ag-PAH-Au contained $33 \text{ mg} \cdot \text{g}^{-1}$ Ag-NPs and $50 \text{ mg} \cdot \text{g}^{-1}$ Au-NPs, respectively. Compared to the contents of Au-NPs and Ag-NPs in SPB-Au-PAsp-Ag, the amount of Au increased because of deposition of PAH-Au, however, the content of Ag-NPs decreased due to the loss during purification.

Although TEM and UV-Vis spectrum couldn't directly confirm that anionic PAsp and cationic PAH were coated onto SPBs, zeta potential could determine the charge of system and thus judge whether polyelectrolyte layers with opposite charge successfully deposited on SPB. As seen in Fig. 5, zeta potential of SPB decreased after Au-NPs deposited onto PAEMH brushes.

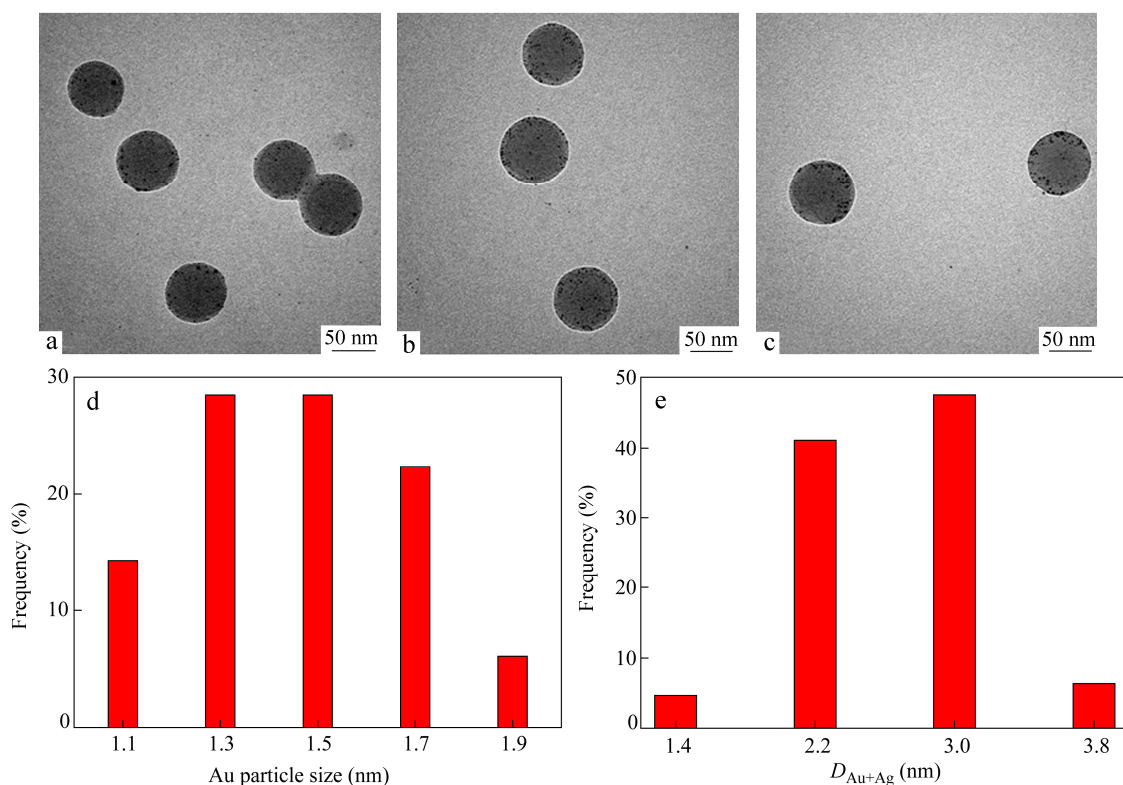


Fig. 3 TEM images of SPB-Au (a), SPB-Au-PAsp-Ag (b), and SPB-Au-PAsp-Ag-PAH-Au (c); Size distribution of the Au-NPs (d) in SPB-Au and both Au-NPs and Ag-NPs (e) in SPB-Au-PAsp-Ag

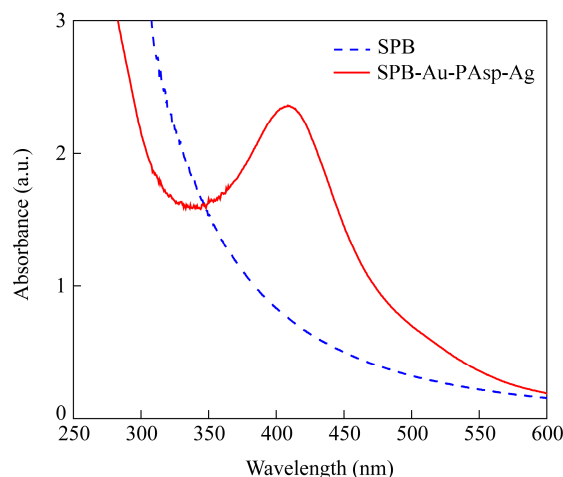


Fig. 4 UV-Vis spectra of cationic SPB and SPB-Au-PAsp-Ag

As the precursor of Au NPs, $AuCl_4^-$ ions were added, although most of them were *in situ* reduced to Au-NPs, the positive charges of PAEMH chains were neutralized partially. The SPB-Au still exhibited positive charge but reduced. However, zeta potential of SPB turned to negative and decreased from 29.8 mV to -42.1 mV after deposition of negatively charged PAsp-Ag. After positively charged PAH-Au deposited onto SPB-Au-PAsp-Ag, zeta potential changed to positive and increased from -42.1 mV to 41 mV. So polyanions PAsp-Ag and polycations PAH-Au alternately loaded on the SPBs-Au by layer-by-layer self-assembly technology successfully.

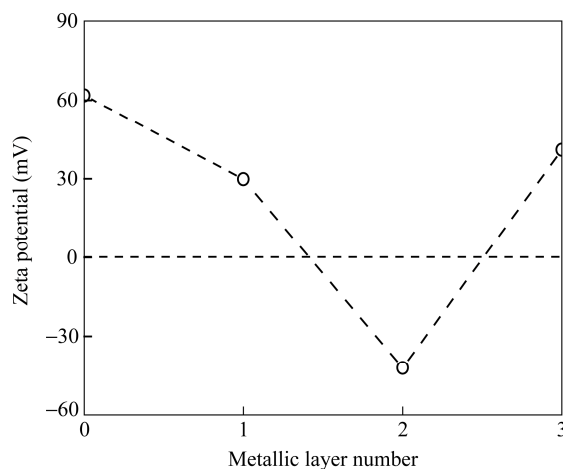


Fig. 5 Zeta potential of SPB, SPB-Au, SPB-Au-PAsp-Ag and SPB-Au-PAsp-Ag-PAH-Au (pH = 5.6)

Catalytic Activity of SPB with Au/Ag Multilayers

The reduction of 4-nitrophenol to 4-aminophenol by sodium borohydride was employed as model reaction to evaluate catalytic activity of SPB-Au and SPB-Au-PAsp-Ag. The initial concentrations of 4-nitrophenol and NaBH_4 were 0.1 and 10 $\text{mmol}\cdot\text{L}^{-1}$, respectively. Sodium borohydride was used in great excess compared to 4-nitrophenol so that the kinetic reaction could be treated as a pseudo-first order reaction^[42]. The reduction reaction of 4-nitrophenol could be monitored by UV-Vis spectroscopy. As shown in Fig. 6, after the addition of SPB-Au-PAsp-Ag, the absorbance of 4-nitrophenol at 400 nm decreased gradually, and a new peak at 290 nm appeared from the product 4-aminophenol.

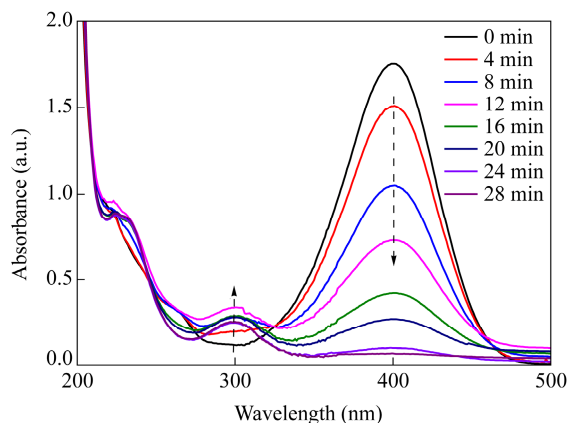


Fig. 6 Monitoring the reduction of 4-nitrophenol at 301 K under the catalysis of SPB-Au-PAsp-Ag by UV-Vis spectroscopy (The concentrations of Au-NPs and Ag-NPs were 0.50 and 0.33 $\text{mg}\cdot\text{L}^{-1}$, respectively.)

Catalytic activity of SPB-Au-PAsp-Ag was evaluated by consumption of 4-nitrophenol at 400 nm in a first order reaction. Extinction of UV-Vis absorption intensity at 400 nm during the reduction reaction could be seen in Figs. 7(a) and 7(b). No reaction occurred without SPB-Au-PAsp-Ag. An induction time existed before reaction started, which decreased with the increase of SPB-Au-PAsp-Ag concentration or temperature.

The reduction reaction could be treated as a pseudo-first-order reaction because NaBH_4 was in great excess whose concentration was almost constant during the reaction. Then the reaction rate was calculated as following:

$$-\frac{dc_t}{dt} = k_{\text{app}}c_t = k_1Sc_t$$

Here k_{app} is the apparent rate constant, c_t is the concentration of 4-nitrophenol at reaction time t , and k_1 is the rate constant normalized to S , the surface area of catalyst nanoparticles normalized to the unit volume of the system^[57].

As shown in Figs. 7(c) and 7(d), plot $\ln(c_t/c_0)$ against time for the reduction of 4-nitrophenol to 4-aminophenol by sodium borohydride at different Ag/Au nanoparticle concentrations and at different temperatures. The reaction rate constant was calculated from the slope of the kinetics curves in Fig. 7(c).

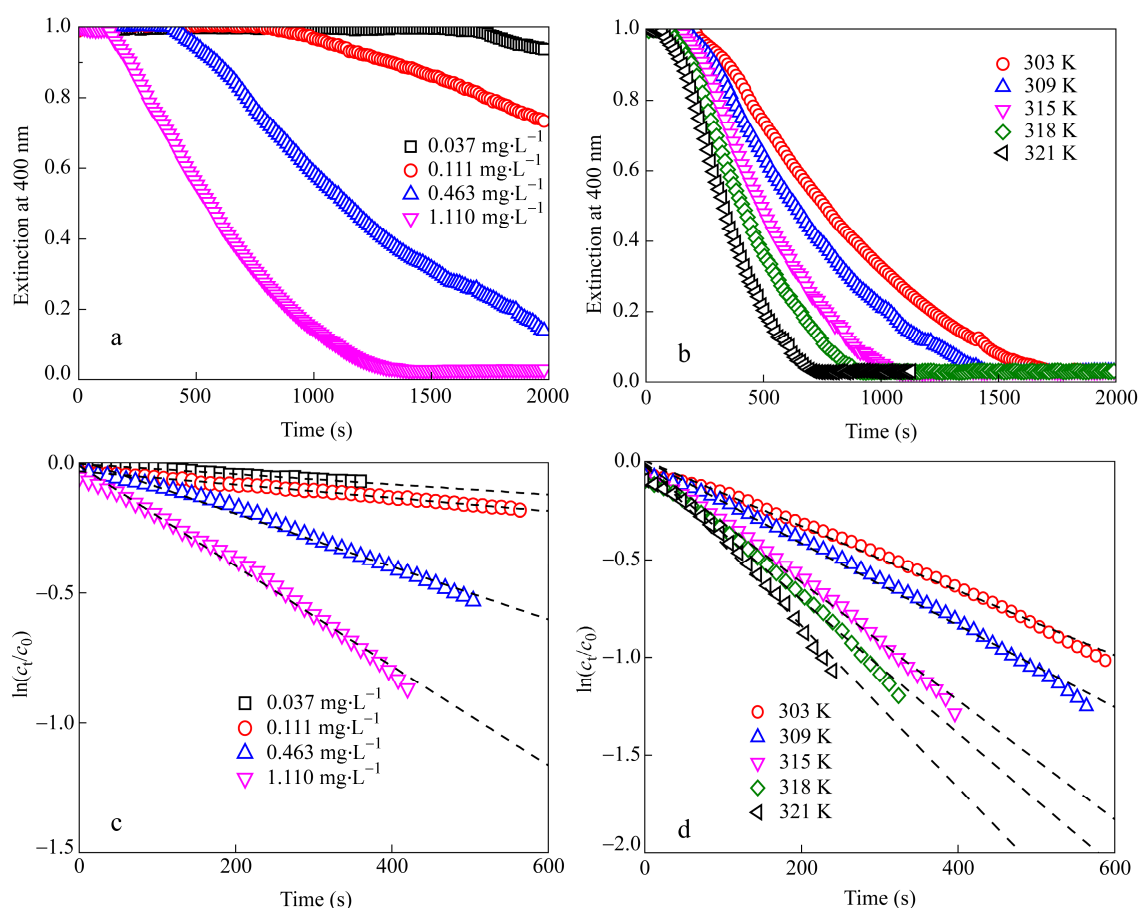


Fig. 7 (a) UV-Vis absorbance at 300 K at different concentrations of SPB-Au-PAsp-Ag for the reduction of 4-nitrophenol to 4-aminophenol by sodium borohydride; (b) Absorbance at various temperatures with the same concentration of SPB-Au-PAsp-Ag containing Au-NPs and Ag-NPs with concentrations of 1 and 0.66 mg·L⁻¹, respectively; (c) Plot of $\ln(c_t/c_0)$ against time at 300 K at different concentrations of SPB-Au-PAsp-Ag; (d) Plot of $\ln(c_t/c_0)$ against time at various temperatures with the same concentration of SPB-Au-PAsp-Ag

Figure 8 shows the linear correlation between k_{app} and both of the concentration of Ag/Au nanoparticles (Au and Ag NPs in Ag/Au nanoparticles with the average diameters of 1.4 and 3.0 nm respectively) and total surface area (S) which was estimated by ICP-AES, TEM, and assumption of spherical structure of metal nanoparticles. Upon increasing the total surface area (S) normalized to the unit volume of the system, the reduction reaction rate constant (k_{app}) increased linearly. Plotting $\ln k_{\text{app}}$ determined from the slope of kinetics reaction at time t versus $1000/T$ (Fig. 9), the apparent activation energy (E_a) was obtained to be 41.2 kJ·mol⁻¹ based on Arrhenius equation. According to the intercept of fitting line, the pre-exponential factor (A) can be calculated to be $2.1 \times 10^4 \text{ s}^{-1}$, and the entropy activation ΔS is obtained to be 82.6 J·(mol⁻¹·K⁻¹) based on the equation $\ln A = \Delta S/R$.

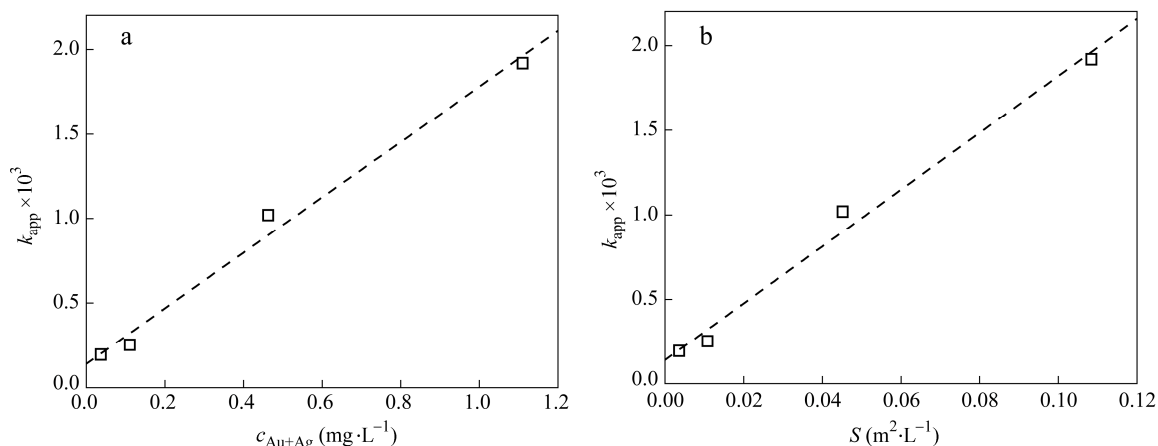


Fig. 8 The apparent rate constant (k_{app}) as a function of the concentration of Au/Ag nanoparticles (a) and surface area of Au/Ag nanoparticles (b) for the reduction of 4-nitrophenol to 4-aminophenol by sodium borohydride

Figure 10 displays the plot of the apparent rate constant against total surface area of different metal nanoparticles immobilized in SPB. As we expected, SPB-Au-PAsp-Ag with Au/Ag bilayer showed high catalytic activity close to that of SPB-Au, but much higher than that of SPB-Ag. More applications of SPB with Au/Ag multilayers in photo-catalysis and photoelectric systems are under way.

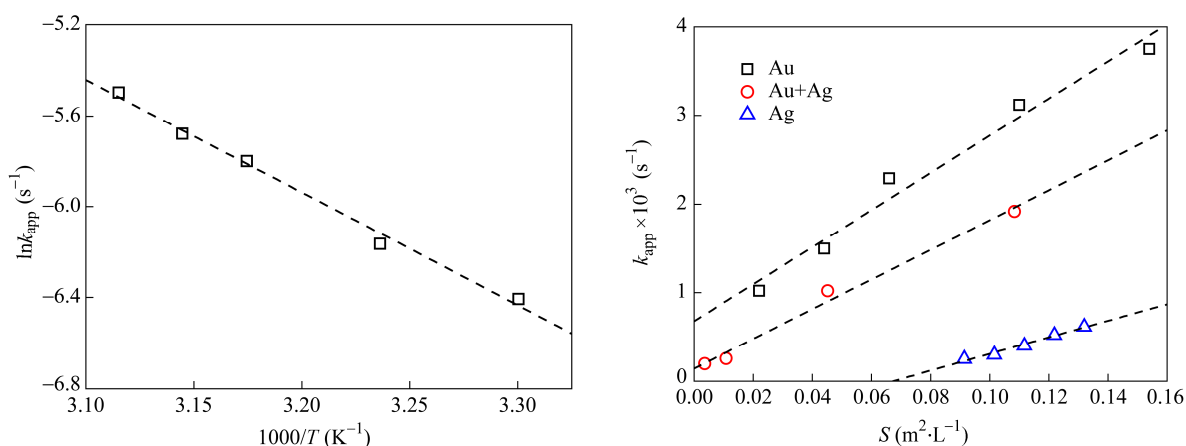


Fig. 9 Plot of $\ln k_{app}$ against $1000/T$ for the reduction of 4-nitrophenol

Fig. 10 The apparent rate constant (k_{app}) as a function of surface area of metal nanoparticles: (Square) Au nanoparticles immobilized in SPB (SPB-Au); (Triangle) Ag nanoparticles immobilized in SPB (SPB-Ag); (Sphere) SPB with Au/Ag nanoparticles bilayer (SPB-Au-PAsp-Ag)

CONCLUSIONS

Au/Ag multilayers on spherical polyelectrolyte brushes (SPBs) were prepared by layer-by-layer deposition technique. Using SPBs as nanoreactors, Au-NPs were generated by *in situ* reduction, and Ag-NPs and Au-NPs were immobilized on polyanion PAsp and polycation PAH by *in situ* reduction reaction, respectively. The negatively charged PAsp-Ag was deposited onto SPB-Au to obtain SPB-Au-PAsp-Ag. Further deposition of positively charged PAH-Au led to the trilayer of SPB-Au-PAsp-Ag-PAH-Au. The structure of multilayer composite nanoparticles were characterized by TEM, DLS, UV-Vis spectroscopy, ICP-AES and zeta potential. The obtained multilayer nanoparticles showed high catalytic activity for the reduction reaction of 4-nitrophenol to 4-aminophenol by $NaBH_4$ as observed by UV-Vis spectroscopy.

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