# Parametric Study on Electrochemical Deposition of Copper Nanoparticles on an Ultrathin Polypyrrole Film Deposited on a Gold Film Electrode

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Monoshaped and monosized copper nanostructured particles have been prepared by potentiostatic electrochemical deposition on an ultrathin polypyrrole (PPY) film, electrochemically grown on a Si(100) substrate sputter-coated with a thin gold film or gold-film electrode (GFE). The crystal size and the number density of the copper nanocrystals have been examined by varying several deposition parameters, including the thickness of the gold film, the PPY film thickness, the applied potential, and the $Cu^{2+}$ and the electrolyte concentrations for copper deposition. Optimal conditions for uniform growth of nanocrystals well-dispersed on the GFE have been determined, along with insight into the mechanism of crystal growth. A minimum gold film thickness of 80 nm is required to eliminate the effects of the gold−silicon interface. The PPY film thickness and homogeneity principally affect the shape uniformity of the nanocrystals, while the copper deposition potential could be used to regulate the size and number density of the nanocrystals. Both the $Cu^{2+}$ and electrolyte concentrations are also found to play important roles in controlling the electrodeposition of nanocrystal growth.

## 1. Introduction

Metallic nanocrystals have been extensively studied because their chemical and physical properties are quite different from the bulk material. These chemical and physical properties strongly depend on the size and distribution of the nanocrystals, which are two important factors for evaluating the fabrication of nanomaterials. Because their unique properties have significant industrial potential in the areas of catalysis, chemical sensors, and magnetic recording, numerous research groups have studied the fabrication and growth of nanocrystals by different approaches. Electrochemical deposition is a promising technique for preparing nanoparticles due to its easy-to-use procedure and low cost of implementation. By reducing metal ions onto selected electrodes from an electrolyte solution, growth of a variety of different sizes and shapes of nanostructured particles has been obtained on metal,[1,2] semiconductor,[3,4] and polymer surfaces.[5] Metal clusters have also been found to grow in a self-organized fashion with atoms efficiently packed to form energetically stable and highly symmetric clusters.[6] As a fcc transition metal with a full d band, copper nanostructured materials are of fundamental interest as prototypical nonmagnetic materials and metallic conductors. Indeed, the formation of copper nanostructured particles and clusters on different substrates using a variety of different methods has been reported by Liu et al.,[7] Guascito et al.,[8] Cioffi et al.,[9] Pászti et al.,[10] Makhloufi et al.,[11] Tsakova et al.,[12,13] Ji et al.,[14] and Sarkar et al.[15,16] As one of the most studied conducting polymers, polypyrrole (PPY) is an excellent material to be used as a substrate or matrix for deposition of metal nanoparticles (including copper, palladium, and hybrid materials) for such applications as catalysis[17] and electronics.[18,19] Our recent work[15,16] examined the growth mechanism of copper nanostructured particles on a thin polypyrrole film electrochemically deposited on polished gold cylinder electrodes. In particular, by manipulating the copper deposition potential and the PPY film thickness, the size and number density of the copper nanocrystals can be effectively controlled,[15,16] and the growth mechanism is found to follow the instantaneous nucleation mechanism.[20]

The chemical and physical properties of the nanoparticles strongly depend on their size and spatial distribution.[21] For applications such as catalysis, optics and electronics, effective control of the size, shape, and number density of the nanoparticles is therefore an important issue. Compared to such "dry" deposition techniques as

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physical vapor deposition, electrochemical deposition can be used to produce uniform and homogeneous distributions of nanoparticles with a similar size. However, reproducible fabrication requires careful control of a large number of growth parameters and conditions, which are poorly understood. In this paper, we describe the results of a parametric study on the growth of copper nanocrystals on a thin PPY film electrochemically deposited on a gold film electrode. By using a single-side polished Si(100) substrate sputter-coated with a thin film of gold as the electrode (the gold film electrode or GFE) instead of the conventional gold cylinder electrode, it is possible to produce a considerably smoother, more uniform electrode surface for PPY electrodeposition with lower roughness and higher PPY film quality. Unlike the gold cylinder electrodes that require careful multistep polishing and other pretreatments, the (disposable) GFE is easier to produce with highly reproducible surface morphology and quality. However, because the gold films are quite thin (less than 120 nm) and could therefore have a higher resistance relative to the gold cylinder electrodes, we examine how the size and density of the copper nanocrystals depend on the gold film thickness of the GFE. For the GFE, we also characterize the effects of other deposition parameters including the PPY film thickness and the applied potential, as well as the concentrations of $CuSO_4$ and the electrolyte $NaClO_4$. By systematically varying these parameters, our goal is to establish the optimal growth conditions for well-dispersed, monoshaped, monosized copper nanocrystals on a GFE. Indeed, the study of the change in the morphology of the nanostructured particles as a function of individual growth parameters promises new insight into the mechanism of copper nanoparticle growth.

## 2. Experimental Details

Single-side polished n-doped Si(100) wafers (0.40 mm thick) with a resistivity of 1.0−1.5 mΩ·cm were cut into $10 \times 4$ mm$^2$ rectangular pieces. The polished side of the Si pieces was gold-coated with a film thickness of 20−120 nm in a magnetron sputter-coater (Denton Vacuum Desk II). The root-mean-square surface roughness of the GFE was determined, by using Atomic Force Microscopy (AFM), to be smaller than 0.6 and 1.5 nm for film thickness below 50 nm and above 50 nm, respectively. With the exception of a native oxide layer on the Si substrate, the GFE so obtained was found to be effectively free from other contaminants (e.g., polishing powders often used in the preparation of conventional gold cylinder electrodes).

A potentio/galvanostat electrochemical workstation (CHI Instrument 660A) was used for all the electrodeposition experiments. PPY films were grown on the GFE at room temperature by chronopotentiometry with a current density of 1.2 mA/cm$^2$ in an aqueous solution of 0.05 M pyrrole and 0.1 M $NaClO_4$, appropriately deoxygenated by bubbling $N_2$ for 20 min. The film thickness of the electropolymerized PPY film can be controlled by varying the amount of charge transferred through the solution to the working electrode (GFE).[22] For a standard 50-nm-thick PPY film, the current was applied typically for 20 s. Other PPY film thicknesses of 20, 100, and 400 nm were also examined in the present work. The film thickness so obtained has been confirmed by independent AFM measurements. The deposited PPY films on the GFE were rinsed thoroughly with Millipore water (with a resistivity of 18.2 MΩ·cm) before use in the nanoparticle deposition experiment.

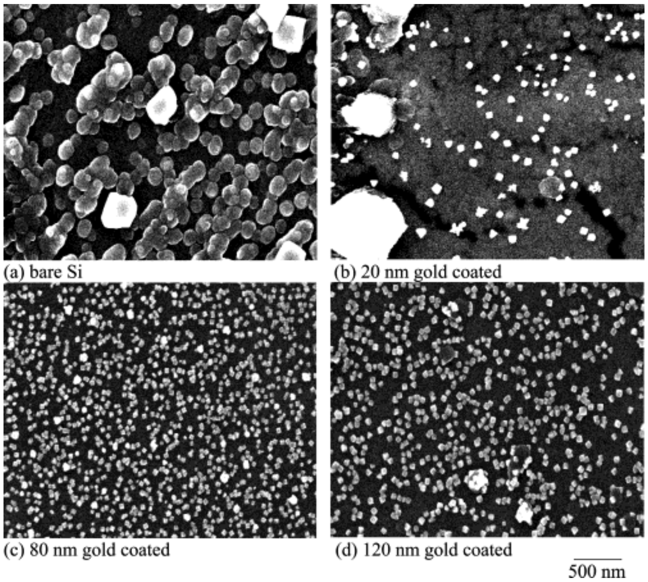

**Figure 1.** SEM images of copper nanocrystals on a 50-nm-thick polypyrrole film deposited on (a) a bare Si(100) substrate and on the Si(100) support covered with a thin gold film (gold film electrode) with gold thicknesses of (b) 20, (c) 80, and (d) 120 nm.

Copper nanocrystals were deposited potentiostatically on the PPY film in a solution of 0.1 M $NaClO_4$ and 0.05 M $CuSO_4$ by using amperometry at preselected potentials. This solution was appropriately deoxygenated by nitrogen bubbling for 20 min. For all the parameters studied, the amount of copper deposited was controlled by the amount of charge transfer, which was fixed to be the equivalent of five monolayers (ML) of copper on the deposited area. It should be noted that hydrogen evolution[23] was not considered in the present charge estimation. Unless stated otherwise, a constant potential of −1.2 V was applied (with respect to a standard Ag/AgCl reference electrode) for a standard nanocrystal deposition. The copper-decorated PPY films were then rinsed thoroughly with water and dried in a drybox flushed with nitrogen. A field-emission scanning electron microscope (LEO FESEM 1530) was used to examine the surface morphology of the films and to characterize the shape, size, and number density of the copper nanoparticles.

## 3. Results and Discussion

**3.1 Effects of Gold Film Thickness of the GFE and of the Film Thickness of the PPY Substrate.** Copper nanocrystals were deposited onto a 50-nm-thick PPY film electrodeposited on the GFE with several gold film thicknesses (20, 80, and 120 nm). Evidently, the SEM micrograph shown in Figure 1a reveals large, uniform, cubic copper nanocrystals on a generally rough PPY film (with spherical nanostructures) grown directly on the bare Si support (i.e., without any gold film coating). These copper crystals appear to have an average size of 200 nm and an approximate number density of $1.5 \times 10^8$ cm$^{-2}$. In contrast, copper nanocrystals deposited on a 50-nm-thick PPY film grown on GFEs with gold film thicknesses of 20 nm (Figure 1b), 80 nm (Figure 1c), and 120 nm (Figure 1d) are found to have average particle sizes in the range of 50 to 100 nm with number densities of $17 \times 10^8$ cm$^{-2}$, $58 \times 10^8$ cm$^{-2}$, and $42 \times 10^8$ cm$^{-2}$, respectively. In all cases, regularly shaped cubic copper nanocrystals are

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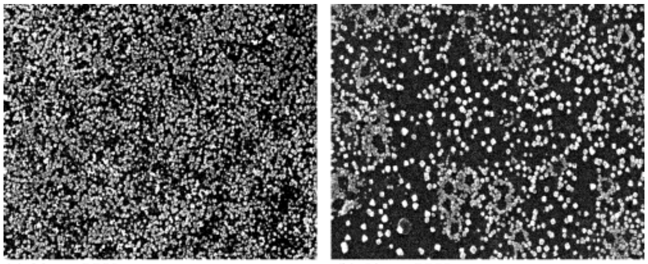
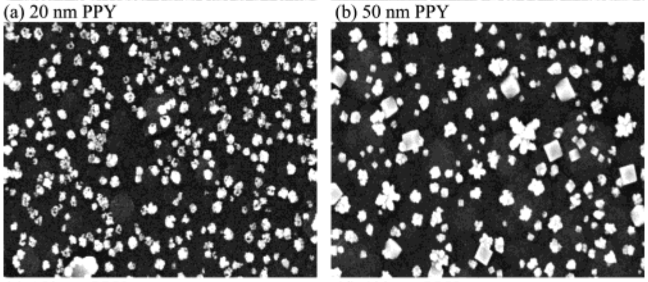


(a) 20 nm PPY (b) 50 nm PPY

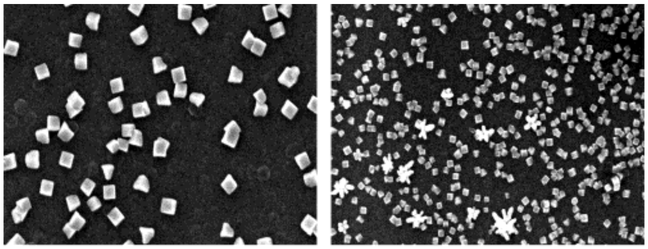


(c) 150 nm PPY (d) 400 nm PPY

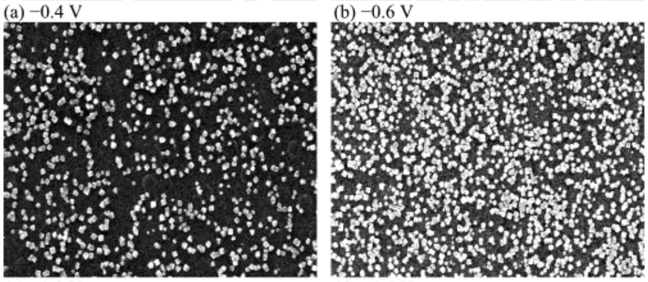
**Figure 2.** SEM images of copper nanocrystals on a polypyrrole (PPY) film on an 80-nm-thick gold film electrode with PPY film thicknesses of (a) 20, (b) 50, (c) 150, and (d) 400 nm.

obtained. However, for the 20-nm-thick GFE, the copper nanocrystals appear to be less evenly dispersed with a larger percentage of irregularly shaped copper clusters than are found for the 80-nm-thick GFE. These variations suggest changes in the conductivity of the GFE with different gold film thicknesses, which apparently have pronounced effects on the quality and morphology of the PPY film.[24] For instance, cracks in the gold film itself are clearly observed in the 20-nm-thick GFE (Figure 1b). These cracks could plausibly lead to variations in the surface conductivity of the GFE, which in turn affect both the PPY film electrodeposition and the subsequent copper nanocrystal deposition. This hypothesis is supported by the rather rough and irregular surface morphology in the corresponding PPY film. In the case of the 120-nm-thick GFE, the PPY surface morphology and the nanocrystal distribution both appear to be quite uniform. Both the resistivity and the roughness of the GFE are expected to affect the film morphology and quality of the PPY substrate and consequently change how the nanocrystals grow. The 80-nm-thick GFE provides a sufficiently thick gold film to produce minimal substrate effects on the shape, size, and uniformity of copper nanocrystal growth and is therefore used in all of the following experiments.

Figure 2 shows the SEM micrographs of copper nanocrystals deposited on PPY electrochemically grown on a 80-nm-thick GFE, with the PPY film thickness set to 20, 50, 150, and 400 nm. As the PPY film thickness is increased from 20 to 400 nm, the average size of the copper nanocrystals is found to increase from 50 to 250 nm with a concomitant decrease in the number density from $150 \times 10^8$ to $14 \times 10^8$ cm$^{-2}$. The observed trends with increasing PPY film thickness are consistent with similar results obtained in our previous work[15] conducted with the conventional gold cylinder electrodes. As before,[15] a thicker PPY film is found to lead to larger variations in both the shape and size of the copper nanocrystals. When the PPY film thickness reaches 400 nm (Figure 2d), both copper nanocubes and nanoclusters are visible, and both morphologies appear to exhibit a large size distribution. In the case of a thinner film, the presence of pinhole defects in the PPY film could also lead to inhomogenities in the copper growth morphology.[25]



(a) −0.4 V (b) −0.6 V



(c) −1.2 V (d) −1.4 V

**Figure 3.** SEM images of copper nanocrystals deposited on a 50-nm-thick polypyrrole film grown on an 80-nm-thick gold film electrode prepared under applied potentials of (a) −0.4, (b) −0.6, (c) −1.2, and (d) −1.4 V, all with respect to a standard Ag/AgCl reference potential.

For electrodeposition with instantaneous nucleation, a lower surface potential is found to lead to fewer nucleation centers (i.e., a lower number density) and a larger particle size. In addition, the thicker the PPY film, the rougher is its surface morphology and therefore the less uniform its surface potential becomes. The latter greater nonuniformity in the surface electrical field changes the copper deposition from an instantaneous, diffusion-limited, controlled growth mechanism to a partially diffusion-controlled mechanism, which could account for the larger size distribution in the copper nanocrystal growth.

**3.2 Effects of the Applied Potential on Copper Nanocrystal Deposition.** The SEM micrographs shown in Figure 3 illustrate the effects of different applied potentials on the morphology and distribution of the copper nanocrystals during amperometric deposition of copper nanocrystals on a 50-nm-thick PPY film deposited on a 80-nm-thick GFE, with all the other deposition parameters kept at their standard values (0.05 M pyrrole, 0.1 M $NaClO_4$ and 0.05 M $CuSO_4$). Consistent with our previous study,[16] the formation of copper nanocrystals on the PPY film begins with instantaneous nucleation followed by diffusion-limited growth. Of all the samples studied here, including those deposited at −0.2 and −0.4 V, nanostructured particle growth is found to occur in the over-peak-potential region. (All the applied potentials are with respect to a standard Ag/AgCl reference electrode.) As summarized in Figure 4, there is a smooth, monotonic decrease in the particle size with more negative potential. The decrease in particle size is accompanied by a corresponding increase in the particle number density, which is consistent with material conservation for a fixed amount of deposited copper chosen for all the samples. It should be noted that the total amount of charge transfer is adjusted for an equivalent of 5 ML of copper atoms during the potentiostatic deposition. Of all the potentials studied, the primary morphology is found to be cubic nanocrystals, while clustering of these nanocrystals could sometimes be observed. For this type of potentiostatic electrodeposition, the applied potential on the working electrode (GFE)

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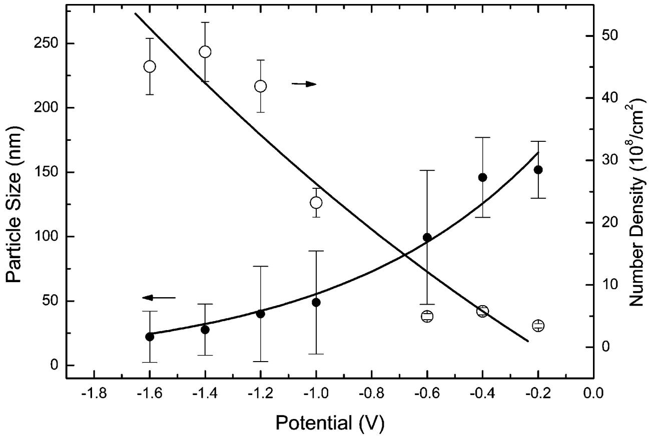
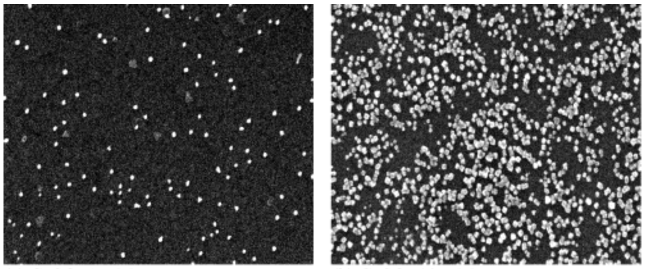


**Figure 4.** Average particle size (left axis) and number density (right axis) of copper nanocrystals deposited on a 50-nm-thick polypyrrole film grown on an 80-nm-thick gold film electrode as a function of the applied potential (with respect to a standard Ag/AgCl reference potential).


(a) $CuSO_4$ 1 mM (b) $CuSO_4$ 10 mM

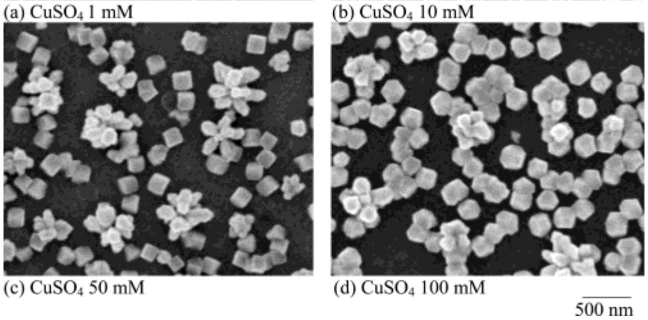

(c) $CuSO_4$ 50 mM (d) $CuSO_4$ 100 mM

**Figure 5.** SEM images of copper nanocrystals deposited on a 50-nm-thick polypyrrole film grown on an 80-nm-thick gold film electrode prepared using different $CuSO_4$ concentrations of (a) 1, (b) 10, (c) 50, and (d) 100 mM.

plays an important role both thermodynamically and kinetically.[26,27] Evidently, a more negative (over-peak-)-potential applied on the working electrode introduces more nucleation sites on the PPY substrate, consistent with the increase in the number density, as depicted in Figure 4. With the larger number density, the more negative potential in effect leads to a faster deposition rate, thereby limiting the ultimate overall size of the nanocrystals for a given charge transfer.

**3.3 The Effects of $CuSO_4$ Concentration and $NaClO_4$ Concentration.** Figure 5 shows the effects of varying the $CuSO_4$ concentration (from 1, 10, and 50 to 100 mM) on the growth morphology of the copper nanoparticles deposited potentiostatically at −1.2 V (with respect to a standard Ag/AgCl reference electrode) on a 50-nm-thick PPY substrate grown on an 80-nm-thick GFE, while keeping the concentration of the electrolyte $NaClO_4$ constant at 0.1 M. The amount of charge transferred to the electrode was equivalent to 5 ML of copper. In the low $Cu^{2+}$ concentration regime, the number density is found to increase with increasing $Cu^{2+}$ concentration. In particular, the copper nanoparticles remain cubic in shape and effectively constant in the size range of 50 ± 10 nm, while the corresponding number density appears to increase dramatically from $12 \times 10^8$ cm$^{-2}$ at 1 mM $Cu^{2+}$ concentration (Figure 5a) to $56 \times 10^8$ cm$^{-2}$ at 10 mM $Cu^{2+}$ concentration (Figure 5b). From 10 mM to 50 mM $Cu^{2+}$ concentration (Figure 5c), a dramatic increase in crystal size to 200 ± 10 nm and a marked reduction in the number density to $8 \times 10^8$ cm$^{-2}$ are observed, while the nanocrystals remain cubic in shape. A further increase in the $Cu^{2+}$ concentration to 100 mM (Figure 5d) produces large polyhedral particles of 200−300 nm in diameter, accompanied by larger clustering of copper nanopolyhedrons.

Although the amount of charge transfer is the same for all the samples prepared at different $CuSO_4$ concentrations, the amount of copper deposited could vary due to the electrochemical reduction of the PPY substrate, which is characterized by the changes in the local chemical environment of N and the removal of the $ClO_4^-$ counterion from the PPY film.[22] This reduction has been verified by X-ray photoelectron spectroscopy (not shown), which shows that the N 1s intensity at 399 eV binding energy (corresponding to the reduction state) is increased while the Cl $2p_{3/2}$ intensity at 207 eV (corresponding to a +7 oxidation state) is diminished after copper deposition. For a complex system such as the electrodeposition of metal (Cu) nanoparticles onto a porous conducting polymer (PPY) substrate, details of the nucleation and growth mechanisms remain largely unexplored due to limitations in the technique and the complexity of the process itself. Since the reduction of the PPY substrate could lead to changes in the conductivity of the substrate during the copper deposition, and the subsequent changes in the local ionic environment could cause further subtle changes in how the metal nanoparticles assemble, it is difficult to determine the precise mechanism underlying the nanoparticle growth. The present results suggest that the initial $CuSO_4$ concentration is an important factor that controls the diffusion rate for mass transport during the electrodeposition process. In the present case, a $CuSO_4$ concentration of 10−50 mM appears to be adequate in providing a uniform nanocrystal morphology.

Finally, copper nanoparticles were deposited potentiostatically at −1.2 V (with respect to a standard Ag/AgCl reference electrode) on a 50-nm-thick PPY substrate grown on an 80-nm-thick GFE with the $CuSO_4$ concentration fixed at 50 mM while varying the $NaClO_4$ (electrolyte) concentration. The SEM micrographs shown in Figure 6 reveal dramatic changes in the morphology of copper nanoparticles as a function of the electrolyte concentration. In particular, the number density of the nanoparticles is found to increase from $5.5 \times 10^8$, $23 \times 10^8$, and $39 \times 10^8$ cm$^{-2}$ to $145 \times 10^8$cm$^{-2}$, while the corresponding particle size is observed to decrease from 300, 150, and 100 nm to 35 nm, with increasing electrolyte concentration respectively from 10 (Figure 6a), 50 (Figure 6b), and 100 mM (Figure 6c) to 200 mM (Figure 6d). At a low electrolyte concentration of 10 mM, there are few crystalline nanocrystals while nanoclusters with a porous structure appear to dominate (Figure 6a). As the electrolyte concentration increases from 50 (Figure 6b) to 100 mM (Figure 6c), nanoclusters become less prominent and the formation of polyhedral nanocrystals (Figure 6b) and regular nanocubes (Figure 6c) is observed. At the highest $NaClO_4$ concentration used in the present study (Figure 6d), clustering of

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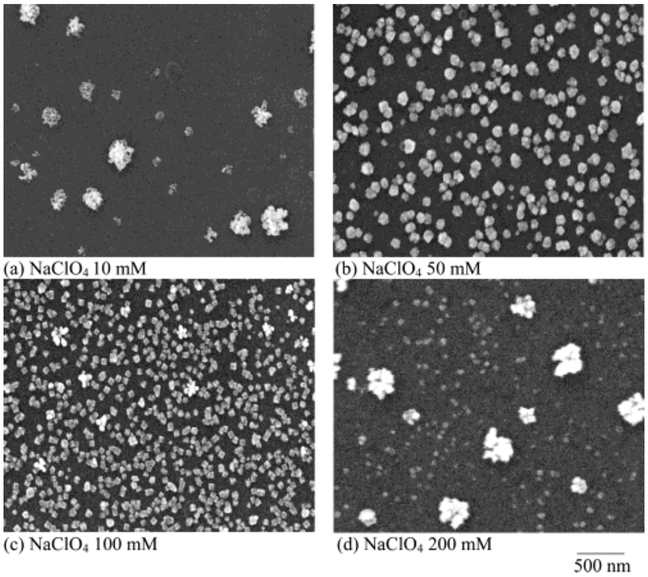

**Figure 6.** SEM images of copper nanocrystals deposited on a 50-nm-thick polypyrrole film grown on an 80-nm-thick gold film electrode prepared using different $NaClO_4$ concentrations of (a) 10, (b) 50, (c) 100, and (d) 200 mM.

nanoparticles and the development of fractal structures apparently emerge, in the presence of remarkably smaller nanoparticles. The underlying mechanism for this bimodal growth behavior remains unknown.

For a diffusion-limited mechanism of copper deposition, the diffusion rate of the $Cu^{2+}$ ions from the solution to the electrode and the subsequent nanocrystal formation is determined by the concentrations of the $Na^+$ and $ClO_4^-$ ions. A lower electrolyte $ClO_4^-$ concentration could decrease the $Cu^{2+}$ diffusion rate, therefore reducing its mass transport from the solution to the electrode, which is consistent with the results shown in Figure 6. A higher electrolyte concentration promotes a faster build-up of the double layer, which is indicated by the dramatic drop in the current with time upon application of the voltage during copper deposition (not shown). The development of the double layer directly affects the diffusion rate of $Cu^{2+}$ to the electrode and the resulting morphology. It should be noted that there is also an inverse relationship between the number density and the particle size of the copper nanoparticles. Between 10 and 100 mM, a higher concentration of electrolyte appears to give rise to a larger number density of copper nanocrystals with a smaller size. As is the case with the $CuSO_4$ concentration, the $NaClO_4$ concentration has a significant effect on the growth morphology of the copper deposits.

## 4. Summary

The growth of uniformly sized and geometrically cubic copper nanocrystals on an ultrathin PPY film substrate electrochemically deposited on a newly introduced gold-film electrode has been demonstrated. Unlike the conventional gold cylinder electrodes, the GFE is found to offer a markedly improved reproducibility in the surface quality of the electrode and a considerable time-saving in the sample preparation. A systematic study of several relevant growth/deposition parameters, including the gold film thickness of the GFE, the film thickness of the PPY substrate, the applied potential, and the concentrations of $Cu^{2+}$ ions and the $NaClO_4$ electrolyte, has been carried out. The present results show that an 80-nm-thick gold film sputter-coated on a polished Si(100) substrate is sufficient to minimize thickness effects due to the GFE on the copper nanoparticle deposition. The effects of the PPY film thickness and of the applied potential on the nanocrystal growth are found to be in good accord with our previous study employing gold cylinder electrodes. However, the GFE gives improved control over the uniformity of the particle size and the structure of the copper nanocrystals. The concentrations of the $CuSO_4$ and the $NaClO_4$ electrolyte offer two additional parameters for manipulating the morphology and quality of the copper nanostructured particles obtained by the electrochemical deposition.

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