Kinetically Controlled Pt Deposition onto Self-Assembled Au Colloids: Preparation of Au (Core)−Pt (Shell) Nanoparticle Assemblies

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Received September 12, 2003. Revised Manuscript Received June 8, 2004

Assemblies of Au (core)−Pt (shell) nanoparticles were prepared by chemical deposition of Pt metal onto colloidal Au particles that self-assembled onto substrates, since $PtCl_6^{2-}$ may be reduced to Pt(0) by the mild reducing agent NH_2OH in the presence of gold nanoparticles. It is shown that the Pt deposition is isotropic and uniform on each particle via the combination of scanning electron microscopy and atomic force microscopy analysis. And the linear dependence of the particle size on the deposition time suggests that the deposition procedure is kinetically controlled. What is more, the kinetics of this Pt deposition onto Au nanoparticles is analyzed, which further reveals that the growth rate of the core−shell nanoparticles depends on the concentration of $PtCl_6^{2-}$, the molar mass and density of Pt metal, and a constant related to the surface reaction.

Introduction

Core−shell bimetallic nanoparticles attract steadily increasing interest because the addition of the second metal provides a method to control chemical or physical properties of the nanoparticle.[1] Now, there have been a variety of such nanoparticles showing fascinating properties and potential application in a broad range of areas, including electronics, biosensors, optics, catalysis, and so on.[2] However, these nanoparticles are often synthesized and exist as a form of colloidal dispersion or matrix materials, and it poses a challenge for their further development into nanodevices. In most cases, future technological applications require the availability of organizing these core−shell nanoparticles into ordered structures on the surface of appropriate substrates.

Among present techniques for the fabrication of nanostructures, chemical self-assembly is in principle considered to be the most desirable one, since it provides the possibility to economically fabricate components of sub-30 nm size into macroscale structures.[3] Although self-assemblies of monometallic nanoparticles are ex-

tensively reported, core−shell bimetallic nanoparticles have received little attention as building blocks so far.[4] Recently, several other groups and we tried to prepare the assemblies of core−shell nanoparticles through depositing other metals onto preformed self-assemblies of Au nanoparticles.[5] The reason for the selection of Au nanoparticle assemblies lies in the ability to prepare monodispersed Au nanoparticles in a wide diameter range (1.5−100 nm), along with the ease to self-assemble Au nanoparticles uniformly onto appropriate substrates.[6] It is expected that the resulting assemblies of core−shell nanoparticles should also possess the favorable morphologic feature of Au nanoparticle assemblies, while the properties could be tailored by the deposited materials.

Herein, we report the preparation of assemblies of Au (core)−Pt (shell) nanoparticles through chemical deposition of Pt metal onto self-assembled Au nanoparticles. The principle of this method lies in the seed growth of metal nanoparticles, which in the present experiment is the reduction of $PtCl_6^{2-}$ in the presence of gold nanoparticles by NH_2OH, a well-known mild reducing agent.[7] As a matter of fact, Schmid et al. previously

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(1) (a) Caruso, F. *Adv. Mater.* **2001**, *13*, 11. (b) Schmid, G. *Chem. Rev.* **1992**, *92*, 1709. (c) Aiken, J. D., III; Finke, R. G. *J. Mol. Catal. A* **1999**, *145*, 1. (d) Henglein, A. *J. Phys. Chem.* **1993**, *97*, 5457.
(2) (a) Aliev, F. G.; Correa-Duarte, M. A.; Mamedov, A.; Ostrander, J. W.; Giersig, M.; Liz-Marzun, L. M.; Kotov, N. A. *Adv. Mater.* **1999**, *11*, 1006. (b) Kamat, P. V.; Flumiani, M.; Dawson, A. *Colloids Surf., A: Physicochem. Eng. Aspects* **2002**, *202*, 269. (c) Lu, P.; Teranishi, T.; Asakura, K.; Miyake, M.; Toshima, N. *J. Phys. Chem. B* **1999**, *103*, 9673. (d) Katsikas, L.; Gutierrez, M.; Henglein, A. *J. Phys. Chem.* **1996**, *100*, 11203.
(3) Fendler, J. H. *Chem. Mater.* **2001**, *13*, 31962.
(4) (a) Colvin, V. L.; Goldstein, A. N.; Alivisatos, A. P. *J. Am. Chem. Soc.* **1992**, *114*, 5221. (b) Ogewa, S.; Hu, K.; Fan, R. F. F.; Bard, A. J. *J. Phys. Chem.* **1997**, *101*, 5707. (c) Freeman, R. G.; Grabar, K. C.; Allison, K. J.; Bright, R. M.; Davis, J. A.; Guthrie, A. P.; Hommer, M. B.; Jackson, M. A.; Smith, P. C.; Walter, D. G.; Natan, M. J. *Science* **1995**, *267*, 1629. (d) Hutter, E.; Fendler, J. H.; Roy, D. *J. Phys. Chem. B* **2001**, *105*, 11159.
(5) (a) Cao, L. Y.; Diao, P.; Liu, Z. F. *Acta Phys.-Chim. Sin.* **2002**, *18*, 1062. (b) Cao, L. Y.; Diao, P.; Tao, Z.; Liu, Z. F. *J. Phys. Chem. B* **2004**, *108*, 3535. (c) Bright, R. M.; Walter, D. G.; Musick, M. D.; Jackson, M. A.; Allison, K. J.; Natan, M. J. *Langmuir* **1996**, *12*, 810. (d) Mrozek, M. F.; Xie, Y.; Weaver, M. J. *Anal. Chem.* **2001**, *73*, 5953.
(6) (a) Cao, L. Y.; Zhu, T.; Liu, Z. F. *Acta Phys.-Chim. Sin.* **2004**, *20*, 211. (b) Grabar, K. C.; Freeman, R. G.; Hommer, M. B.; Natan, M. J. *Anal. Chem.* **1995**, *67*, 735.
(7) (a) Schmid, G.; Lehnert, A.; Malm, J.; Bovin, J. *Angew. Chem., Int. Ed. Engl.* **1991**, *7*, 30. (b) Schmid, G.; West, H.; Mehles, H.; Lehnert, A. *Inorg. Chem.* **1997**, *36*, 891.

reported the preparation of bimetallic nanoparticles with an 18 nm Au core surrounded by a 5 nm Pt shell through reducing $PtCl_6^{2-}$ by NH_2OH in the presence of gold sol.[7] Some other techniques have also been explored to synthesize the core−shell bimetallic nanoparticles, such as radiolytic reduction and photolytic reduction.[8] But all of these resulting core−shell nanoparticles were synthesized in colloidal dispersion or matrix materials, and there has been little kinetic investigation of the metal deposition.[9] In the present experiment, the Au nanoparticles were immobilized onto silanized silicon wafers before the $PtCl_6^{2-}$ reduction by NH_2OH, which led to the formation of assemblies of Au (core)−Pt (shell) nanoparticles. In addition, they may serve as models for studying the growth kinetics of Au (core)−Pt (shell) nanoparticles, which is shown to be kinetically controlled.

Experimental Section

Chemicals. $HAuCl_4·3H_2O$, *p*-aminothiophenol, and (3-aminopropyl)trimethoxysilane were obtained from Aldrich. H_2PtCl_6, $NH_2OH·HCl$, and other reagents were analytical grade. All chemicals were used as received. Au colloids with $13 ± 1.0$ nm diameter were prepared by the Frens method[10] and characterized on a JEM-200CX (JEOL, Japan) transition electron microscope.

Preparation of Au Nanoparticle Self-Assemblies. Silicon wafers (10 mm × 10 mm) were sonicated successively in toluene, acetone, ethanol, and water. Then the wafers were cleaned in a bath of 4:1 (by volume) H_2SO_4/H_2O_2 (piranha solution) at 85 °C for 5 min. After being rinsed successively in water and ethanol, the wafers were immersed in 0.1% (by volume) (3-aminopropyl)trimethoxysilane ethanol solution for 1 h. Then they were removed, rinsed with ethanol thoroughly, dried in a stream of high-purity nitrogen gas, and baked at 120 °C for 30 min. Such silanized wafers were immersed in as-prepared Au colloids for several minutes, and colloidal Au particles would self-assemble onto these substrates.

Chemical Deposition of Pt. The substrates with self-assembled Au nanoparticles were immersed into a mixture of 1000 mL of 0.01 wt % H_2PtCl_6 aqueous solution and 9 mL of 1 wt % NH_2OH solution at 60 °C. After reaction for different times varying from 45 min to 48 h, the substrates were removed and rinsed with water.

Raman Spectrum Measurement. The nanoparticle assemblies (with or without Pt deposition) were immersed in 0.1 vol % *p*-aminothiophenol/ethanol solution for 24 h. After being removed, they were rinsed with ethanol and dried in a stream of high-purity nitrogen gas. Raman spectra of these samples in the region of 800−1800 cm^{-1} were collected via the method of backscattering.

Instruments. An LEO-1530 (Germany) scanning electron microscope and Nanoscope (DI, U.S.) atomic force microscope operating in tapping mode were used to characterize the morphology of nanoparticle assemblies. X-ray photoelectron spectroscopy (XPS) spectra were collected on an ESCALab 220i-XL (VG, U.K.). A Renishaw System 1000 spectrometer (Renishaw, U.K.) with a laser wavelength of 632.8 nm was used to collect Raman spectra.
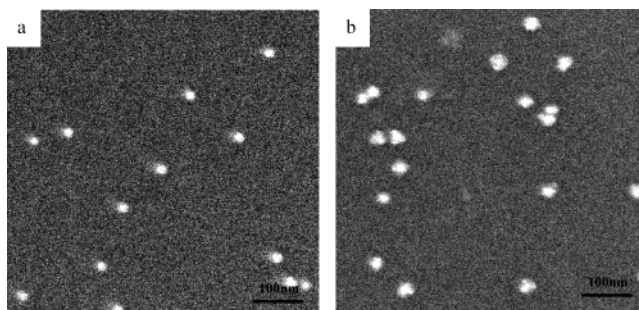
(8) (a) Henglein, A. *J. Phys. Chem. B* **2000**, *104*, 2201. (b) Liz-marzan, L. M.; Philips, A. P. *J. Phys. Chem.* **1995**, *99*, 15120. (c) Remita, S.; Picq, J.; Khatouri, J.; Mostafavi, M. *Radiat. Phys. Chem.* **1999**, *54*, 463. (d) Harada, M.; Asakura, K.; Toshima, N. *J. Phys. Chem.* **1993**, *97*, 5103. (e) Damle, C.; Biswas, K.; Sastry, M. *Langmuir* **2001**, *17*, 7156. (f) Heng Yu, H.; Gibbons, P. C.; Kelton, K. F.; Buhro, W. E. *J. Am. Chem. Soc.* **1997**, *119*, 10382.

(9) (a)Baletto, F.; Mottet, C.; Ferrando, R. *Phys. Rev. Lett.* **2003**, *90*, 135504. (b) Baletto, F.; Mottet, C.; Ferrando, R. *Phys. Rev. B* **2002**, *66*, 155420.

(10) Frens, G. *Nat. Phys. Sci.* **1973**, *241*, 20.

Figure 1. SEM images of assemblies of Au nanoparticles (a) before and (b) after being immersed into the H_2PtCl_6 and NH_2OH solution for 9 h.

Results and Discussion

Chemical Pt Deposition onto Self-Assembled Au Nanoparticles. It is well-reported that $PtCl_6^{2-}$ could be reduced to Pt(0) by NH_2OH on the surface of colloidal Au particles.[7] Thus, if self-assembled Au nanoparticles are immersed into the H_2PtCl_6 and NH_2OH solution, we should expect the formation of assemblies of Au (core)−Pt (shell) nanoparticles due to the deposition of Pt metal onto the gold surface. Figure 1 shows typical scanning electron microscopy (SEM) images of the original self-assembled Au nanoparticles (Figure 1a) and the counterparts which were immersed into the NH_2OH and H_2PtCl_6 solution for 9 h (Figure 1b). From this figure, we observe that the sizes of the nanoparticles exposed to the immersion (Figure 1b, ca. 28 nm) are obviously larger than those of the original Au nanoparticles (Figure 1a, ca. 13 nm). This result indicates that the deposition of Pt metal happened during the course of the immersion. However, judging from detailed analysis of numerous different SEM images, there is no obvious difference between the assembly densities of particles for the two nanoparticle assemblies. Therefore, the appearance of larger nanoparticles after this immersion (Figure 1b) is due to the Pt deposition onto preformed Au nanoparticles, rather than the formation of separate Pt particles. In fact, it has already been reported that NH_2OH is a mild reducing agent and only in the presence of seed particles can it reduce such metal ions as $AuCl_4^-$.[11]

Colloidal Au particles are well-known as ideal surface-enhanced Raman scattering (SERS) active substrates; that is, the intensity of the Raman signal from molecules adsorbed onto them can be enhanced greatly,[4c] which is not the case for Pt nanoparticles.[12] So, it is possible to characterize the Pt deposition by monitoring the Raman spectra of probe molecules. In the present experiment, *p*-aminothiophenol was used as the probe molecule, because it could absorb onto the surface of Au and Pt metals in the form of a monolayer,[13] and its Raman spectrum was investigated extensively.[14] The Raman spectra of the original self-assembled Au nanoparticles and the counterpart after the above-mentioned

(11) (a) Turkevich, J.; Stevesson, P. C.; Hiller, J. *J. Discuss. Faraday Soc.* **1951**, *11*, 55. (b) Brown, K. R.; Natan, M. J. *Langmuir* **1998**, *14*, 726.

(12) Tian, Z. Q.; Bin Ren, B.; Wu, D. Y. *J. Phys. Chem.* **2002**, *106*, 9463.

(13) Schreiber, F. *Prog. Surf. Sci.* **2000**, *65*, 151.

(14) (a) Joo, T. H.; Kim, M. S.; Kim, K. *J. Raman Spectrosc.* **1987**, *18*, 57. (b) Osama, M.; Matsuda, N.; Yoshil, K.; Uchida, I. *J. Phys. Chem.* **1994**, *98*, 12702.
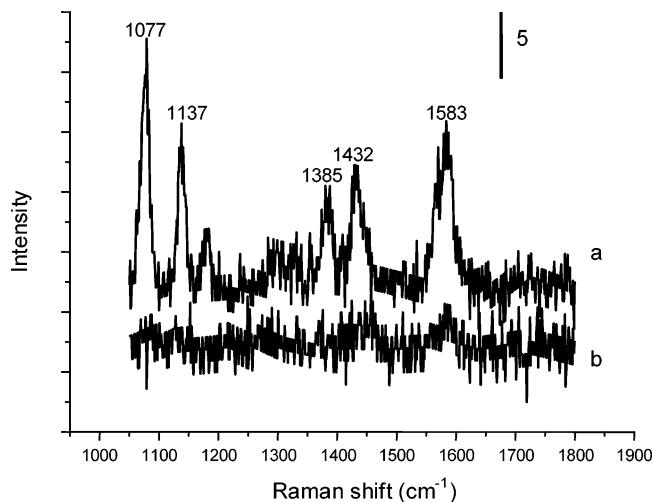
Figure 2. Raman spectra of a PATP monolayer adsorbed onto (a) the original Au nanoparticle assemblies and (b) Au nanoparticle assemblies after being immersed into the H_2PtCl_6 and NH_2OH solution for 9 h (ν_{7a}, 1077 cm^{-1}; ν_{9b}, 1137 cm^{-1}; ν_3, 1385 cm^{-1}; ν_{19b}, 1432 cm^{-1}; ν_{8a}, 1583 cm^{-1}; the vibration assignments referring to ref 14).

immersion are shown in Figure 2. We find that the intensities of the Raman bands (ν_{7a}, 1077 cm^{-1}; ν_{9b}, 1137 cm^{-1}; ν_3, 1385 cm^{-1}; ν_{19b}, 1432 cm^{-1}; ν_{8a}, 1583 cm^{-1}; the vibration assignments referring to ref 14) of the original Au nanoparticles are much greater than those of the substrate exposed to the Pt deposition, the latter even almost vanishing into the background. This result suggests that the Au nanoparticles on the latter substrate were coated by Pt metal.

When it comes to bimetallic nanoparticles, it is important to understand its fine structure, which is studied by XPS in the present experiment. Figure 3 shows typical XPS spectra of bimetallic Au−Pt nanoparticle assemblies with different sizes. In both of the spectra, we observe two subpeaks at 70.8 and 74.3 eV, Pt 4f peaks, which show the existence of pure Pt. On the other hand, we also observe a small Au 4f peak at about 84 eV in the case of smaller Au−Pt nanoparticles ($\sim$25 nm), while this Au 4f peak does not appear in the case of larger Au−Pt nanoparticles ($\sim$61 nm). It is expectable since the probe depth of our XPS instrument is about 10 nm. In the case of 25 nm Au−Pt nanoparticles, the Pt layer is not thick enough, and the instrument can detect the signal of Au, while in the other case of 61 nm Au−Pt nanoparticles, the Au signal cannot be detected due to the thick Pt layer. According to this XPS result, it is reasonable to propose that the Au−Pt bimetallic nanoparticles should have a core−shell structure, that is, a Au core being coated by a shell of Pt metal. Previously, Schmid et al. characterized the fine structure of bimetallic Au−Pt nanoparticles prepared with the same method in bulk solution by EDX microanalysis, and also showed that the core of Au nanoparticles was surrounded by an outer layer of Pt metal.[7a] However, these Au (core)−Pt (shell) nanoparticles might not be thermodynamically stable, since Pt metal has higher M−M bonding than Au metal. According to a previous paper, as for bimetallic particles, the metal with higher M−M bonding being the core should be more thermodynamically stable.[15]
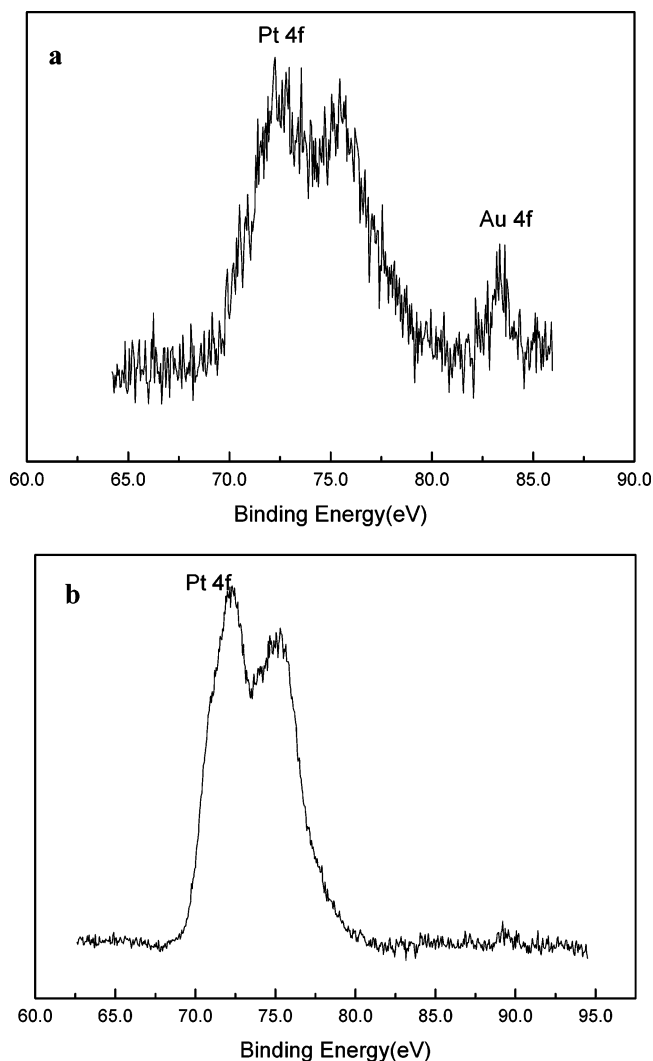

Figure 3. XPS spectra of bimetallic Au−Pt nanoparticles of size (a) 25 nm and (b) 61 nm.

To further understand the deposition procedure, we studied the morphology of Au (core)−Pt (shell) assemblies by a combination of SEM and atomic force microscopy (AFM) analysis, since SEM is able to measure the particle dimension in the *x*−*y* plane (parallel to the substrate surface), while AFM can give the precise particle height in the *z* direction (perpendicular to the substrate surface). Figure 4 shows SEM images of the assemblies of Au (core)−Pt (shell) nanoparticles prepared with different deposition times, 45 min, 3 h, 9 h, and 18 h. Figure 5 shows the corresponding AFM images and typical section scans, the *z* scale covering 50 nm for each image. The morphologic data are listed in Table 1.

As shown in Table 1, the size increase in the *x*−*y* plane ($D_{xy} - D_{Au}$) is 2 times that in the *z* direction ($D_z - D_{Au}$), where D_{Au}, D_{xy}, and D_z represent the size of the original Au particles as well as the dimensions of the Au (core)−Pt (shell) nanoparticles in the *x*−*y* plane and the *z* direction, respectively. As illustrated in Scheme 1, this result indicates that the deposition amounts of Pt metal are equal in every direction (*x*, *y*,

(15) (a) Watzky, M. A.; Finke, R. G. *Chem. Mater.* **1997**, *9*, 3083 and ref 38 therein. (b) Schmidt, G.; West, H.; Malm, J.-O.; Bovin, J.-O.; Grenthe, C. *Chem.−Eur. J.* **1996**, *2*, 147.
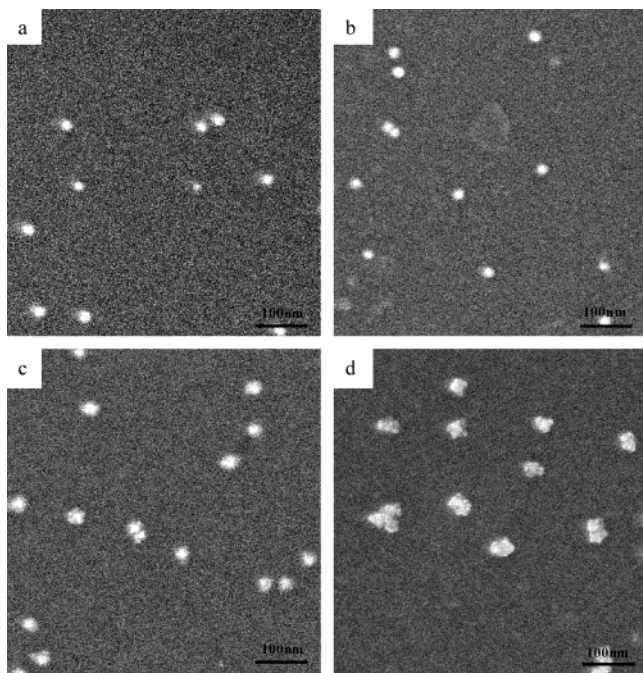
Figure 4. SEM images of Au (core)−Pt (shell) nanoparticle assemblies prepared with different deposition times: (a) 45 min, (b) 3 h, (c) 9 h, and (d) 18 h.

Table 1. Morphological Parameters of Au (Core)−Pt (Shell) Particles

	$D_z{}^a$ (nm)	$D_z - D_{Au}$ (nm)	$D_{xy}{}^b$ (nm)	$D_{xy} - D_{Au}$ (nm)	RSD^d (%)
a	13 ± 1.3	0	14 ± 1.5	1	9.7
b	16 ± 1.2	3	19 ± 2.3	6	7.7
c	20 ± 2.1	7	28 ± 4.2	15	11
d	26 ± 3.1	13	42 ± 6.1	28	12
$D_{Au}{}^c$ (nm)			13 ± 1.0		

^{a} D_z is the average diameter of core−shell particles in the z direction. ^{b} D_{xy} is the average diameter of core−shell particles in the $x−y$ plane. ^{c} D_{Au} is the average diameter of the original Au nanoparticles. ^{d} RSD is the relative standard deviation of the diameter of core−shell particles in the z direction.

Scheme 1. Deposition of Pt Metal onto Fixed Au Nanoparticles
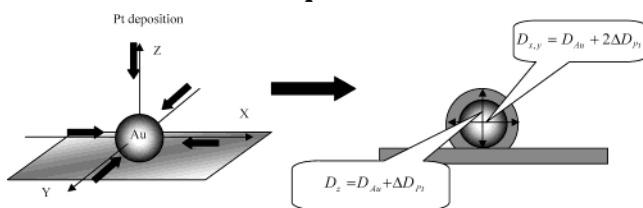
and z). In other words, the Pt deposition is isotropic. For a reference, in the deposition of gold metal onto self-assembled Au nanoparticles via a similar method, Brown et al. observed the particles preferentially grew in the $x−y$ plane over the z direction, which we think might be associated with the great affinity between Au metal and the organic film.[16a] On the other hand, from Figures 4 and 5, we find that these core−shell particles appear nearly monodisperse.[16b] Especially, at a low deposition amount, the relative standard deviations

(RSDs) of the Au (core)−Pt (shell) nanoparticles are all about 10% (Table 1), which is similar to those of the original Au nanoparticles (13 ± 1.0 nm). This result suggests that the Pt deposition is uniform on each metal nanoparticle, and thereby the morphologic feature of Au nanoparticles is inherited.

Figure 6 shows the size of Au (core)−Pt (shell) nanoparticles (D_z, that in the z direction) as a function of the deposition time, t, and, as a reference, the size of the original Au nanoparticles is also plotted. It can be seen that the particle size depends linearly on the deposition time, and that the slope is 1.2×10^{-2} nm/min, demonstrating the growth rate of the particles. According to the growth law of colloidal particles, the particle size will show a linear dependence on time if the growth procedure is kinetically controlled, and vice versa.[11a,17] Therefore, the linear relationship of the particle size, D_z, vs the deposition time suggests that the Pt deposition onto the metal nanoparticles is a kinetically controlled procedure; that is, the rate-determining step is the surface reaction, i.e., the reduction of $PtCl_6{}^{2-}$ by NH_2OH on the surface of metal nanoparticles. In fact, as for the synthesis of core−shell bimetallic nanoparticles, it is well-recognized that the general principle is a seeded autocatalytic surface growth mechanism, but the rate-determining step has not been determined in previous papers, which might depend on specific systems.[7,18] In addition, as for the famous statement that the rate of change of the diameter with time is constant in kinetically controlled growth, there has also been no direct experimental observation to offer proof for it until now. This is because this statement is derived for particles growing in a region where the concentration of reagents remains constant,[11a,17] which was almost impossible to satisfy in previous experiments. However, in the present experiment, the involved components consist of Au nanoparticles self-assembled onto small Si wafers (10 mm × 10 mm) and a voluminous solution of 1000 mL of 0.01 wt % H_2PtCl_6 mixed with 9 mL of 1 wt % NH_2-OH. The consumed amount of reagents (H_2PtCl_6 and NH_2OH) during the Pt deposition was less than 1% of the whole, and thus, the concentration change of the reagents could be negligible. Therefore, just by taking advantage of the voluminous solution and localized reaction, we manage to observe the linear dependence of the particle size on the growth time.

In short, judging from SEM images, SERS measurement, and XPS spectra, we conclude that the self-assembled Au nanoparticles are coated by Pt metal when immersed into the $PtCl_6{}^{2-}$ and NH_2OH solution. With the combination of SEM and AFM analysis, the Pt deposition is shown to be isotropic and uniform on each particle. In addition, this Pt deposition procedure is considered to be kinetically controlled due to the linear relationship of the particle size vs deposition time. The detailed analysis of the growth kinetics is given below.

Growth Kinetics of Au (Core)−Pt (Shell) Nanoparticles. Generally speaking, the growth procedure of

(16) (a) Brown, K. R.; Lyon, L. A.; Fox, A. P.; Reiss, B. D.; Natan, M. J. *Chem. Mater.* **2000**, *12*, 314. (b) As for the definition of "monodisperse" and "nearly monodisperse", please see: *J. Mol. Catal. A* **1996**, *114*, 29 and ref 7 therein.

(17) Overbeek, J. T. G. *Adv. Colloid Interface Sci.* **1982**, *15*, 251.
(18) (a) Watzky, M. A.; Finke, R. G. *J. Am. Chem. Soc.* **1997**, *119*, 10382 and the note in refs 22 and 23 therein. (b) Widegren, J. A.; Aiken, J. D., III; Ozkar, S.; Finke, R. G. *Chem. Mater.* **2001**, *13*, 312.
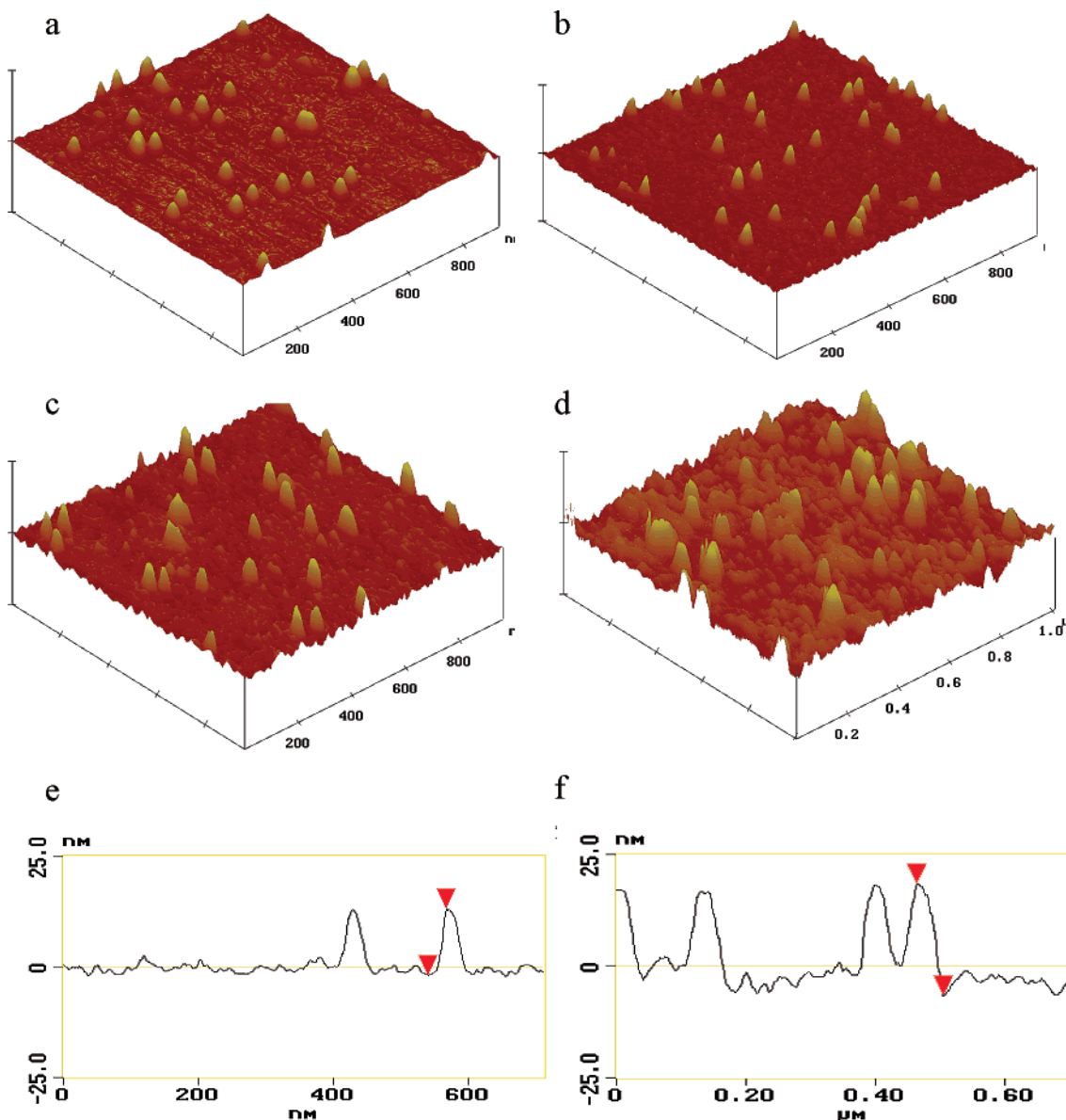
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Figure 5. AFM images of Au (core)−Pt (shell) nanoparticle assemblies prepared with different deposition times: (a) 45 min, (b) 3 h, (c) 9 h, and (d) 18 h. The z scale covers 50 nm for each image. Sectional analyses of (e) sample b and (f) sample d are also given.

colloidal particles can be divided into two kinds, diffusion-controlled and kinetically controlled, according to the rate-determining step.[11a] As for the diffusion-controlled procedure, Reiss developed the growth kinetics model quantitatively and proposed formulations for the evolution of particle sizes with time,[19] which was extensively cited and applied in various preparations of nanoparticles.[20] When it comes to the kinetically controlled procedure, although it is well-recognized that the change rate of the particle size with time is constant, no well-established quantitative model has been given to offer proof for this proposition. Herein, referring to the approach of Reiss,[19] we analyze the kinetics of the growth of Au (core)−Pt (shell) nanoparticles, which supports that famous proposition and provides further insight into the procedure of Pt deposition.
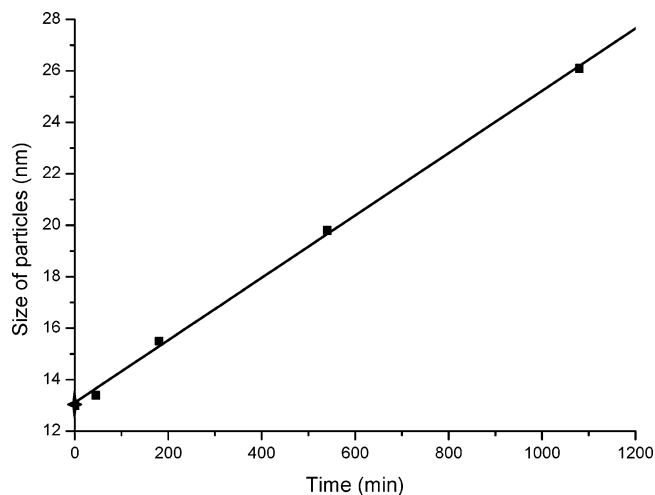

Figure 6. Average size of the Au (core)−Pt (shell) nanoparticles in the z direction as a function of deposition time. The bold plus sign on the vertical axis indicates the average size of the original Au nanoparticles.

(19) Reiss, H. J. Chem. Phys. **1951**, 19, 482.
(20) (a) Ngo, T. T.; Williams, R. S. Appl. Phys. Lett. **1995**, 66, 1906. (b) Liu, H.; Penner, R. M.. J. Phys. Chem. B **2000**, 104, 9131. (c) Scharifker, B. R. J. Electroanal. Chem. **1998**, 458, 253.

Scheme 2. Model of a Single Au (Core)−Pt (Shell) Particle on the Substrate
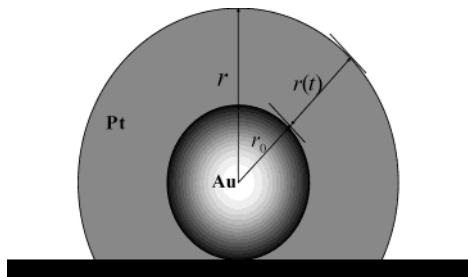
It is assumed initially that there is an individual Au nanoparticle of radius r_0, and then at any time, the particle radius can be denoted as a function of time:

$$r \propto r(t) + r_0 \qquad (1)$$

where r is the radius of the core−shell particle and $r(t)$ is the thickness of the deposited Pt shell, as illustrated in Scheme 2. The volume of the Pt shell, V_{Pt}, can be written as

$$V_{Pt} = \frac{2}{3}\pi r^3 + \pi r^2 r^0 - \frac{1}{3}\pi r_0{}^3 \qquad (2)$$

and the amount of deposited Pt metal, N_{Pt}, is

$$N_{Pt} = V_{Pt}\frac{\rho_{Pt}}{M_{Pt}} \qquad (3)$$

where M_{Pt} and ρ_{Pt} are the molar mass and density of Pt metal. In this experiment, the rate of Pt deposition, v_{Pt}, should be defined as the differentiation of N_{Pt} over the deposition time, t, and the area of the particle surface, S:

$$v_{Pt} = \frac{d^2 N_{Pt}}{dt\, dS} \qquad (4)$$

Considering that the deposition is isotropic, that is, the deposition rate is identical for each point at the nanoparticle surface, eq 4 can be derivated as
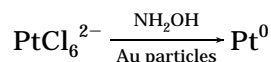
$$\frac{dN_{Pt}}{dt} = v_{Pt}S \qquad (5)$$

According to Scheme 2, S can be calculated as

$$S \propto 2\pi r(r + r_0) \qquad (6)$$

With eqs 1−6 combined, we obtain

$$\frac{dr}{dt} = v_{Pt} \cdot \frac{M_{Pt}}{\rho_{Pt}} \qquad (7)$$

As discussed above, the rate-determining step in the Pt deposition is the surface reaction, which can be written as follows:

$$PtCl_6{}^{2-} \xrightarrow[\text{Au particles}]{NH_2OH} Pt^0$$

Obviously, v_{Pt} is also equal to the reduction rate of $PtCl_6{}^{2-}$:

$$v_{Pt} = KC \qquad (8)$$

where K is a parameter associated with the surface reaction, which should be a constant since the experimental conditions (reactant concentration, temperature, and so on) did not change during the present experiment, and C is the concentration of $PtCl_6{}^{2-}$ in the bulk solution.

Substituting eqs 1 and 8 into eq 7, we obtain

$$\frac{dr(t)}{dt} = KC\frac{M_{Pt}}{\rho_{Pt}} \qquad (9)$$

Equation 9 indicates that the change rate of the particle size with time is constant if the reagent concentration remains constant. Taking the boundary condition into account

$$t = 0, \quad r(t) = 0 \qquad (10)$$

we obtain the following equation through the integration of eq 9 with respect to t:

$$r(t) = KC\frac{M_{Pt}}{\rho_{Pt}}t \qquad (11)$$

Equation 11 demonstrates the growth law of a single nanoparticle, but in the real experiment there is an ensemble of particles with different sizes. We assume that the size distribution of the original Au nanoparticles is $n(r_0)$; in other words, the number of particles with radii lying in the range between r_0 and $r_0 + dr_0$ is $n(r_0)\, dr_0$. Because there was no nucleation during the Pt deposition, the size distribution function of Au (core)−Pt (shell) nanoparticles, $m(r)$, can be given by

$$m(r)\, dr = n(r_0)\, dr_0 \qquad (12)$$

and the average radii of Au and Au (core)−Pt (shell) nanoparticles can be written as follows:

$$\bar{r}_0 = \frac{1}{n}\int n(r_0)\, r_0\, dr_0 \qquad (13)$$

$$\bar{r} = \frac{1}{n}\int m(r)\, r\, dr \qquad (14)$$

where n is the number of total particles. With the combination of eqs 1, 11, 13, and 14, we obtain

$$\bar{r} \propto KC\frac{M_{Pt}}{\rho_{Pt}}t + \bar{r}_0 \qquad (15)$$

Equation 15 shows that the average size of Au (core)−Pt (shell) nanoparticles is linear over the deposition time, which is consistent with the experimental result given in Figure 6. From Figure 6, we easily find

$$KC\frac{M_{Pt}}{\rho_{Pt}} = 1.2 \times 10^{-2}\ \text{nm/min} \qquad (16)$$

where $C = 2.5 \times 10^{-4}$ mol/L, $M_{Pt} = 195.1$ g/mol, and $\rho_{Pt} = 21.4$ g/cm^3, and then K can be worked out as

$$K = 5.3 \times 10^{-2} \text{ cm/min} \qquad (17)$$

In addition, eq 15 also shows that the increase of the particle size should be linearly associated with the concentration of $PtCl_6^{2-}$, C. This prediction already proved to be true in our experiments (data shown in the Supporting Information).

The above analysis provides solid evidence for the linear dependence of particle size on growth time in the kinetically controlled procedure, and demonstrates that the growth rate of Au (core)−Pt (shell) nanoparticles depends on the concentration of $PtCl_6^{2-}$, the molar mass and density of Pt metal, and a constant associated with the surface reaction.

Conclusion

The assemblies of Au (core)−Pt (shell) nanoparticles were prepared by chemical deposition of Pt onto Au colloids self-assembled on substrates. The Pt deposition is isotropic and uniform on each particle. It is also shown that the deposition procedure is kinetically controlled, and kinetics analysis reveals that the growth rate of Au (core)−Pt (shell) nanoparticles depends on the concentration of $PtCl_6^{2-}$, the molar mass and density of Pt metal, and a constant associated with the surface reaction. This result provides the principles to exactly control the thickness of the deposited shell.

Supporting Information Available: Dependence of Au (core)−Pt (shell) nanoparticle size in the z direction on the concentration of $PtCl_6^{2-}$ (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

CM0348491