

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/40694888>

A Facile and Controllable Strategy to Synthesize Au-Ag Alloy Nanoparticles within Polyelectrolyte Multi layer Nanoreactors upon Thermal Reduction

ARTICLE *in* LANGMUIR · DECEMBER 2009

Impact Factor: 4.46 · DOI: 10.1021/la9040612 · Source: PubMed

CITATIONS

30

READS

260

5 AUTHORS, INCLUDING:



Li Shang

Karlsruhe Institute of Technology

63 PUBLICATIONS 2,998 CITATIONS

SEE PROFILE



Shaojun Guo

Brown University

128 PUBLICATIONS 9,042 CITATIONS

SEE PROFILE



Junfeng Zhai

Chinese Academy of Sciences

50 PUBLICATIONS 1,599 CITATIONS

SEE PROFILE



Shaojun Guo

Peking University

307 PUBLICATIONS 10,434 CITATIONS

SEE PROFILE

A Facile and Controllable Strategy to Synthesize Au–Ag Alloy Nanoparticles within Polyelectrolyte Multilayer Nanoreactors upon Thermal Reduction

Li Shang, Lihua Jin, Shaojun Guo, Junfeng Zhai, and Shaojun Dong*

State Key Laboratory of Electroanalytical Chemistry, Changchun Institute of Applied Chemistry, Graduate School of the Chinese Academy of Sciences, Chinese Academy of Sciences, Changchun, 130022, China

Received October 26, 2009. Revised Manuscript Received November 27, 2009

A new synthesis strategy has been developed for the preparation of bimetallic gold–silver (Au–Ag) alloy nanoparticles by the virtue of polyelectrolyte multilayer (PEM) nanoreactors. By controlling the assembly conditions, gold and silver ions can be effectively loaded onto the PEM composed of polyethylenimine (PEI) and poly(acrylic acid) (PAA) simultaneously. Upon further thermal treatment, Au–Ag alloy nanoparticles with sizes of ca. 3.8 nm formed in the PEM, which were characterized in detail by UV–vis absorption spectroscopy, transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), and energy-dispersive X-ray (EDX) analysis. Appearance of a single plasmon band in the visible region and lack of apparent core–shell structures in the TEM images confirm the formation of homogeneous Au–Ag alloy nanoparticles. In addition, the surface plasmon absorption band of the Au–Ag alloy nanoparticles shows linear blue-shift with increasing Ag content, which also supported the formation of alloy nanoparticles. Several key parameters of the present strategy have been investigated, which showed that pH of both the assembly solution and gold salt solution and the choice of polymers for constructing PEM, as well as the reduction approach, all played an important role in successfully synthesizing bimetallic Au–Ag nanoparticles. The formation mechanism of alloy nanoparticles has also been discussed based on the spectral evolution during the thermal reduction.

Introduction

Nanomaterials are at the leading edge of the rapidly developing field of nanotechnology.¹ The development of reliable experimental strategies for synthesizing nanomaterials with well-controlled composition, high monodispersity, and multifunction is one of the challenging themes in current nanotechnology.² Metal particles in the nanometer size regime show distinct size-dependent properties than those of bulk metals, which led to extensive investigations involving metal nanoparticles, especially gold/silver, as building blocks for nanoscale materials and devices in the last 2 decades.³ Recently, bimetallic nanoparticles with either alloyed or core–shell structures have gained significant interest due to new properties that arise from the combination of different compositions of metals on the nanoscale.⁴ In particular, the properties of these bimetallic particles can be facily tailored by the composition besides the usual size and shape manipulation. Their unique

properties have been utilized in electronic⁵ and optical⁶ as well as catalysis applications,⁷ which proves to be more effective than monometallic nanocrystals. For example, one recent study indicated that bimetallic Au–Ag nanoparticles displayed considerably more sensitivity in SERS analysis as biosensors than individual components.⁸

A number of synthetic strategies have been developed for the preparation of bimetallic nanoparticles, including wet chemical approach,⁹ photochemical method,¹⁰ electroless plating,¹¹ electrochemical synthesis,¹² and thermal reduction.¹³ However, most previous studies have been carried out in liquid mixtures or solutions.^{9–12} In many cases, in order to manipulate and process these nanoparticles for practical applications such as optoelectronics and sensor devices, they have to be embedded within polymer matrixes, or on solid substrates.^{6b,13a,14} Although bimetallic nanoparticles which are presynthesized in solution can be

*To whom correspondence should be addressed. Fax: +86-431-85689711. E-mail: dongsj@ciac.jl.cn.

(1) (a) Roduner, E. *Chem. Soc. Rev.* **2006**, *35*, 583. (b) Zhao, Y.; Fu, H.; Peng, A.; Ma, Y.; Xiao, D.; Yao, J. *Adv. Mater.* **2008**, *20*, 2859. (c) Service, R. F. *Science* **2008**, *321*, 1036. (d) Zhang, L. J.; Webster, T. J. *Nano Today* **2009**, *4*, 66.

(2) (a) Perro, A.; Reculosa, S.; Ravaine, S.; Bourgeat-Lami, E.; Duguet, E. *J. Mater. Chem.* **2005**, *15*, 3745. (b) Park, J.; Joo, J.; Kwon, S. G.; Jang, Y.; Hyeon, T. *Angew. Chem., Int. Ed.* **2007**, *46*, 4630. (c) Berti, L.; Burley, G. A. *Nat. Nanotechnol.* **2008**, *3*, 81.

(3) (a) Shenhar, R.; Rotello, V. M. *Acc. Chem. Res.* **2003**, *36*, 549. (b) Liao, H. W.; Nehl, C. L.; Hafner, J. H. *Nanomedicine* **2006**, *1*, 201. (c) Baron, R.; Willner, B.; Willner, I. *Chem. Commun.* **2007**, 323. (d) Lee, J. S.; Kim, Y. M.; Kwon, J. H.; Shin, H.; Sohn, B. H.; Lee, J. *Adv. Mater.* **2009**, *21*, 178.

(4) (a) Ferrando, R.; Jellinek, J.; Johnston, R. L. *Chem. Rev.* **2008**, *108*, 845.

(b) Major, K. J.; De, C.; Obare, S. O. *Plasmonics* **2009**, *4*, 61.

(5) Nishida, N.; Shiraishi, Y.; Kobayashi, S.; Toshima, N. *J. Phys. Chem. C* **2008**, *112*, 20284.

(6) (a) Hunyadi, S. E.; Murphy, C. J. *J. Mater. Chem.* **2006**, *16*, 3929. (b) Sharma, A. K.; Gupta, B. D. *Nanotechnology* **2006**, *17*, 124. (c) Zou, X.; Ying, E.; Dong, S. *J. Colloid Interface Sci.* **2007**, *306*, 307.

(7) (a) Li, X.; Li, B.; Cheng, M.; Du, Y.; Wang, X.; Yang, P. *J. Mol. Catal. A: Chem.* **2008**, *284*, 1. (b) Huang, J.; Vongehr, S.; Tang, S.; Lu, H.; Shen, J.; Meng, X. *Langmuir* **2009**, *25*, 11890–11896.

(8) Liu, Y. C.; Yu, C. C.; Hsu, T. C. *Electrochem. Commun.* **2007**, *9*, 639.

(9) (a) Link, S.; Wang, Z. L.; El-Sayed, M. A. *J. Phys. Chem. B* **1999**, *103*, 3529.

(b) Mallin, M. P.; Murphy, C. J. *Nano Lett.* **2002**, *2*, 1235. (c) Kariuki, N. N.; Luo, J.; Maye, M. M.; Hassan, S. A.; Menard, T.; Naslund, H. R.; Lin, Y.; Wang, C.; Engelhard, M. H.; Zhong, C. J. *Langmuir* **2004**, *20*, 11240. (d) Rodriguez-Gonzalez, B.; Burrows, A.; Watanabe, M.; Kiely, C. J.; Marzan, L. M. L. *J. Mater. Chem.* **2005**, *15*, 1755. (e) Raveendran, P.; Fua, J.; Wallen, S. L. *Green Chem.* **2006**, *8*, 34.

(10) (a) Peng, Z.; Spliethoff, B.; Tesche, B.; Walther, T.; Kleinermanns, K. *J. Phys. Chem. B* **2006**, *110*, 2549. (b) Gonzalez, C. M.; Liu, Y.; Scaiano, J. C. *J. Phys. Chem. C* **2009**, *113*, 11861.

(11) (a) Zhang, Q.; Xie, J.; Liang, J.; Lee, J. Y. *Adv. Funct. Mater.* **2009**, *19*, 1387. (b) Wang, C.; Peng, S.; Chan, R.; Sun, S. *Small* **2009**, *5*, 567.

(12) (a) Zhou, M.; Chen, S.; Zhao, S.; Ma, H. *Physica E* **2006**, *33*, 28. (b) Alqudami, A.; Annapoorni, S.; Shivaprasad, G. S. M. *J. Nanopart. Res.* **2008**, *10*, 1027.

(13) (a) Pal, S.; De, G. *Chem. Mater.* **2005**, *17*, 6161. (b) Prvulescu, V. I.; Prvulescu, V.; Endruschat, U.; Filoti, G.; Wagner, F. E.; Kubel, C.; Richards, R. *Chem.—Eur. J.* **2006**, *12*, 2343. (c) Som, T.; Karmakar, B. *Nano Res.* **2009**, *2*, 607.

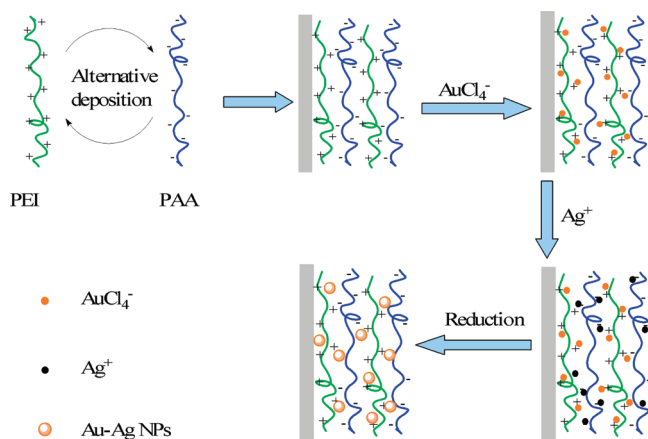


Figure 1. Schematic of the PEM buildup and subsequent reduction process.

further deposited on a support, their original structure, size, and morphology are hardly retained.^{14b} Moreover, it would be more favorable to combine the synthesis and immobilization of nanoparticles within one step, which suggests the importance and urgency to develop an in situ synthesis strategy of bimetallic nanoparticles within the films or other support.

Recently, polyelectrolyte multilayer (PEM) films, constructed through the electrostatic layer-by-layer self-assembly of oppositely charged polyelectrolytes, is of great interest as a facile means for creating functional nanomaterials.¹⁵ These PEM are promising nanoreactors which have been applied for synthesizing a broad range of nanomaterials, because the multilayer films can be facily tuned with desired composition and thickness, deposited onto different substrates with predetermined morphologies, and easily removed after nanomaterials synthesis.^{15a} Many groups including us have reported the successful synthesis of monometallic nanoparticles (such as Au, Ag, and Pt) within PEM,¹⁶ which demonstrated its great potential for synthesizing nanoparticles in a simple and controllable approach. Herein, we further extended the utilization of PEM to synthesize bimetallic alloy nanoparticles. To the best of our knowledge, this is the first report of preparing bimetallic nanoparticles by the virtue of PEM nanoreactors. As an example of this strategy, we will report the synthesis of Au–Ag alloy nanoparticles within the PEM composed of weak polyelectrolytes. The Au–Ag bimetallic system was chosen based on the following reasons. First, Au and Ag are known to have very similar lattice constants and are completely miscible in all proportions, forming homogeneous alloys in bulk phases.¹⁷ Second, Au–Ag nanoparticles show interesting optical properties and the plasmon absorption band depends on the alloy composition.^{9b,18} Third, Au–Ag alloy nanoparticles combine both merits of Au and Ag, which leads to their promising application

in the fields including optical devices, heterogeneous catalysis, and biomedical research.^{5,6,7b,14}

The principle of our strategy is schematically shown in Figure 1. In general, multilayer films via layer-by-layer deposition of polyethylenimine (PEI) and poly(acrylic acid) (PAA) are fabricated first. Then AuCl_4^- and Ag^+ are incorporated into the assembled PEM films sequentially via the interaction between the polyelectrolytes and the metal ions. Upon further thermal reduction, Au–Ag alloy nanoparticles are formed within PEM films. The present protocol is simple and controllable, which can be easily extended to synthesize other bimetallic or multicomponent nanoparticles.

Experimental Section

Reagents. Branched polyethylenimine (PEI, $M_w = 25000$), linear polyethylenimine (LPEI, $M_n = 423$), Poly(methacrylic acid) (PMAA, $M_w = 9500$), poly(diallyldimethylammonium chloride) (PDDA, $M_w = 20000$), and poly(sodium styrenesulfonate) (PSS, $M_w = 70000$) were purchased from Sigma-Aldrich. Poly(acrylic acid) (PAA, $M_w = 240000$) was bought from Alfa Aesar. Hydrogen tetrachloroaurate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$) and AgNO_3 were purchased from Beijing Chemical Co. (China). All reagents were of analytical reagent grade, and used as received. Indium–tin oxide (ITO) covered glass plates were purchased from Shenzhen Hivac Vacuum Photoelectronics Co. Ltd. (China, resistivity $< 15 \Omega$). The water used throughout this work was ultrapure water ($18 \text{ M}\Omega^{-1}$) produced by a Milli-Q system.

Preparation of Multilayer Films. Quartz and glass wafers were cleaned by immersing in slightly boiled piranha solution (7:3 mixture of 98% H_2SO_4 and 30% H_2O_2) for 40 min and then rinsed with copious amounts of water (*Caution: Piranha solution reacts violently with organic materials and should be handled carefully*). The multilayer films were then prepared by alternately immersing the substrate into PEI (5 mg/mL, pH 7.0) and PAA (5 mg/mL, pH 3.5) solutions for 10 min each until the desired number of layers was achieved. The films were carefully washed with water after each dipping step and then dried with nitrogen stream. For energy-dispersive X-ray (EDX) analysis, multilayer films were also prepared on the ITO surfaces. ITO was cleaned by sonicating sequentially for 20 min each in soapy water, 10% NaOH in ethanol, and distilled water. To facilitate the presentation, a PEM notation of (PEI x /PAA y) n is used in the following text, where x represents the assembly pH of PEI solution, y represents the assembly pH of PAA solution, and n is the bilayer numbers.

Adsorption of Metal Ions and In Situ Reduction. As-prepared PEI/PAA multilayer films were first immersed in 5 mM HAuCl_4 solution (pH 2.0) in the dark for 15 min, followed by thoroughly washing with distill water twice, and then dried with nitrogen stream. Gold ions-incorporated films were then immersed in 10 mM AgNO_3 solution (pH 6.5) in the dark for a certain time, followed by thoroughly washing with distill water twice, and then dried with nitrogen stream. The relative content of Ag in the film can be monitored by controlling the immersing time, and the molar ratio of Ag/Au was measured by energy-dispersive X-ray (EDX) analyzer. Finally, the freshly prepared Au–Ag ions-incorporated PEI/PAA multilayer films were heated at 473 K in air for 1 h. While heating at other temperatures can also result in the formation of nanoparticles, we chose 473 K in order to facilitate the spectroscopic monitoring of the reduction process in the experiments.

Characterization. UV–vis absorption spectra were recorded with a Cary 500 UV–vis–NIR spectrometer (Varian). X-ray photoelectron spectroscopy (XPS) measurements were carried out on an ESCALAB-MKII spectrometer (VG Co., U.K.) with $\text{Al K}\alpha$ X-ray radiation as the X-ray source for excitation. A XL30 ESEM scanning electron microscope (SEM) equipped with an energy-dispersive X-ray (EDX) analyzer was used to analyze the composition of the PEM, which was prepared on the ITO

(14) (a) Ong, B. H.; Yuan, X. C.; Tjin, S. C. *Fiber Integr. Opt.* **2007**, *26*, 229. (b) Liu, X.; Wang, A.; Yang, X.; Zhang, T.; Mou, C.; Su, D.; Li, J. *Chem. Mater.* **2009**, *21*, 410.

(15) (a) Shi, X.; Shen, M.; Mohwald, H. *Prog. Polym. Sci.* **2004**, *29*, 987. (b) Srivastava, S.; Kotov, N. A. *Acc. Chem. Res.* **2008**, *41*, 1831. (c) Wang, Y.; Angelatos, A. S.; Caruso, F. *Chem. Mater.* **2008**, *20*, 848.

(16) (a) Xiong, H.; Cheng, M.; Zhou, Z.; Zhang, X.; Shen, J. *Adv. Mater.* **1998**, *10*, 529. (b) Dai, J.; Bruening, M. L. *Nano Lett.* **2002**, *2*, 497. (c) Wang, T. C.; Rubner, M. F.; Cohen, R. E. *Langmuir* **2002**, *18*, 3370. (d) Chen, H.; Dong, S. *Talanta* **2007**, *71*, 1752. (e) Shang, L.; Wang, Y.; Huang, L.; Dong, S. *Langmuir* **2007**, *23*, 7738. (f) Chia, K. K.; Cohen, R. E.; Rubner, M. F. *Chem. Mater.* **2008**, *20*, 6756. (g) Kgo, H. Y.; Choi, W. S.; Park, J. H.; Kim, D. Y. *Macromol. Rapid Commun.* **2008**, *29*, 520. (h) Zan, X.; Su, Z. *Langmuir* **2009**, *25*, 12355–12360.

(17) Okamoto, H.; Massalski, T. B. *Phase Diagrams of Binary Gold Alloys*; ASM International: Metals Park, OH, 1987.

(18) Senapati, S.; Ahmad, A.; Khan, M. I.; Sastry, M.; Kumar, R. *Small* **2005**, *1*, 517.

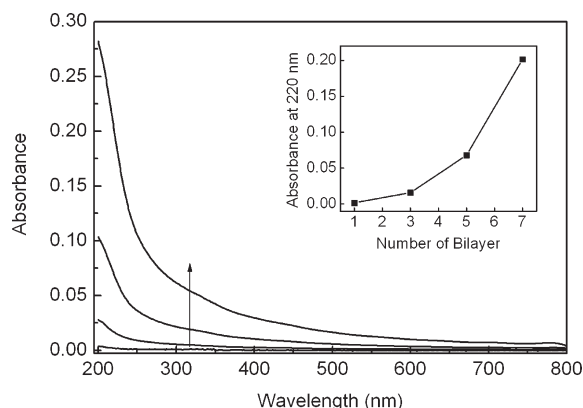


Figure 2. UV-vis absorption spectra of (PEI 7.0/PAA 3.5)_n multilayer film with $n = 1, 3, 5$, and 7 (from the bottom to top). Inset plots the absorbance of PEM at 220 nm as a function of n .

surfaces. TEM images were obtained with a JEM-2100F high-resolution transmission electron microscope operating at 200 kV. For TEM observation, a small piece of the PEM loaded with nanoparticles was peeled off from the substrate in hydrofluoric acid, floated in water, sonicated, and transferred to carbon-coated copper grids. The X-ray diffraction (XRD) analysis of the resulting PEM, fabricated on the glass surface, was carried out on a D/MAX 2500 V/PC X-ray diffractometer using Cu (40 kV, 30 mA) radiation.

Results

Buildup of PEI/PAA Multilayer Films. PEI and PAA were chosen as the functional assembling units in the present strategy to construct the PEM reactors for synthesizing bimetallic Au–Ag nanoparticles. When at suitable pH conditions, both PEI (pH 7.0) and PAA (pH 3.5) can be partially ionized,¹⁹ which provides the basis for the buildup of multilayer films via electrostatic interactions. Meanwhile, the remaining free amine groups of PEI and carboxylic acid groups of PAA are expected to provide the possible binding sites for metal ions. PEM of (PEI/PAA)_n were first assembled on the quartz surfaces to enable the spectroscopic monitoring of assembly process in the UV region, since both polymers possess weak absorption in the visible region. As shown in Figure 2, with increasing number of bilayers (n), the absorption of PEM in the UV region increased gradually, which indicated the successful buildup of PEI/PAA multilayer films. The subtle increase in the visible region should be caused by the scattering effect due to the increase of film thickness. It is interesting to note that the films exhibit exponentially growth in the present experimental conditions, as evidenced by the absorption results plotted in the inset of Figure 2. It has been well established that, depending on the assembly conditions, there are two growth modes of PEM: linearly and exponentially.²⁰ Many previous works have reported the similar exponentially growth of PEM, such as in the case of polystyrenesulfonate (PSS)/polyallylamine (PAH) multilayer system,²¹ and poly(diallyldimethylammonium chloride) (PDDA) and poly(acrylic acid) (PAA) multilayer system²² as well as PEI/PAA multilayer systems.²³ According to

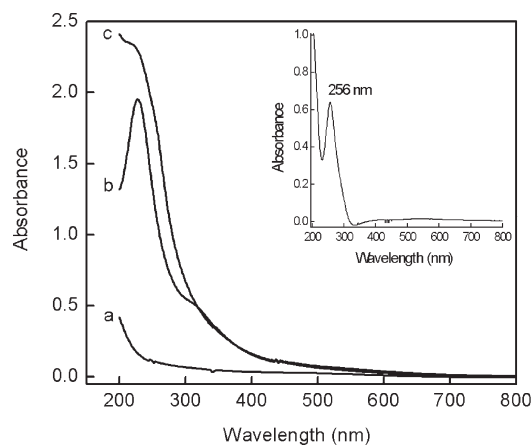


Figure 3. Absorption spectra of the (PEI 7.0/PAA 3.5)₇ PEM before (curve a) and after (curve b) immersing in 5 mM HAuCl₄ solution (pH 2.0) for 15 min, followed by immersing in 10 mM AgNO₃ solution for 15 min (curve c). The inset displays the difference spectrum obtained by subtracting curve b from curve c.

previous studies, such an exponentially growth of PEM in our case is believed to be caused either by the swelling of weak polyelectrolytes (PAA in our case) during rinsing steps which reduces the diffuse flux, or the formation of an energetic barrier at the film surface which prevents the free polycations (PEI in our case) from moving out of the film.²³

Adsorption of Metal Ions and In Situ Reduction. As mentioned above, the PEM films of (PEI/PAA)_n were assembled at the pH where free amine groups and carboxylic acid groups are available, thus we expect the as-prepared PEM films are capable of incorporating metal ions into the film. While amine groups are known to bind anionic gold complex ions,^{16f} carboxylic acid groups can serve as the binding sites for silver ions.^{16c} Figure 3 presents the spectral results of (PEI/PAA)₇ films after immersing in HAuCl₄ solution (pH 2.0), and AgNO₃ solution (pH 6.5), successively. As shown, a new absorption band at 227 nm appeared in the absorption spectrum of PEM accompanying with a weak band at around 315 nm after immersing in HAuCl₄ solution (curve b). In contrary, the original PEM possessed no observable absorption peak in this region (curve a), which indicated the successful loading of gold ions into the film.²⁴ Further immersing the gold ions-loaded films in AgNO₃ solution resulted in a distinct absorbance increase in the region below 300 nm (curve c). The inset in Figure 3 shows the result of difference spectrum, obtained by subtracting curve b from curve c, where a strong absorption band centered at 256 nm can be observed. This clearly indicated the incorporation of Ag⁺ into the PEM films.²⁵ Therefore, both gold and silver ions have been successfully introduced into PEM films of PEI/PAA via a very simple approach.

The PEM films loaded with gold and silver ions were then followed by thermal reduction. The formation of metal nanoparticles was visually observed from the change in color of the film from transparent (before reduction) to orange (after reduction). The intensity of color gradually increased with increasing the heating time. Also, absorption spectroscopy was employed to follow the growth of metal nanoparticles in the PEM films upon the thermal reduction. Figure 4 presents the evolution of the absorption spectra of Au/Ag ions-containing (PEI/PAA)₇ films

(19) Clark, S. L.; Hammond, P. T. *Langmuir* **2000**, *16*, 10206.

(20) Hoda, N.; Larson, R. G. *J. Phys. Chem. B* **2009**, *113*, 4232.

(21) Ruths, J.; Essler, F.; Decher, G.; Riegler, H. *Langmuir* **2000**, *16*, 8871.

(22) Srivastava, S.; Ball, V.; Podsiadlo, P.; Lee, J.; Ho, P.; Kotov, N. A. *J. Am. Chem. Soc.* **2008**, *130*, 3748.

(23) (a) Yoo, P. J.; Nam, K. T.; Qi, J.; Lee, S. K.; Park, J.; Belcher, A. M.; Hammond, P. T. *Nat. Mater.* **2006**, *5*, 234. (b) Ji, J.; Fu, J.; Shen, J. *Adv. Mater.* **2006**, *18*, 1441. (c) Podsiadlo, P.; Michel, M.; Lee, J.; Verploegen, E.; Kam, N. W. S.; Ball, V.; Lee, J.; Qi, Y.; Hart, A. J.; Hammond, P. T.; Kotov, N. A. *Nano Lett.* **2008**, *8*, 1762.

(24) Goia, D. V.; Matijevic, E. *Colloid. Surf. A* **1999**, *146*, 139.

(25) Wang, Q.; Yu, H.; Zhong, L.; Liu, J.; Sun, J.; Shen, J. *Chem. Mater.* **2006**, *18*, 1988.

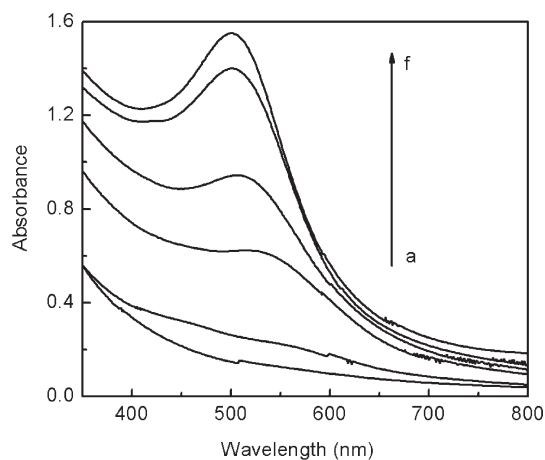


Figure 4. Spectra evolution of (PEI 7.0/PAA 3.5)₇ PEM after incorporating both gold and silver ions upon thermal reduction at 473 K for different times. The corresponding heating time: (a) 0 s; (b) 30 s; (c) 2 min; (d) 10 min; (e) 30 min; (f) 1 h.

after heating at 473 K for different times. As observed, after heating for 30 s, the absorbance in the range from 400 to 650 nm increased obviously (curve b). Two min later, an intense peak centered at 520 nm was observed (curve c). With extending the heating time, the absorbance of plasmon band increased gradually, accompanying with a blue shift of the maximum absorption. After heating for 1 h, the maximum absorption shifted to 501 nm (curve f), and further heating would result in no distinguishable spectral change, which suggested the finish of reduction process.

Noble metal nanoparticles (e.g., Au, Ag) are known to display strong surface plasmon resonance (SPR) in the visible region due to the collective oscillation of the free conduction electrons induced by an interacting electromagnetic field.²⁶ The fact that the absorption band of PEM after reduction showed only one plasmon band centered at 501 nm, which located between the Ag-SPR (ca. 420 nm) and Au-SPR (ca. 540 nm), indicated the formation of Au–Ag alloy nanoparticles.^{9b} The absence of two or more plasmon bands rules out the possibility for a mixture of monometallic Au nanoparticles and Ag nanoparticles or core–shell type bimetallic nanoparticles, as suggested in many previous studies.^{10a,13a,18} The single plasmon band also implies that the particles are spherical rather than rods or triangles, which are expected to have two or three bands, respectively.²⁷ Moreover, the plasmon band of Au–Ag nanoparticles was found to be dependent on the Ag/Au molar ratio. The Ag/Au ratio can be controlled by controlling the immersing time of gold ions-loaded PEM films in AgNO₃ solution. The corresponding absorption spectra of PEM after reduction are shown in Figure 5. It can be observed with increasing the Ag/Au ratio, the maximum absorption peak shifts from 544 nm (curve a, 0% Ag + 100% Au) to 501 nm (curve d, 60% Ag + 40% Au). Further analysis, as shown in the inset of Figure 5, resulted in a linear dependence of the peak position with the metal ratio in the film, which is generally indicative of homogeneous mixing of metal in the particles.^{4a,9b} This suggested that as the ratio of Ag/Au increased, Ag coreduces with Au to form Au–Ag alloy nanoparticles.

Characterization of Alloy Nanoparticles-Incorporated PEM. TEM was first utilized to analyze the size and morphology of the alloy nanoparticles formed within PEM. The typical TEM images are presented in Figure 6A, and the histogram of size

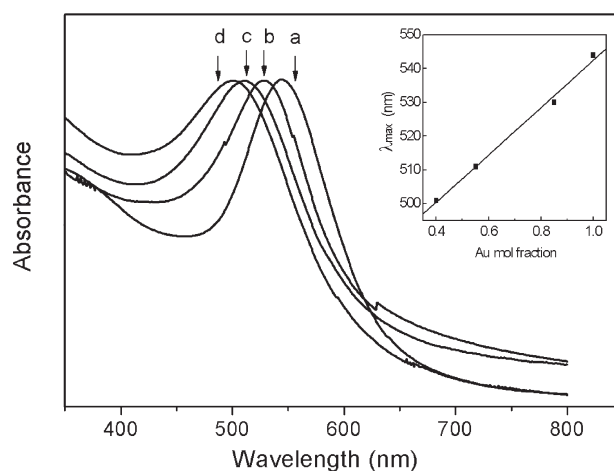


Figure 5. Absorption spectra of Au–Ag alloy nanoparticles with various ratios of Ag and Au: (a) 0% Ag + 100% Au; (b) 15% Ag + 85% Au; (c) 45% Ag + 55% Au; (d) 60% Ag + 40% Au. The inset shows the plots of the wavelength corresponding to the maximum absorbance as a function of Au molar fraction.

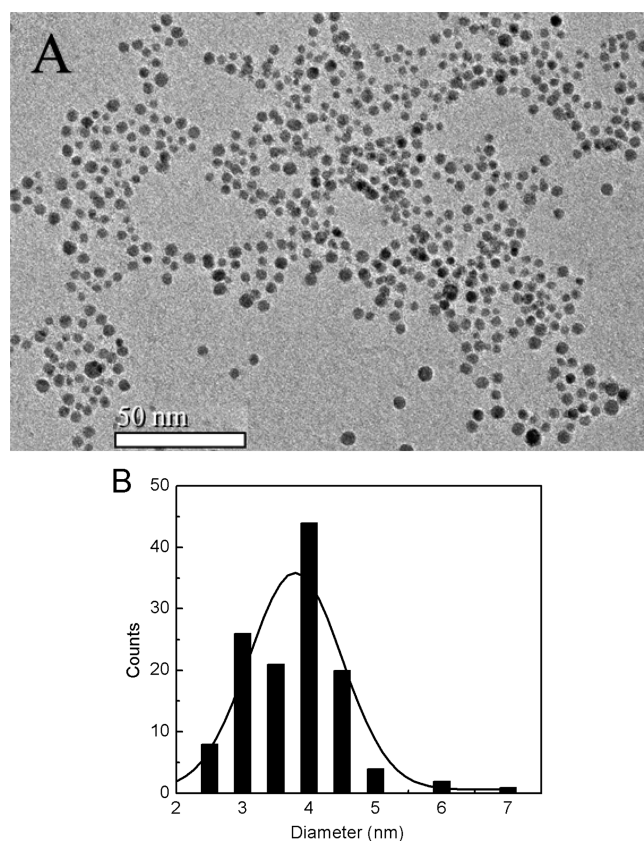


Figure 6. TEM images of (PEI 7.0/PAA 3.5)₇ PEM after thermal treatment at 473 K for 1 h (A), and the corresponding histograms of alloy nanoparticles (B).

distribution are shown in Figure 6B. Clearly, abundant alloy nanoparticles formed in the PEM films upon thermal reduction. The shape of the nanoparticles was spherical, which agreed with the spectroscopic results. Also, the diameter was measured to be 3.8 ± 0.8 nm, as judged from more than 100 individual particles. Previous works with core–shell bimetallic nanoparticles showed an obvious electron density banding with a dark Au core and a lighter Ag shell.^{9d,10b,13c} However, TEM analysis herein showed that most of nanoparticles (over 95% of observed particles)

(26) Noguez, C. *J. Phys. Chem. C* **2007**, *111*, 3806.

(27) Sun, Y.; Xia, Y. *Science* **2002**, *298*, 2176.

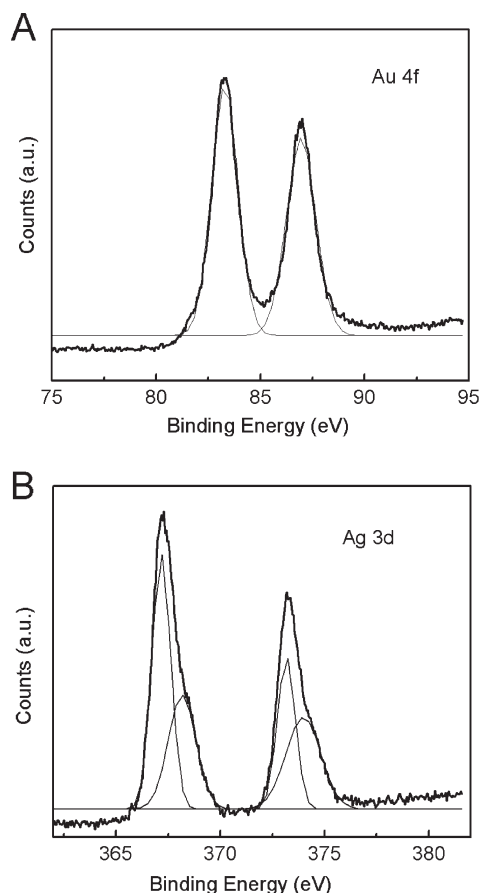


Figure 7. High-resolution XPS data of the (PEI 7.0/PAA 3.5)₇ PEM after thermal treatment at 473 K for 1 h: (A) Au 4f; (B) Ag 3d.

exhibited virtually uniform electron density within each other. This further supported the notion that the formed nanoparticles within the PEM films were mainly alloyed rather than core-shell.^{9b}

XPS spectra can provide us with further information regarding the chemical state of the alloy nanoparticles in the PEM films. Figure 7 presents high-resolution XPS spectra displaying the (A) Au 4f, and (B) Ag 3d spectral regions. As shown in Figure 7A, the Au 4f_{7/2} and Au 4f_{5/2} peaks occur at a binding energy (BE) of 83.7 and 87.1 eV, respectively, which are assigned to metallic Au.²⁸ Figure 7B shows the Ag 3d spectrum, where both Ag 3d_{5/2} and Ag 3d_{3/2} could be resolved into two peaks, respectively. According to previous literatures, while the Ag 3d_{5/2} (368.2 eV) and Ag 3d_{3/2} (374.0 eV) peaks could be assigned to metallic Ag, the Ag 3d_{5/2} (367.3 eV) and Ag 3d_{3/2} (373.2 eV) peaks could be assigned to oxidized Ag.²⁹ Considering XPS mainly reflects the information on the surface of samples, we believe the presence of partially oxidized silver in PEM may be due to the exposure to air during sample handling.^{14b}

Since Au and Ag have very similar lattice parameters of 0.409 and 0.408 nm,³⁰ it is very difficult to distinguish them by XRD pattern. However, the presence of metallic nanoparticles can be detected by XRD studies. Figure 8 shows XRD spectra of the alloy nanoparticles-containing PEM films (60% Ag + 40% Au), which showed a weak peak at $2\theta = 38.3^\circ$ due to Au/Ag (111)

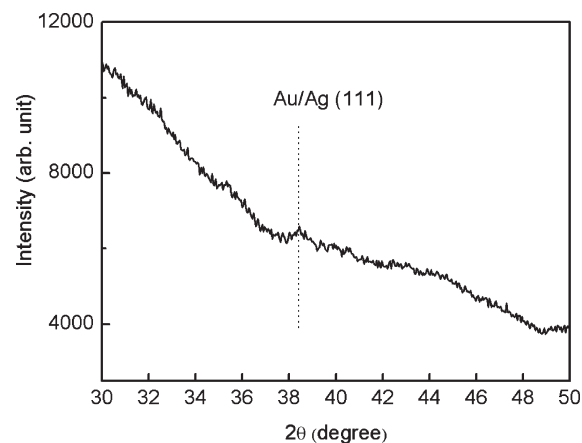


Figure 8. XRD spectrum of the (PEI 7.0/PAA 3.5)₇ PEM films containing Au–Ag alloy nanoparticles.

reflections.^{13a} We then attempted to use SEM-EDX to analyze the elemental distribution of Au/Ag on each individual nanoparticle, which was unsuccessful because the size of alloy nanoparticles was beyond the resolution of the instrument. However, SEM-EDX allows one to analyze the average Au/Ag ratio on randomly selected areas in the PEM films. The results suggested a relative standard deviation (RSD) of less than 10% for the obtained Au/Ag ratio from seven different areas in the film (data not shown). This suggested a homogeneous distribution of Au and Ag throughout the film, which accorded with our notion that the formed particles in the film were Au–Ag bimetallic nanoparticles rather than a mixture of monometallic nanoparticles.

Discussion

Key Factors of the Strategy. Although PEM has been widely applied as the nanoreactors for the preparation of metal or semiconductor nanoparticles in recent years, most of previous studies focused on the synthesis of monometallic nanoparticles in PEM films. One possible difficulty of synthesizing bimetallic nanoparticles within PEM is the lack of an effective strategy of loading both metal ions simultaneously into the film. Herein, we developed a facile approach to incorporate both gold and silver ions into PEM of (PEI/PAA)_n, which allowed further preparation of Au–Ag alloy nanoparticles upon thermal reduction.

It is noteworthy pH plays a critical role in the present strategy for the successful synthesis of bimetallic nanoparticles, since both polymers utilized in the PEM assembly are weak polyelectrolytes. First, pH of the assembly solution needs to be adjusted to charge the polyelectrolytes to ensure the successful buildup of PEM via electrostatic interactions. Meanwhile, under the assembly conditions, enough free amine groups of PEI and carboxylic groups of PAA should be remained in the resultant films so that they are capable of incorporating metal ions into the film. In our experiment, PEM was assembled at pH 7.0 and 3.5 for PEI and PAA, respectively, which proved to be very effective. To demonstrate the importance of pH, we also attempted to synthesize bimetallic nanoparticles in three representative PEM systems: (PEI 3.0/PAA 3.5)₇, (PEI 7.0/PAA 8.0)₇, and (PEI 3.0/PAA 8.0)₇. The results showed that in all three cases, the resultant PEM films displayed very weak capabilities of preparing bimetallic nanoparticles than the case of (PEI 7.0/PAA 3.5)₇.

In addition, pH of HAuCl₄ solution was also important for effective loading of gold ions into the PEM films, as suggested by Rubner and co-workers in one recent work where they reported

(28) Moulder, J. F.; Stickle, W. F.; Sobol, P. E.; Bomben, K. D. *Handbook of X-Ray Photoelectron Spectroscopy*; Perkin-Elmer: Eden Prairie, MN, 1992.

(29) Chimentao, R. J.; Kirm, I.; Medina, F.; Rodriguez, X.; Cesteros, Y.; Salagre, P.; Sueiras, J. E.; Fierro, J. L. G. *Appl. Surf. Sci.* **2005**, 252, 793.

(30) Kittel, C. *Introduction to Solid State Physics*; Wiley: New York, 1996.

the in situ synthesis of gold nanoparticles in amine-rich PEM nanoreactors.^{16f} For PEM composed of (PEI 7.0/PAA 3.5)₇, when immersing at HAuCl₄ solution with pH < 2.0, for example at pH 1.8, the strong acidic condition would convert too many carboxylate groups into protonated carboxylic acid groups, thereby breaking the COO⁻-NH₃⁺ electrostatic linkages formed during PEM assembly. As a result, the structure of PEM films would be broken, and large porosity can be visually observed in the film. On the other hand, when immersing PEM at HAuCl₄ solution with pH > 2.0, the binding ability of PEM toward gold complex ions would decrease with increasing pH, because less amine groups that are capable of binding gold ions were available (seen in Figure S1 in the Supporting Information).^{16f} Therefore, we adopted a HAuCl₄ solution with pH 2.0 for loading gold ions into the film.

To probe other factors responsible for the synthesis of bimetallic Au–Ag alloy nanoparticles in the present approach, we also conducted other control experiments. First, we performed the same preparation by changing either or both PEI/PAA with other common polyelectrolytes such as PDDA, PSS, LPEI and PMAA. The results showed that PEM composed of (PDDA/PSS)_n, (PDDA/PAA)_n, or (PEI/PSS)_n all failed in synthesizing bimetallic nanoparticles. In contrary, PEM composed of (LPEI/PAA)_n, (PEI/PMAA)_n, or (LPEI/PMAA)_n could obtain similar alloy nanoparticles at suitable assembly conditions. These results clearly suggested the importance of coexisting amine groups and carboxylic groups in the PEM films, which accorded with our notion that both groups were necessary for adsorbing metal ions. Second, we attempted to reduce metal ions by other approaches rather than thermal treatment. While reduction by immersing metal ions-containing PEM films in the NaBH₄ (0.01 M) could proceed very fast within 10 min and form alloy nanoparticles, the resultant film was found to exhibit poor stability, which was possibly caused by the harsh reaction conditions. Photoreduction by radiating the film with a UV lamp at 365 nm could also result in the production of bimetallic nanoparticles, but the reaction proceeded too slowly (longer than 24 h). Therefore, thermal reduction was adopted in our experiment.

Mechanism for Alloy Formation. We then try to probe the possible formation mechanism of alloy nanoparticles in our system. Since gold and silver have similar lattice constants and can form homogeneous alloys in bulk phases, the formation of alloy nanoparticles was actually not unexpected for PEM incorporated with both Au and Ag ions in the films. On the basis of the evolution of absorption spectra of PEM upon thermal reduction as shown in Figure 4, we speculated the possible alloy formation processes as following. When the metal ions-loaded films were subjected to heating at 473 K, gold ions in the film will first be reduced to form small clusters due to its redox advantage over silver.^{6a,27} During this process, the plasmon absorption will be dominated by the SPR of gold. Further heating will cause the nearby Ag ions being coreduced along with gold ions on the surface of small gold clusters, and the plasmon band will blue-shift correspondingly due to the doping of Ag within the particles. With extending the heating time, alloy nanoparticles will grow gradually until they reach a size with a surface area that can be stabilized by the surrounding polymers. Moreover, previous studies indicated that high concentration of metal ions within the films could also favor alloying of metal nanoparticles.³¹

Although the detailed growth mechanism of alloy nanoparticle is not well understood at present, the formation of alloy nanoparticles

can be well supported by our experimental results. The spectral evidence came from the appearance of a single plasmon band in the visible range as shown in Figure 4 and the linear blue-shift in the plasmon peak with the increase in Ag/Au ratio (Figure 5). Also the lack of apparent core–shell structures in the TEM images (Figure 6) and homogeneous Au/Ag distribution throughout the film by EDX analysis further supported the formation of gold–silver alloy nanoparticles.

Merits of the Strategy. Compared with previous methods for synthesizing Au–Ag alloy nanoparticles, the present strategy by utilizing PEM nanoreactors possesses several distinct advantages:

(a) The structure and composition of PEM are variable and tunable via the choice of polyelectrolytes, which allows the facile introduction of additional function/property into the films accompanying with the formation of alloy nanoparticles.^{15a} For example, the choice of polymers with electroactive groups is expected to endow the resultant nanostructured films with electroactive property. Moreover, the strategy of PEM nanoreactors is favorable for synthesizing ultrasmall nanoparticles due to the restricting effect of surrounding polyelectrolytes to the growth of nanoparticles, such as Au–Ag alloy particles with sizes of ca. 3.8 nm in our case. Previous studies indicated that these small-sized metal nanoparticles showed particularly high reactivities, which was favorable for their catalytic applications.^{14b}

(b) The concentration, composition, and optical properties of the nanoparticles in the film could be readily tuned by manipulating the multilayer processing conditions. As shown in Figure 5, while the Ag/Au ratio can be controlled by controlling the immersing time in AgNO₃, the optical properties of the nanostructured films can be changed correspondingly. This suggested the feasibility of modulating the optical properties of the film. In addition, the concentration and size of metal nanoparticles in the films can also be facilely controlled by tuning the assembly conditions such as metal salt concentration, pH, and bilayer number. As an example, absorption spectra of PEM with different bilayer numbers (*n* = 1–7) after loading metal ions and subjected to thermal reduction were investigated (seen in Figure S2 in the Supporting Information). The results showed that the absorbance of formed alloy nanoparticles increased gradually and exponentially with increasing the bilayer numbers, which accorded well with the result in Figure 2 that the (PEI/PAA)_n film grows in an exponential mode. The results herein also suggested the feasibility of tuning the density of nanoparticles in the film in a facile approach.

(c) The resultant alloy nanoparticles-embedded films were found to exhibit good chemical stability, as evidenced by negligible spectral changes after aging the film in the air for over 1 month. We attributed this stability to the following two reasons. On one hand, since the alloy nanoparticles were in situ formed within multilayer films, due to the association of metal with the component of the film, movement of the formed nanoparticles was restricted and hence improved the stability of the resulting film.^{16e} On the other hand, previous studies indicated that reduction of metal ions by heating could result in the cross-linking of PEI/PAA systems via heat-induced amide formation from carboxylate-ammonium complexes,^{16b} which could also strengthen the film.

(d) Finally, the present strategy can be extended to prepare other bimetallic or multicomponent nanoparticles within PEM nanoreactors, provided the assembling polyelectrolytes possess necessary binding groups for the respective metal ions. In addition, this method can be applicable to synthesize bimetallic nanoparticles on either planar or curve surfaces, for example,

(31) Roy, R. K.; Mandal, S. K.; Pal, A. K. *Eur. Phys. J. B* **2003**, *33*, 109.

on the surface of colloid particles, which can further extend the application of formed nanoparticles.

Conclusions

In summary, we have reported a general strategy of synthesizing small-sized, composition-controllable Au–Ag alloy nanoparticles within PEM nanoreactors. By controlling assembly conditions, gold and silver ions can be effectively incorporated into PEM of (PEI/PAA)_{*n*}. Upon further thermal reduction, alloy nanoparticles can be obtained, which is confirmed by both absorption spectroscopy and TEM results. The concentration and composition of nanoparticles, the component and optical properties of the film can all be readily tuned by controlling the experimental conditions. This work not only presents a new strategy of preparing Au–Ag alloy nanoparticles, but also extends the applicability of PEM nanoreactors from synthesizing monometallic nanoparticles to bimetallic nanoparticles.

Moreover, such a strategy can be extended for synthesizing a wide variety of other composite nanoparticles other than the present model system (Au–Ag), which is expected to be of great importance for both synthesis and further application of these attractive nanomaterials.

Acknowledgment. This work was supported by the National Natural Science Foundation of China (No. 20820102037) and the Special Funds for Major State Basic Research Projects of China (973 Project 3010CB933603).

Supporting Information Available: Figures showing the absorption spectra of PEM film after immersing in the HAuCl₄ solution at different pH and absorption spectra of as-prepared nanoparticles in PEM film with different bilayer numbers. This material is available free of charge via the Internet at <http://pubs.acs.org>.