

Synthesis of Icosahedral Gold Nanocrystals: A Thermal Process Strategy

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We demonstrate a one-step thermal process route to the synthesis of icosahedral gold nanocrystals. By regulating the concentrations of poly(vinyl pyrrolidone) (PVP) and HAuCl_4 or changing the temperature, we can readily access the shapes of icosahedral nanocrystals with good uniformity. These gold nanostructures, with unique geometrical shapes, might find use in areas that include photonics, optoelectronics, and optical sensing. We also observed that these gold nanocrystals have a strong tendency to be immobilized spontaneously on the glass substrate.

Metal nanostructures have drawn considerable interest in recent years because of their applications in catalysis, biosensing, optics, and magnetic devices where they have been exhibiting particular performance over their bulk counterparts.^{1–4} In the past decade, many efforts have been devoted to the shape-controlled synthesis of metal micro- and nanostructures.^{5–8} Among them, Au nanocrystals are particularly interesting because they have unique electrical and optical properties. Various approaches have been reported for fabricating gold nanocrystals with various morphologies, such as rods,^{9–13} cubes,¹⁴ prisms,^{15,16} disks,¹⁷ plates,^{18–22} and branched nanocrystals.^{23–25} For instance, Wang et al.⁹ reported the synthesis of gold nanorods by electrochemical reduction of a gold precursor in organic solution. Triangular gold nanoprisms were prepared with a biological synthesis method, where a plant extract was used to react with aqueous chloraurate ions to produce the desired product shapes.¹⁵ Large-scale synthesis of Au microplates was accomplished through a mild wet-chemical route based on the reduction of HAuCl_4 by *ortho*-phenylenediamine in aqueous solution.¹⁹ However, few reports on the preparation of shape-controlled gold nanoparticles have appeared in the past decade. Murphy and Sau²⁶ adopted a seed-mediated growth method to control the morphology and dimensions of Au nanocrystals. Various structural architectures with rod-, rectangle-, hexagon-, cube-, triangle-, and starlike gold nanocrystals were synthesized by manipulation of the experimental parameters in the presence of cetyltriethylammonium bromide (CTAB). Polymer (such as PVP) has been extensively applied in the synthesis of nanomaterials. By controlling parameters, reasonable control of size and shape of nanoparticles can be achieved. Yang and co-workers²⁷ recently reported the formation of platonic (including icosahedral) gold nanocrystals using the polyol process in the presence of PVP. By regulating the ratio of PVP to gold precursor, platonic nanogold with well-defined shapes was prepared. Xie et al. prepared shape-controlled gold nanoparticles by introducing a small amount of salt into an *N,N*-

dimethylformamide (DMF) solution containing PVP and changing the temperature or the concentration of the gold precursor.²⁸ Herein, we report a simple one-step synthesis of icosahedral gold nanocrystals in aqueous solution by a thermal process. By elevating the synthesis temperatures and modifying the concentration of PVP, gold nanocrystals with icosahedral structure were obtained. To our knowledge, this is the first report that describes the synthesis of icosahedral gold nanocrystals in aqueous solution by a thermal process. Upon adjusting the concentration of gold precursor, the icosahedral and platelike structures with dominating dispersion were prepared, respectively.

In a typical experiment, a 5 mL PVP (0.12 M) solution and a 5 mL HAuCl_4 (5 mM) solution were mixed and stirred with a magnetic bar. The solution was heated to reflux in a water bath at 100 °C. The solution turned iridescent purple within 60 min, indicating formation of gold nanoparticles. The solution was aged for 2 h to ensure that the reaction was complete. A glass slide (Shanghai Baio technology Co., LTD) was cleaned in aqua regia (HCl/HNO_3 1:3) for 20 min and rinsed with triply distilled water. The glass slide suspended the as-prepared gold nanocrystal solution for ~48 h. The gold nanocrystal film was formed spontaneously on the surface of glass slides, evident by the color change (clear to iridescent yellow) on the glass slide. Then, the material on the glass slide was slowly evaporated at room temperature for scanning electron microscopy (SEM) and X-ray diffraction (XRD) characterizations.

Figure 1a shows the typical transmission electron microscopy (TEM) image of the products prepared by the simple thermal process at 100 °C. Observation by TEM indicates that the majority of the particles have a projected quasi-spheroid shape with sizes of 220 ± 40 nm (inserted is a histogram of particle sizes). Some triangular and hexangular structures are also found with sizes of ~800 and ~780 nm, respectively. The lower-magnification SEM image (Figure 1b) indicates that the nanocrystals consist of a large amount of quasi-spheroid particles accompanied with few platelike structures, while the higher-magnification image (Figure 1c) clearly reveals that the quasi-spheroid particles are polyhedron structures, dominantly icosahedral.

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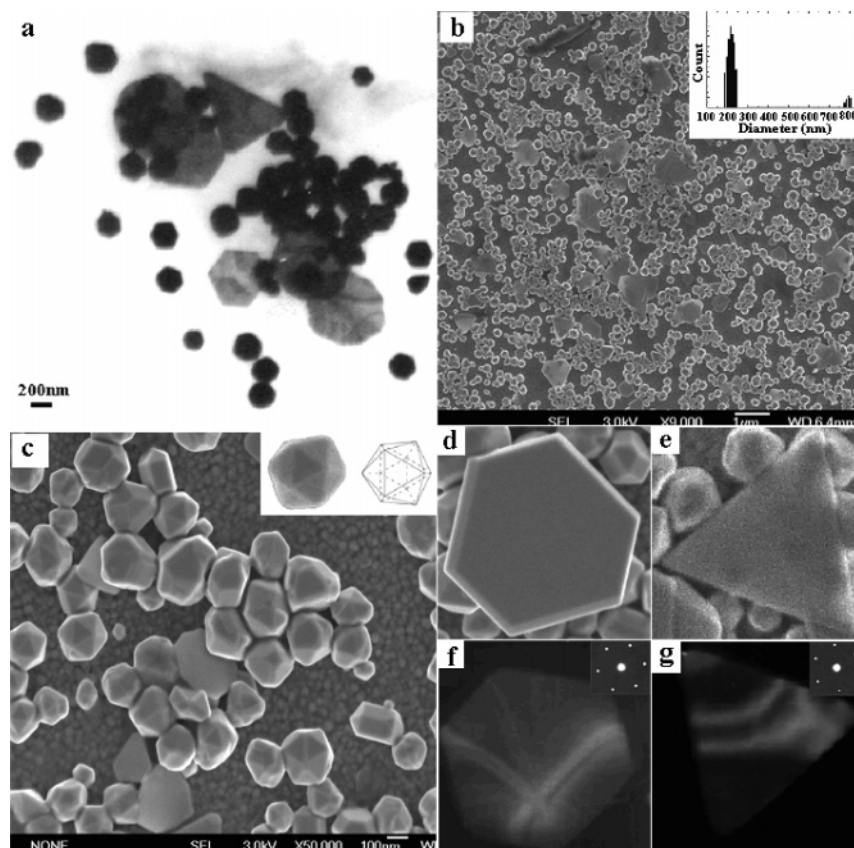


Figure 1. (a) Representative TEM image of the gold nanocrystals synthesized with the thermal process. (b) Low- and (c) high-magnification images of the same patch of gold nanocrystals. The insets in parts b and c show one icosahedral nanocrystal and its geometrical structure. SEM and TEM images of typical (d, f) hexagonal and (e, g) triangular nanoplates, respectively. The insets in parts f and g show the diffraction pattern recorded by triangular and hexagonal nanoplates, respectively.

hedral in shape (inset Figure 1c). These Au icosahedral particles have uniform sizes from ~ 180 to ~ 250 nm, in agreement with the TEM characterizations. The icosahedron is one of the platonic structures, which consists of 20 triangle planes with $\{111\}$ surface. Some of the particles are thin hexangular and triangular plates (Figure 1d,e, respectively), whose shapes and sizes are consistent with TEM images (Figure 1f,g, respectively). The insets show the electron diffraction (ED) pattern (inset Figure 1f,g) obtained by directing the electron beam perpendicular to one of the faces of the corresponding nanoplate. The ED patterns reveal a hexagonal-symmetry diffraction spot pattern, demonstrating that the Au nanoplates are single crystal with a preferential growth direction along the gold $\{111\}$ plane.²⁹

The chemical compositions of these particles are determined by energy-dispersive X-ray spectroscopy (EDS). The EDS spectrum (Figure 2a) shows only peaks corresponding to Au, which indicates that the particles are pure metallic Au. The XRD pattern recorded from the same batch of sample (supported on a glass substrate as in Figure 2b) shows sharp peaks corresponding to the $\{111\}$, $\{200\}$, and $\{222\}$ diffraction peaks of Au, which demonstrates that the as-prepared nanoparticles are composed of pure crystalline Au with face-centered cubic (fcc) structure. The lattice constant calculated from this pattern is 4.0764 Å, in agreement with the value report in the literature ($a = 4.0768$ Å, JCPDS, file no. 4-0784).³⁰ Also indicated is the higher intensity from the $\{111\}$ plane. These observations confirm that our nanocrystals are primarily dominated by $\{111\}$ facets, and thus, their $\{111\}$ planes tend to be preferentially oriented parallel to the surface of the supporting substrate. As is well-known, the optical properties of metal nanoparticles are

highly dependent on the size and shape of the particles. Several groups have theoretically simulated the optical properties of metal nanoparticles with arbitrary shapes and found distinctive shape-dependent behaviors.^{33–35} Figure 2c,d shows a photograph and an absorption spectrum of the as-prepared Au particles in aqueous solution. The solution is iridescent purple in color (Figure 2c). Different from the UV–vis spectra of spherical gold nanoparticles in solution that displayed surface plasma resonance (SPR) bands located at about 520 nm, the UV–vis spectra collected on the resulting solution clearly show two SPR bands at about 570 and 640 nm (Figure 2d). The spectral features of the icosahedral nanocrystals are fairly consistent with previous reports.²⁷ The additional broad near-IR band is most likely due to quadrupole plasmon resonance of the nanoparticles.

More interestingly, after a glass slide is immersed in the solution for 48 h, immobilization of the nanocrystals occurs spontaneously on the glass substrate. SEM characterizations of the immobilized nanocrystals (Figure 3) clearly show that they are nearly monodispersed and well-dispersed on the glass surface. This process is probably driven by electrostatic interactions between the particles that are carrying positive charges because of adsorption of unreacted gold ions and the negatively charged SiO_2 surface.³¹ Control over the immobilization of nanocrystals on the solid surface has great importance for the further use of nanocrystals in many applications, such as surface-enhanced Raman spectroscopy.³²

The morphology and dimensions of the as-synthesized nanostructure were found to strongly depend on the reaction conditions such as temperature, the concentration of PVP, and the concentration of HAuCl_4 . For example, when the temperature was 50 °C, the shape of the product was dominated with

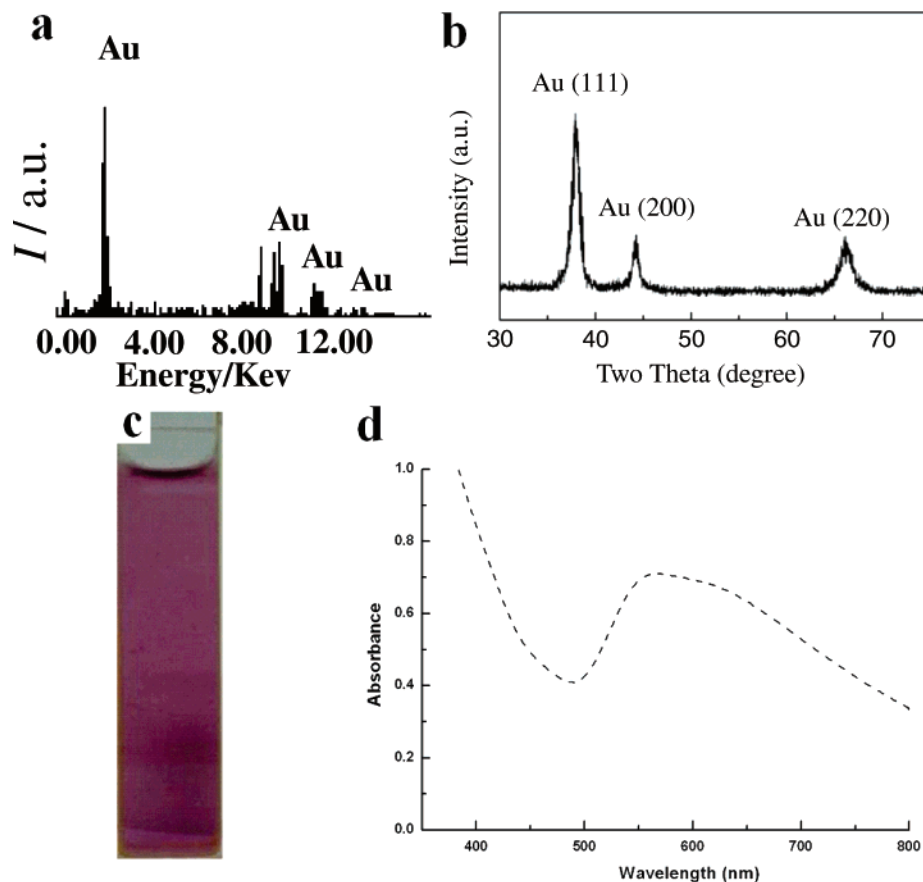


Figure 2. EDS spectrum (taken with SEM) (a) and XRD pattern (b) of gold nanocrystals. Photograph (c) and UV-vis spectrum (d) of the gold particles suspended in aqueous solution.

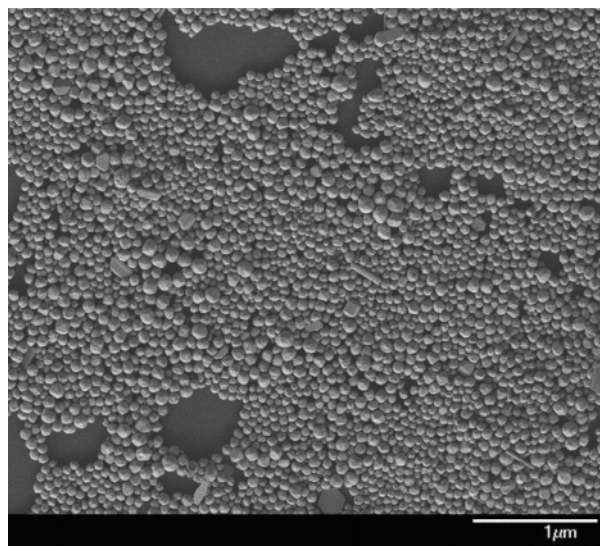


Figure 3. The as-prepared gold nanocrystals immobilized on a glass substrate.

spherical structures (Figure 4a). Upon thermal treatment to 80 °C, an obvious change occurred. Some icosahedral and polygonal plate nanostructures appeared accompanied by spheres (Figure 4b). As shown in Figure 4c, however, an obvious change appeared after synthesis at 100 °C. The predominant structures of the products were icosahedral and platelike nanocrystals. It is also worthwhile mentioning that the quantity of PVP in the solution is an important factor in determining the morphology of the final Au particles. By decreasing this concentration, the percentage of irregular nanostructures increased. In one particular example, the PVP concentration was decreased to 0.60

M while keeping the concentration of the gold precursor constant. Figure 4d showed that a large quantity of nanoparticles had a projected irregular shape. It was also found that the particle shapes were sensitive to the concentration of the gold precursor used in the experiments. Control reactions in which various concentrations of gold precursor were added under otherwise identical conditions were performed. Figure 4e,f shows typical SEM images of Au products obtained with initial gold precursor of 1 mM (Figure 4e) and 50 mM (Figure 4f). They clearly indicate that the products are mostly icosahedral at low gold precursor concentrations. However, the amount of platelike nanostructures increased significantly at high HAuCl_4 concentrations. These results indicate that it is possible to tune the shape of the gold nanocrystals by simply controlling the experimental conditions.

As a result of the above reduction process, nucleation and growth processes of Au yielded a mixture of icosahedral nanocrystals and polygonal plates. The surface-regulating polymer (PVP) is believed to play a key role here. PVP that contains an $\text{N}-\text{C}=\text{O}$ group is easily attached to the surface of these nanocrystals and slows the growth speed of the crystal faces. As a kinetic controller of the growth rates of different crystalline faces through adsorption and desorption, PVP adsorbed on specific crystalline surfaces could significantly decrease their growth rates and lead to a highly anisotropic growth. Selective interactions between PVP and the different surface planes of the gold nanocrystals may greatly enhance the growth rate along the $\{111\}$ direction, and/or reduce the growth rate along $\{100\}$ direction, and ultimately result in particles with icosahedral shapes.

In conclusion, we present our preliminary findings that large-scale of icosahedral Au nanocrystals can be synthesized by a

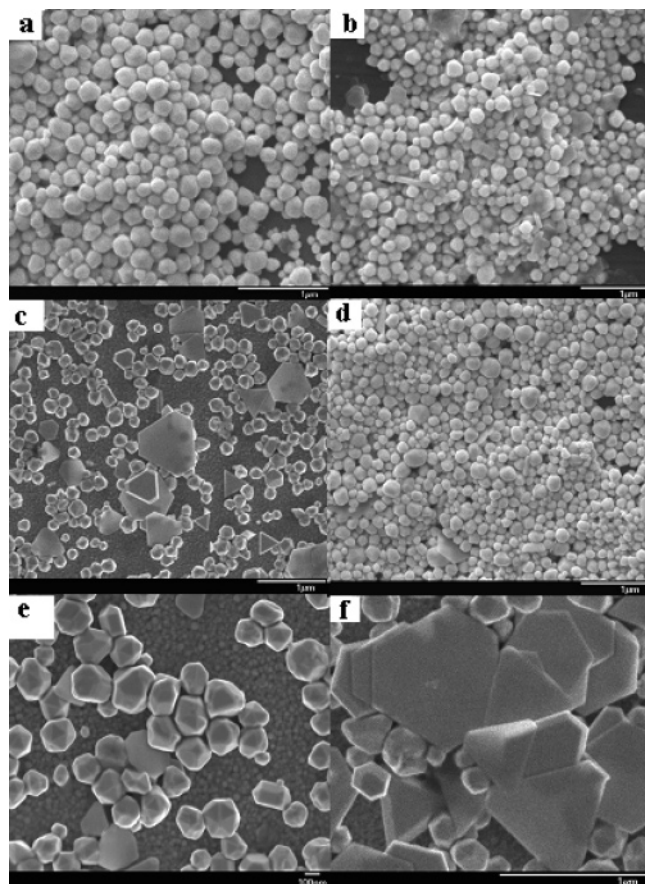


Figure 4. SEM images of gold nanocrystals synthesized under different conditions. (a–c) The same as in Figure 1b, except that the reaction temperatures were from 50 to 80 and 100 °C, respectively. (d) The same as in Figure 1b, except that the PVP concentration was 0.60 M. (e, f) The same as in Figure 1b, except that the HAuCl₄ concentrations were 1 and 50 mM, respectively.

simple one-step wet-chemical route, carried out by the thermal process of HAuCl₄ with PVP in aqueous media. The study suggests that the temperatures and concentrations of PVP and Au precursor in the solution are key factors to producing Au nanocrystals in certain shapes. The successful preparation of gold nanocrystals exemplifies the exquisite shape control that can be achieved through careful growth-rate regulation along different crystallographic directions and demonstrates a strategy that may be generally applicable to other material systems.

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References and Notes

- (1) Milliron, D. J.; Hughes, S. M.; Cui, Y.; Manna, L.; Li, J. B.; Wang, L. W. *Nature (London)* **2004**, *430*, 190.
- (2) Wang, J. F.; Gudiksen, M. S.; Duan, X. F.; Cui, Y.; Lieber, C. M. *Science* **2001**, *293*, 1455.
- (3) Jin, R.; Cao, Y.; Hao, E.; Métraux, G. S.; Schatz, G. C.; Mirkin, C. A. *Nature (London)* **2003**, *425*, 487.
- (4) Kim, J. U.; Cha, S. H.; Shin, K.; Jho, J. Y.; Lee, J. C. *Adv. Mater.* **2004**, *16*, 459.
- (5) Sun, Y.; Xia, Y. *Adv. Mater.* **2003**, *15*, 695.
- (6) Ahmadi, T. S.; Wang, Z. L.; Green, T. C.; Henglein, A.; El-Sayed, M. A. *Science* **1996**, *272*, 1924.
- (7) Kim, F.; Song, J.; Yang, P. *J. Am. Chem. Soc.* **2002**, *124*, 14316.
- (8) Sun, Y.; Gates, B.; Mayers, B.; Xia, Y. *Nano Lett.* **2002**, *2*, 165.
- (9) Yu, Y.; Chang, S. S.; Lee, C. L.; Wang, C. R. *J. Phys. Chem. B* **1997**, *101*, 6661.
- (10) Gai, P. L.; Harmer, M. A. *Nano Lett.* **2002**, *2*, 771.
- (11) Kim, F.; Song, J. H.; Yang, P. *J. Am. Chem. Soc.* **2002**, *124*, 14316.
- (12) Nikoobakht, B.; El-Sayed, M. A. *Chem. Mater.* **2003**, *15*, 1957.
- (13) Busbee, B. D.; Obare, S. O.; Murphy, C. J. *Adv. Mater.* **2003**, *15*, 414.
- (14) Sun, Y.; Xia, Y. *Science* **2002**, *298*, 2176.
- (15) Shankar, S. S.; Rai, A.; Ankamwar, B.; Singh, A.; Ahmad, A.; Sastry, M. *Nat. Mater.* **2004**, *3*, 482.
- (16) Millstone, J. E.; Park, S.; Shuford, K. L.; Qin, L.; Schatz, G. C.; Mirkin, C. A. *J. Am. Chem. Soc.* **2005**, *127*, 5312.
- (17) Simakin, A. V.; Voronov, V. V.; Shafeev, G. A.; Brayner, R.; Bozon-Verduraz, F. *Chem. Phys. Lett.* **2001**, *348*, 182.
- (18) Malikova, N.; Pastoriza-Santos, I.; Schierhorn, M.; Kotov, N. A.; Liz-Marzan, L. M. *Langmuir* **2002**, *18*, 3694.
- (19) (a) Shao, Y.; Jin, Y.; Dong, S. *Chem. Commun.* **2004**, *9*, 1104. (b) Sun, X.; Dong, S.; Wang, E. *Angew. Chem., Int. Ed.* **2004**, *46*, 6360. (c) Sun, X.; Dong, S.; Wang, E. *Langmuir* **2005**, *21*, 4710.
- (20) (a) Ibano, D.; Yokota, Y.; Tominaga, T. *Chem. Lett.* **2003**, *32*, 574. (b) Tsuji, M.; Hashimoto, M.; Nishizawa, Y.; Tsuji, T. *Chem. Lett.* **2003**, *32*, 1114. (c) Wang, L.; Chen, X.; Zhan, J.; Sui, Z.; Zhao, J.; Sun, Z. *Chem. Lett.* **2004**, *33*, 720. (d) Wang, L.; Chen, X.; Zhan, J.; Chai, Y.; Yang, C.; Xu, L.; Zhuang, W.; Jing, B. *J. Phys. Chem. B* **2005**, *109*, 3189.
- (21) Stoeva, S. I.; Prasad, B. L. V.; Uma, S.; Stoimenov, P. K.; Zaikovski, V.; Sorensen, C. M.; Klabunde, K. J. *J. Phys. Chem. B* **2003**, *107*, 7441.
- (22) Zhou, Y.; Wang, C. Y.; Zhu, Y. R.; Chen, Z. Y. *Chem. Mater.* **1999**, *11*, 2310.
- (23) Kuo, C.; Huang, M. H. *Langmuir* **2005**, *21*, 2012.
- (24) Chen, S.; Wang, Z. L.; Ballato, J.; Foulger, S. H.; Carroll, D. L. *J. Am. Chem. Soc.* **2003**, *125*, 16186.
- (25) Hao, E.; Bailey, R. C.; Schatz, G. C.; Hupp, J. T.; Li, S. *Nano Lett.* **2004**, *4*, 327.
- (26) Sau, T. K.; Murphy, C. J. *J. Am. Chem. Soc.* **2004**, *126*, 8648.
- (27) Kim, F.; Connor, S.; Song, H.; Kuykendall, T.; Yang, P. *Angew. Chem., Int. Ed.* **2004**, *43*, 3673.
- (28) Chen, Y.; Gu, X.; Nie, C.; Jiang, Z.; Xie, Z.; Lin, C. *Chem. Commun.* **2005**, *33*, 4181.
- (29) Zhou, Y.; Wang, C. Y.; Zhu, Y. R.; Chen, Z. Y. *Chem. Mater.* **1999**, *11*, 2310.
- (30) Bayliss, P. *Mineral Powder Diffraction File Date Book*; JCPDS: Swarthmore, PA, 1986.
- (31) Sarkar, A.; Kapoor, S.; Mukherjee, T. *J. Phys. Chem. B* **2005**, *109*, 7698.
- (32) Gole, A.; Orendorff, C. J.; Murphy, C. J. *Langmuir* **2004**, *20*, 7117.
- (33) Mock, J. J.; Barbic, M.; Smith, D. R.; Schultz, D. A.; Schultz, S. *J. Chem. Phys.* **2002**, *116*, 6755.
- (34) Kelly, K. L.; Coronado, E.; Zhao, L. L.; Schatz, G. C. *J. Phys. Chem. B* **2003**, *107*, 668.
- (35) Sosa, I. O.; Noguez, C.; Barrera, R. G. *J. Phys. Chem. B* **2003**, *107*, 6269.