# Uniform Electrochemical Deposition of Copper onto Self-Assembled Gold Nanoparticles

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Assemblies of gold(core)/copper(shell) nanoparticles could be prepared through the electrochemical deposition of copper metal onto self-assembled gold colloids that are immobilized via an organic film onto conductive substrates. In principle, the deposition on each particle is required to be independent of those on other particles, to develop monodispersed core–shell particles. From a simplified model, we derive formulas for the criteria to ensure the deposition independence, demonstrating the required experimental conditions of particle size, assembly density, and the ratio of the surface concentration to the bulk concentration of depositing species. In the electrolyte of 1.0 mM $CuSO_4$/0.10 M $Na_2SO_4$, we then manage to realize the experimental conditions lying in the independent region through applying a potential of −0.030 V(vs SCE) onto self-assembled gold particles 13 ± 1.0 nm in size, with a density of 350 $\mu m^{-2}$. The resulting core–shell nanoparticles show high monodispersity, especially at a relatively smaller size, because the particle size is <20 nm (with a relative standard deviation of RSD < 10%).

## Introduction

Because self-assembled gold nanoparticles that have been immobilized via an organic film onto conductive substrates are electrochemically addressable,[1,2] such conditions offer the possibility to prepare assemblies of gold(shell)/metal(shell) nanoparticles through the electrochemical deposition of other metals onto the gold nanoparticles.[3–5] Such core–shell nanoparticle assemblies are interesting, because assemblies such as these should possess both desirable features of the gold nanoparticle as well as the deposited metals, and their properties might be conveniently tailored by altering the composition or size of the deposited materials.[6] In principle, this approach of electrochemical deposition is desirable, considering that electrochemistry is versatile and powerful; it could be applicable to almost all metals and provides various channels to control the deposition procedure (for example, electrochemical potential can be used to control the deposition rate and coulometry can be used to monitor the deposition quantity exactly). However, according to present reports that demonstrate such electrochemical deposition, the resulting particles often show polydispersity, because of the nonuniformity of metal deposition.[3] This phenomenon brings us to explore how to realize uniform deposition and, thus, prepare assemblies of core–shell nanoparticles with high monodispersity.

Generally speaking, instantaneous nucleation and independent growth are the key requirements for the achievement of uniform growth of a particle ensemble on planar substrates.[7–10] In other words, the procedure of particle nucleation should be separated from that of particle growth, and each particle grows indepen-

dently of the others. Previously, we reported the electrochemical deposition of copper onto preformed gold nanoparticle self-assemblies, and the separation of nucleation and growth was realized by taking the advantage of organic molecules with long alkyl chains.[4] In that case, the organic monolayer was sufficiently compact to inhibit direct electron transfer through the organic molecules. Thus, copper metal was selectively deposited onto the surface of gold nanoparticles, rather than that of the organic film. Therefore, there was no nucleation of new separate particles besides from the growth of preformed ones. However, as for the development of uniform core–shell nanoparticles, the question of independent growth or independent deposition remains unresolved.

In the present paper, we first demonstrate the relationship between experimental conditions of particle size, assembly density, and the ratio of the surface concentration to the bulk concentration of depositing species, which is required for the achievement of independent disposition. We then manage to realize experimentally the independent deposition by controlling the applied potential to produce uniform core–shell particles.

## Experimental Section

**Chemicals.** $HAuCl_4 \cdot 3H_2O$ (from Aldrich) and amino-undecylthiol (AUDT) and Decanthiol (DT) (both from TCI) were used. Other reagents were analytical grade. All these compounds were used as received. Gold nanoparticles with a diameter of 13 ± 1.0 nm were prepared using the Frens method[11] and characterized by transmission electron microscopy (TEM) (model JEM-200CX, JEOL, Tokyo, Japan).

**Preparation of Gold Nanoparticle Self-Assemblies.** Gold substrates were prepared by sputtering high-purity gold onto cleaned silicon wafers that had a titanium adhesion layer (10 nm of titanium and 150 nm of gold). The resulting gold substrates were cleaned by being first sonicated successively in ethanol and water and then immersed in a bath of 7:3 (by

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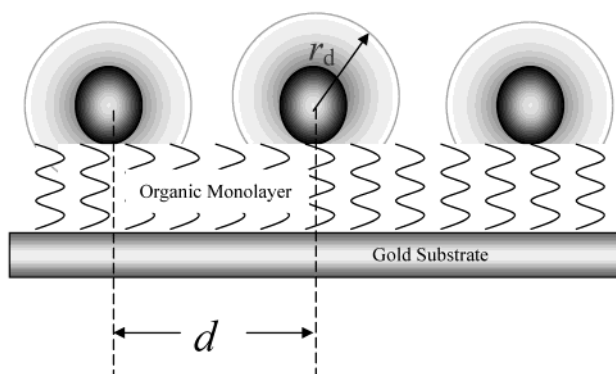‡ Present address: Department of Applied Chemistry, Beihang University, Beijing 100083, PRC.

**SCHEME 1. Geometric Relation of the Assembled Particles and Their Diffusion Layer in a Simplified Model**

**Top view**
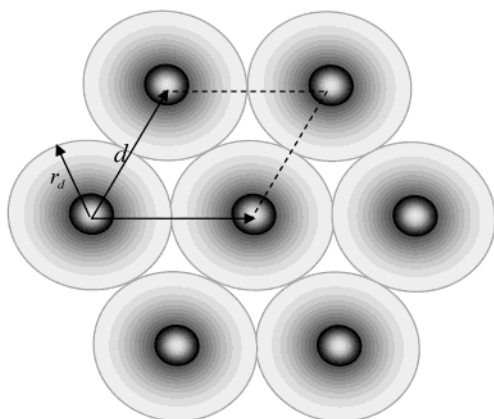
**Side view**

volume) 98% $H_2SO_4$:30% $H_2O_2$ (piranha solution) at 85 °C for 5 min. After being rinsed successively in water and ethanol, cleaned substrates were placed in 1.0 mM AUDT−ethanol solution for 24 h, then removed and rinsed with ethanol thoroughly. AUDT-modified gold substrates were immersed in 1.0 mM DT ethanol solution for 48 h, then removed and rinsed with ethanol and water successively. Finally, such organic-modified substrates were immersed in as-prepared gold colloids for 2 h, and colloidal gold particles would deposit onto the substrates in a density of ∼350 $\mu m^{-2}$ (i.e., 350 particles on a 1 $\mu m^2$ surface).

**Electrochemical Deposition of Copper.** All electrochemical experiments were performed using a electrochemical workstation (model CHI660A). A saturated calomel electrode (SCE), a platinum wire, and gold colloid−derivated gold substrates were used as the reference, counter, and working electrodes, respectively. A 1.0 mM $CuSO_4$/0.10 M $Na_2SO_4$ mixture was used as the electrolyte solution. Scanning electron microscopy (SEM) (model LEO-1530, LEO Elektronenmikroskopie GmbH, Germany) was used to characterize the morphology of the nanoparticle assemblies.

**Results and Discussion**

**Criteria for Independent Deposition.** In electrochemical experiments, self-assembled gold nanoparticles on conductive substrates will act as an ensemble of microelectrodes.[2] For the sake of simplicity, we assume a regular hexagonal
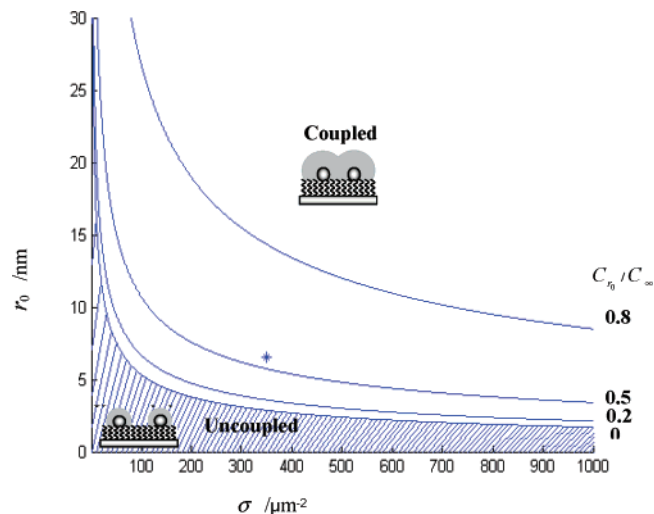
**Figure 1.** Calculation of diffusion coupling as a function of particle radius ($r_0$), assembly density ($\sigma$), and four indicated values of the concentration ratio ($C_S/C_\infty = 0$, 0.2, 0.5, 0.8), using eq 8. The asterisk star symbol denotes the initial conditions before electrochemical deposition in the present experiment.
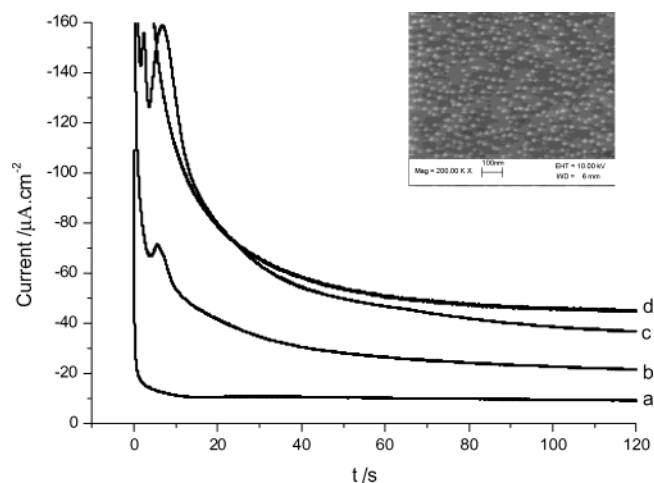
**Figure 2.** Current-versus-time profile for copper electrodeposition onto gold nanoparticle self-assemblies at different potentials: (a) −0.030 V, (b) −0.10 V, (c) −0.15 V, and (d) −0.20 V (vs SCE). Inset is a typical SEM image of a gold nanoparticle self-assembly before electrochemical deposition.

array to model the particle assemblies, just as shown in Scheme 1, although the real assemblies seem somewhat random.

According to previous papers, to achieve independent deposition, avoidance of the diffusion interference between adjacent microelectrodes is required.[12] Although no exact solution is known for the extent of diffusion interference, several groups proposed some approaches to evaluate the diffusion interference.[12−15] Penner et al. reported that, for diffusion interference to be negligible, the edge of the diffusion layer, which was defined to be located where the concentration of metal ion is 90% of that in the bulk solution, should not couple each other.[15] In this experiment, as illustrated in Scheme 1, this requirement can be denoted as

$$d \geq 2r_d \tag{1}$$

where $d$ is the central distance of two most neighboring particles and $r_d$ is the radius of the diffusion layer. An expression

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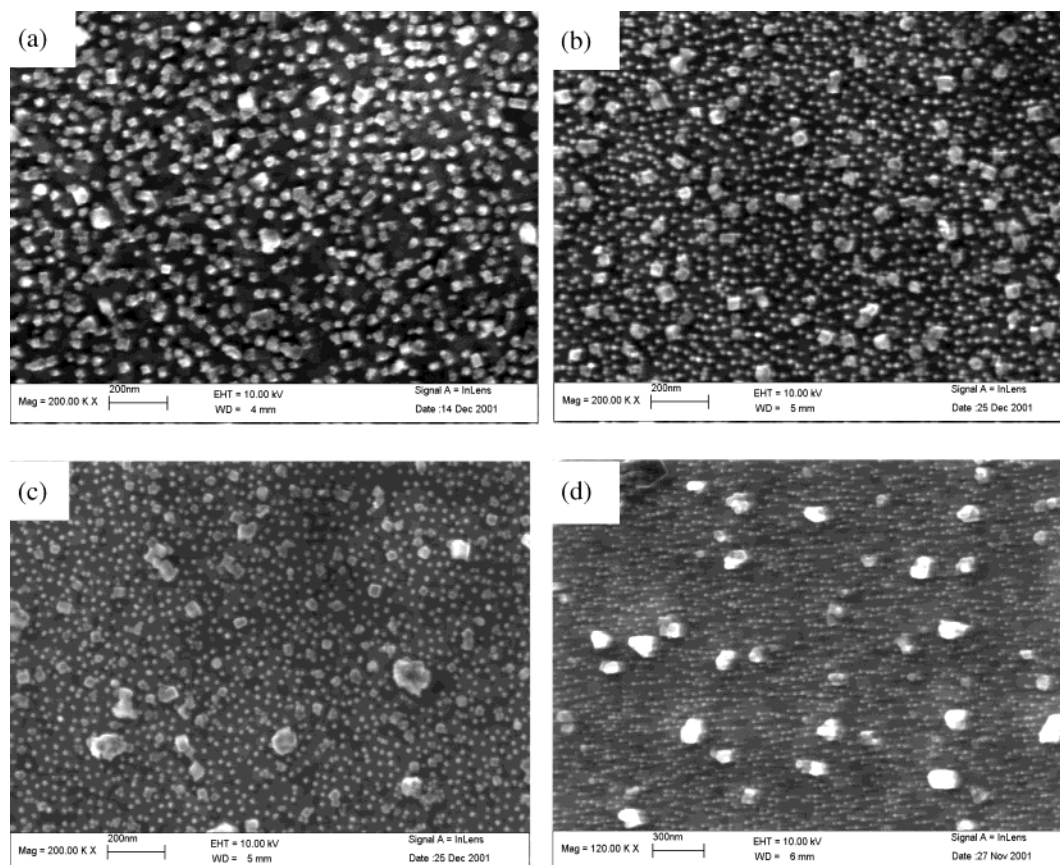*J. Phys. Chem. B, Vol. 108, No. 11, 2004* **3537**



**Figure 3.** SEM images of gold nanoparticle self-assemblies after the electrodeposition of copper at different potentials: (a) −0.030 V, (b) −0.10 V, (c) −0.15 V, and (d) −0.20 V. Deposited amounts are approximately similar to each other.

of $d$ can be derived from the spatial relationship shown in Scheme 1:

$$A = SN \qquad (2)$$

$$S = \left(\frac{\sqrt{3}}{2}\right)d^2 \qquad (3)$$

$$\sigma = \frac{N}{A} \qquad (4)$$

and, thus,

$$d = \left(\frac{\sqrt{3}}{2}\sigma\right)^{1/2} \qquad (5)$$

where $A$ is the total area of the planar working electrode, $N$ the total number of the particles, $S$ the occupied area of single quadrangle unit (as shown in Scheme 1, top view), and $\sigma$ the assembly density of particles on the electrode. In regard to the expression of $r_d$, it can be derived as follows. In the electrochemical deposition of a hemispherical electrode under diffusion control, if a steady state is attained, the reagent concentration at the radial distance of $r$, $C(r)$, can be given as[15−17]

$$C(r) = C_\infty - \frac{(C_\infty - C_S)r_0}{r} \qquad (6)$$

where $C_S$ and $C_\infty$ are the concentration of metal ion on the surface of nanoparticle electrodes and in the bulk of solution,

respectively, and $r_0$ is the radius of nanoparticles. Thus, $r_d$ can be derived as[15]

$$r_d = \frac{(C_\infty - C_S)r_0}{0.1C_\infty} \qquad (7)$$

Combining eqs 1, 5, and 7, we can obtain the following expression:

$$1 \geq 200\sqrt{3}\sigma\left[\left(1 - \frac{C_S}{C_\infty}\right)r_0\right]^2 \qquad (8)$$

For diffusion interference to be negligible, the inequality shown in eq 8 must be achieved; the involved relations between experimental parameters are plotted as Figure 1. This figure schematically shows the experimental parameters—$r_0$, $\sigma$, and $C_S/C_\infty$—under which the diffusion layers will (or will not) couple with each other. The upper-right-hand region of these curves represents the coupled region (where diffusion interference is significant), whereas the lower-left-hand region of these curves represents the uncoupled region (where diffusion interference is negligible). Figure 1 also shows that the smaller the values of $r_0$ and $\sigma$, or the greater the value of $C_S/C_\infty$, the easier it is to achieve uncoupled electrodeposition. This result provides guidance to control the experimental conditions necessary for the achievement of independent deposition. There should be three possible approaches to move the experiments conducted in the coupled region into the uncoupled region: decrease the value of $r_0$, decrease the value of $\sigma$, or increase the value of $C_S/C_\infty$. The parameters $r_0$ and $\sigma$ can be conveniently changed in the procedure of particle synthesis and self-assembly, whereas $C_S/C_\infty$ can be adjusted by controlling the applied potential.[17]
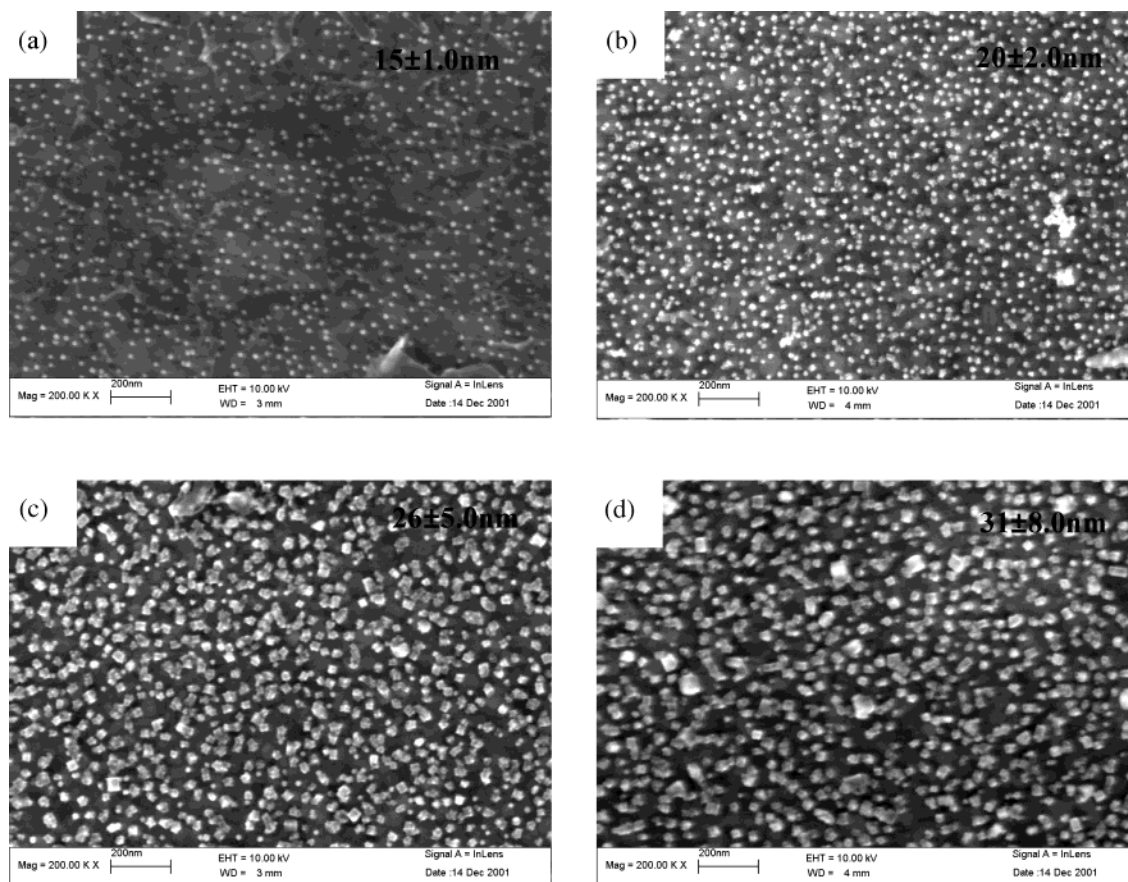
**Figure 4.** SEM images of gold (core)/copper (shell) nanoparticle assemblies prepared via the electrodeposition of copper onto self-assembled gold nanoparticles at −0.030 V for different times: (a) 2, (b) 15, (c) 50, and (d) 150 s. Morphological information is given in each corresponding image.

The aforementioned result provides guidance to achieve the independent deposition of metal on preformed gold nanoparticle self-assemblies under diffusion control. Because it is only related to the geometrical features of nanoparticle assemblies, this result should be, in principle, applicable to the electrochemical deposition of any metal onto such gold colloid-derived conductive substrates.

**Achievement of Independent Deposition.** Obviously, we can achieve an independent deposition of copper metal onto gold nanoparticle self-assemblies. In the present experiment, the initial experimental parameters are given as follows: the average diameter of the gold nanoparticles ($r_0$) is $13 \pm 1.0$ nm, the assembly density ($\sigma$) is $\sim350\ \mu m^{-2}$, and the $Cu^{2+}$ concentration in the bulk solution ($C_\infty$) is 1.0 mM, whereas the concentration on the particle surface ($C_S$) remains to be tailored.

The electrochemical experiments were performed in the 1 mM $CuSO_4$/0.1 M $Na_2SO_4$ electrolyte. To seek favorable $C_S$/$C_\infty$ values, we controlled the electrochemical potential to be −0.030 V (vs SCE), −0.10 V, −0.15 V, and −0.20 V. Correspondingly, Figure 2 shows the current-versus-time transients. From this figure, we can observe that all the deposition currents exponentially decrease initially and then have a tendency to be approximately constant, which indicates that the electrodeposition occurred under diffusion control.[15−17] During the diffusion-controlled procedure, when a steady state is attained, the expression of current ($i$) is given as[15−17]

$$i = nFA^*m_0(C_\infty - C_{r_0}) \qquad (9)$$

where $n$ is the number of electrons required to reduce a single $Cu^{2+}$ ion, $A^*$ the electrode area, $F$ the Faraday constant, and $m_0$ the mass-transfer coefficient of the $Cu^{2+}$ cations. Because

the steady-state current response at −0.15 V is similar to that at −0.20 V, which is also almost equal to those at even more-negative potentials (data not shown), the current at −0.20 V defines the diffusion-controlled limit in the present experiment. With the combination of eq 9 and the curves given in Figure 2, we can estimate the concentration of $Cu^{2+}$ cations on the microelectrode surface ($C_S$) at different potentials. At −0.030 and −0.10 V, $C_S$ is calculated to be $\sim$0.80 and 0.50 mmol/L, respectively, because the corresponding currents at steady state are approximately one-fifth and one-half of that of −0.20 V. Thus, the $C_S$/$C_\infty$ values at −0.030 and −0.10 V are 0.8 and 0.5, respectively. According to Figure 1, we can come to know that the deposition at −0.030 V may occur in the uncoupled region until the particle radius increases up to $\sim$15 nm, whereas in the case of −0.10 V or more-negative potentials, the diffusion layers will couple with each other as soon as the deposition begins.

Typical SEM images of the resulting particle assemblies are shown in Figure 3. We can observe that the size distribution of particles becomes obviously worse as a more-negative potential is applied. In the case of −0.030 V, almost each particle grew larger; thus, the particles seem to be relatively uniform. However, at −0.10 V, the sizes of $\sim$10% of the particles increased up to $\sim$50−60 nm, whereas those of others did not exhibit any obvious changes. In regard to the potentials of −0.15 and −0.20 V, we can find that there are fewer particles with larger size, compared to that at −0.10 V. This result indicates that the extent of diffusion interference increases with the overpotential, and that the potential of −0.030 V is favorable for uniform deposition, which is consistent with the preceding discussion. The Natan group reported a nonuniform deposition

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of silver onto gold nanoparticle self-assemblies,[3] and we think that it may be due to the fact that their experiment was conducted in a coupled region.

On the basis of this result, we select $-0.030$ V as the preferred potential to conduct the electrochemical copper deposition. Figure 4 shows SEM images of the resulting assemblies after being electrodeposited for different times (2, 15, 50, and 150 s). From these images, we can observe that the particle assemblies all show good uniformity, especially at low deposition time. The relative standard deviation (RSD) is $<10\%$ when the particle size is $<20$ nm but increases sharply as the particles continue to become larger. This result could be ascribed to two possible reasons: (i) as the size increases, some neighboring particles have a tendency to coalescence and form larger particles, which is apparent if one examines Figure 4c and 4d closely; and (ii) considering the random distribution of particles, there are certainly some particles that suffer from significant diffusion interference, the extent of which increases as the particle growth increases, which results in nonuniform deposition. However, similar to the principle given in Figure 1, a decrease of the assembly density $\sigma$ and particle size $r_0$ should be favorable to improve the uniformity of the resultant particles further.

## Conclusion

A formula was derived for the achievement of independent metal deposition onto self-assembled gold nanoparticles: $1 \geq 200\sqrt{3}\sigma[(1 - C_S/C_\infty)r_0]^2$. With its guidance, during the electrochemical deposition of copper metal in the electrolyte of 1.0 mM $CuSO_4$/0.10 M $Na_2SO_4$, the independent electrodeposition was achieved by applying a potential of $-0.030$ V on self-assembled gold nanoparticles ($13 \pm 1.0$ nm in diameter) with a assembly density of 350 $\mu m^{-2}$. The resulting gold (core)/copper (shell) nanoparticles show good monodispersity, especially in the case of low deposition amounts.

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