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Synthesis of Gold Nanorices on ITO Substrate Using Silver Seed-Mediated Growth Method

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Abstract: Herein, we propose a seed-mediated growth method for synthesis of gold nanorices directly grown on the substrate using silver seed. The as prepared sample was characterized using UV-Vis spectrometer, field emission scanning electron microscopy (FESEM), and X-Ray diffraction (XRD). The UV-Vis spectrum of the sample shows transversal surface plasmon resonance (t-SPR) peak at wavelength 541 nm and longitudinal surface plasmon resonance (l-SPR) peak at wavelength 730 nm. The FESEM image confirmed the morphology of gold nanostructures are rice-like shape. Typically, the nanorices have long axis (a) 55.54±3.30 nm, short axis (b) 28.71±2.30 nm, and aspect ratio (a/b) 1.98±0.09. The XRD pattern of the sample at diffraction angle (2θ) in the range of 10º-70º reveals three peaks at 38.18º, 44.48º, and 64.67º which corresponding to (111), (200), and (220) Bragg's reflection of face centers cubic lattice Gold (ICSD file No. 98-005-3763). The strong peak intensity at 38.18º represents the nanorices growth in the (111) direction. The gold nanostructures with rice-like shape which exhibit two localized surface plasmon resonance (LSPR) thus it has very potential for application in plasmonic sensing.

Keywords: Localized surface plasmon resonance, gold nanoparticles, gold nanorices, plasmonic sensor

1. Introduction

Metal nanoparticles, especially gold, have a unique optical, electronics, and catalytic properties [1,2]. Due to these characteristics, research in gold nanoparticles has received a lot of attention in recent years [3]. The properties of gold nanoparticles can be tuned by controlling their size and shape. Gold nanoparticles with various shape such as spherical [4], rod [5], tripod [6], wire [7], cube [8], and plate [9] have been successfully synthesized by different method and reaction condition. Subsequent experiments showed that method and reaction condition strongly affect to the size or shape of gold nanoparticles obtained.

When light hits the gold nanoparticles, free electron in conduction band will oscillate. The collective oscillation of free electron on the surface of metal nanoparticles are called as surface plasmon resonance [10]. The SPR of the gold nanoparticles strongly dependent on their size and shape. For example, gold nanosphericals with diameter 15 nm possess SPR at wavelength around 520 nm. This SPR red shifted as the size of gold nanoparticles increase. Gold nanorods possess two SPR corresponding to the electron along the transverse axes (t-SPR) and longitudinal axes (l-SPR). The l-SPR of gold nanorods can be tailored by tuning its length and diameter, as well as the aspect ratio. Gold nanoshells also possess two SPR arising from the plasmon on the inner (denoted as bonding SPR) and outer surface (denoted as antibonding SPR) of the shell. The bonding and antibonding SPR of gold nanoshells can be tuned by varying the relative size of inner and outer radius of the shell. Gold nanoparticles shaped like rice, namely as gold nanorices is one of the gold nanoparticles geometry which have SPR that combines the SPR properties of both gold nanorods and gold nanoshells in single structure. This hybrid SPR properties makes gold nanorices potentially useful in plasmonic sensing application [11].

In this work, we used bottom up method namely seed-mediated growth method (SMGM) to synthesis gold nanorices. This method was initially by formation of seed and further growth are accomplished in sequential steps. The main advantage of SMGM is it flexibility in control shape and size of nanoparticles by simply modified seed or growth condition [12]. Herein, we modified reaction condition for gold nanospherical by changing gold seeds with silver seeds. The introduction of silver seed assumed will affect growth behavior and thus giving the morphological effect onto obtained gold nanoparticles, i.e. the gold nanostructures with rice-like shape, namely gold nanorices.

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2. Experimental

2.1 Chemicals

Gold (III) chloride trihydrate ($HAuCl_4.3H_2O$, ≥99.9%), trisodium citrate dihydrate ($C_6H_5Na_3O_7.2H_2O$), sodium borohydride ($NaBH_4$, 98%), hexadecyltrimethylammonium bromide or CTAB ($C_{19}H42BrN$, ≥98%), Silver Nitrate ($AgNO_3$, 99.8-100.5%), and L-ascorbic acid ($C_6H_8O_6$) were purchased from Sigma Aldrich (USA). All reagents were used as received without further purification. De-Ionized water (DIW) with resistivity 18.2 MΩcm was used for all solution preparations, which was prepared using a Millipore RiOs water purification system. Indium tin oxide (ITO) coated glass slide with surface resistivity of 8-12 Ω/sq was used as substrate. All glassware and substrate were cleaned by sonication in DIW, acetone (R&M Chemicals), and 2-propanol (R&M Chemicals) for 15 minutes, respectively, and then dried in oven with temperature 50 ºC.

2.2 Synthesis

The gold nanorices are synthesized using seed-mediated growth method (SMGM). This method requires two basic process, namely seeding and growth processes. Seeding process was performed to plant nanoseeds. This nanoseeds was used to promote growth avoid randomness of natural crystal growth and controlling critical parameters. Meanwhile growth process was carried out to growing the nanoparticles from nanoseeds.

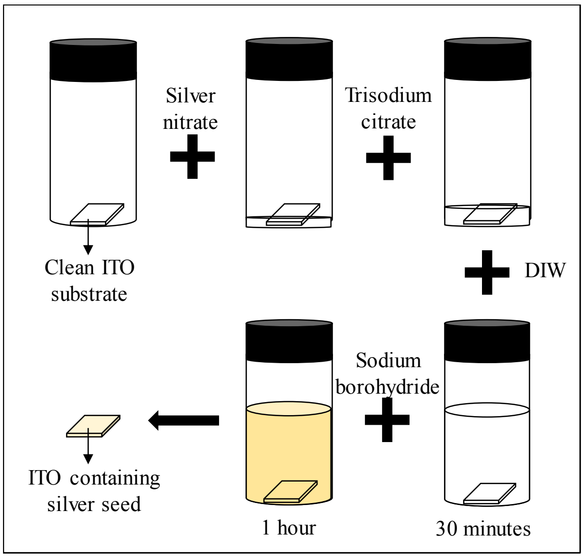

Fig. 1 Schematic of seeding process of silver seeds.

The citrate-stabilized silver nanoseeds was prepared from the method of Oyama and co-workers [13] with minor modification. In typical process, seed process was carried out by placed clean ITO substrate (5 mm x 5 mm) in bottom of glass vial. Then, 0.5 ml of 0.01 M silver nitrate, 0.5 ml of 0.01 M trisodium citrate, and 19 ml DIW were mixed in a glass vial and assisted by gently shaking for 5 minutes to ensure efficient mixing. This solution left undisturbed at temperature 28 ºC. After 30 minutes, freshly prepared 0.5 ml ice-cold 0.1 M $NaBH_4$ was rapidly injected into the solution and color of the solution drastically changes from colorless to yellow, which indicating the formation of silver seed. The solution was left undisturbed at temperature 28 ºC for another 1 hour. After 1 hour, the ITO substrate containing silver seeds was taken out from the seed solution and rinsed with DIW. The remained water on the sample surface was removed by touching the edges of the sample on the tissue paper. After that, the sample was dried in oven at temperature 50 ºC for 1 hour. Before further use in growth process, the sample was placed in petri dish and sealed with parafilm. The schematic of silver seeding process is shown in Fig. 1.

The growth of gold nanorices was carried out by immersing the ITO containing silver seed sample into growth solution which was prepared by mixing 0.5 ml of 0.01 M $HAuCl_4$, 20 ml of 0.1 M CTAB, and 0.12 ml of 0.1 M ascorbic acid in temperature 28 ºC. After 45 minutes, the sample was carried out from growth solution and rinsed with DIW for three times. Lastly, the sample was dried in oven with temperature 50 ºC for 1 hour and annealed at temperature 100 ºC for 1 hour to remove the surfactant and organic compounds. Fig. 2 shows schematic of gold nanorices growth process.

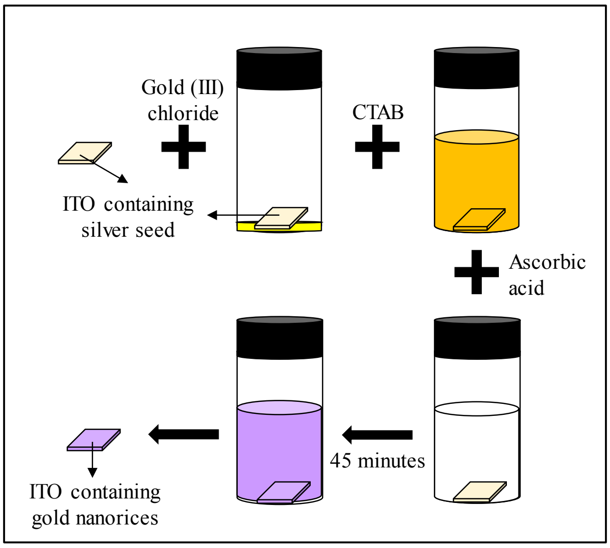

Fig. 2 Schematic of the growth process of gold nanorices.

In order to compare the structure of gold nanoparticles, synthesis process using gold nanoseeds was performed. ITO containing gold nanoseeds were obtained by immersing clean ITO substrate in gold seed solution which prepared by mixed 0.5 ml of 0.01 M $HAuCl_4$, 0.5 ml of 0.01 M trisodium citrate, and 19 ml of DIW for 30 minutes. Then, 0.5 ml ice-cold 0.1 M $NaBH_4$ was injected into this solution and left undisturbed for another 1 hour. Lastly, ITO substrate was rinsed with DIW and dried in an oven with temperature 50 ºC. Further, ITO containing gold nanoseed are immersing into growth solution which prepared at same condition for gold nanorices. The difference between these two synthezing processes is metal source used in seeding process; silver and gold.

2.3 Characterization

The optical properties of the sample were recorded by using UV-Vis spectrophotometer brand Shimadzu model UV-1800 (Japan) in the range of wavelength from 400 to 800 nm. A field emission scanning electron microscopy (FESEM) from Joel JSM-7600F Schottky (USA) was employed to characterize the morphology of the sample. The structural properties of the samples were characterized using a X'Pert Powder X-Ray diffractometer from PANalytical (Netherlands) with CuKα radiation at a wavelength (λ) of 0.1540 nm with a step size of 0.03º. The detected data was taken in a 2θ range of 10º to 70º

3. Results and Discussion

Gold nanorices synthesized using silver seed had been successfully attached on ITO substrate using seed-mediated growth method. UV-Vis absorption spectrum of the sample is shown in Fig. 3. The result shows that UV-Vis spectrum of the gold nanorices exhibit two distinct peaks. First peak observed at wavelength 541 nm and second peak observed at wavelength 730 nm. The first and second peak are assigning to a transversal surface plasmon resonance (t-SPR) absorption band and a longitudinal (l-SPR) absorption band for cylindrical gold nanoparticles, respectively [14], [15].

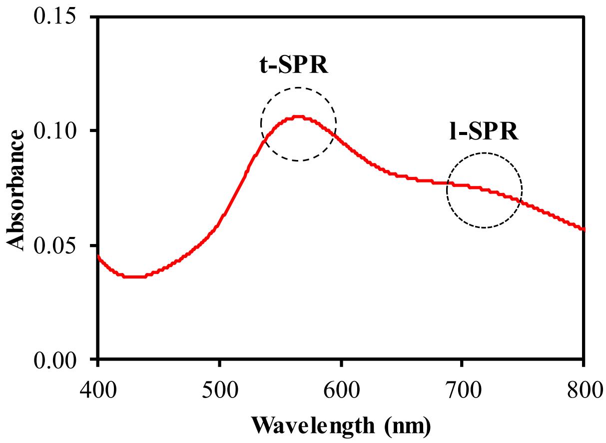

Fig. 3 UV-Vis absorption spectrum of the gold nanorices.

Fig. 4 provides FESEM image of the sample. Fig. 4a is a low magnification FESEM image of the sample. it reveals that gold nanoparticles, represent by white grain, are achieved using this approach. Magnified FESEM images of individual gold nanorices are shown in Fig. 4b and 4c. The analysis for long axis and short axis of nanorices were done using ImageJ software. This software calculated area gold nanoparticles at 304 x 304 pixels with total area of FESEM image is 8.39×10^5 nm^2. The gold nanorices obtained have average long axis size (a) of 55.54±3.30 nm and short axis size (b) of 28.71±2.30 nm. The aspect ratio of gold nanorices are 1.98±0.09 determined by calculation of long axis over short axis (a/b).

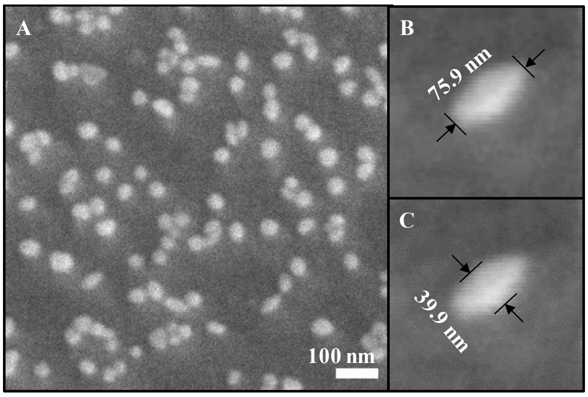

Fig. 4 FESEM image of the obtained gold nanorices grown on substrate (a) at magnification 50K, (b) single gold nanorices and its long axis size and (c) single gold nanorices and its short axis size obtained from magnification 100K.

Furthermore, the structure of the sample was examined by XRD characterization. Fig. 5 shows XRD pattern of as prepared sample. Three diffraction peaks were obtained at 2θ = 38.18º, 44.48º, and 64.67º. All these Bragg peaks can be indexed to (111), (200), and (220). These results were matched with data for bulk gold materials standard of ICSD file No. 98-005-3763. The remarkable peaks confirmed that the as prepared nanoparticles are gold. From the pattern, the silver characteristic peaks can't be observed. This finding suggests that the surface composition of the nanoparticles prepared using this method have phase purity of gold nanocrystals. It was also found from the XRD pattern that the intensity ratio between the (111) plane and the other peak is high. This result indicating that the gold nanostructured were characterized by dominant (111) planes [16]. The detailed of all peaks are listed in Table 1.

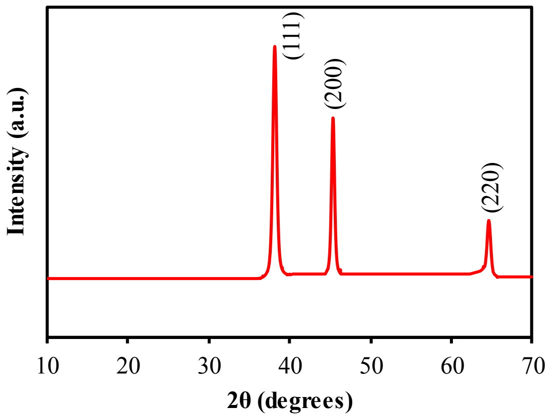

Fig. 5 XRD pattern of the gold nanorices.

Table 1 Detailed of XRD result for gold nanorices.

No.	Peak (degree)	Plane	Intensity (a.u.)
1	38.18	(111)	713.92
2	44.48	(200)	648.77
3	64.67	(220)	555.49

Likewise, in the experiments using gold nanoseeds, UV-Vis absorption spectrum of gold nanoparticles obtained exhibit only one SPR spectrum peak observed at wavelength 545 nm as shown in Fig. 6. The absorption spectrum peak is consistent with the SPR of gold nanoparticles with the spherical shape as reported in elsewhere [17], [18]. However, for good sensitivity, more than one peak resonance is required.

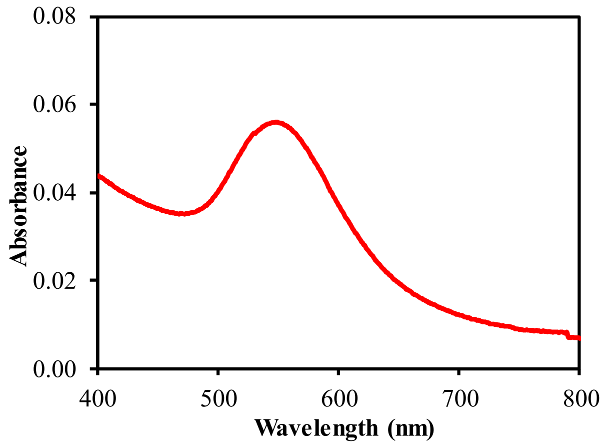

Fig. 6 UV-Vis absorption spectrum of the gold nanoparticles prepared by growth using gold nanoseeds.

FESEM images of gold nanoparticles synthesized using gold nanoseeds are shown in Fig. 7. In present experiment protocol, gold nanoparticles obtained mostly have a spherical shape. Moreover, the average diameter of gold nanosphericals is 22.24±1.58 nm, estimated by calculation using ImageJ. Hence, the gold source can only produces gold nanosphericals using this recipe not gold nanorices.

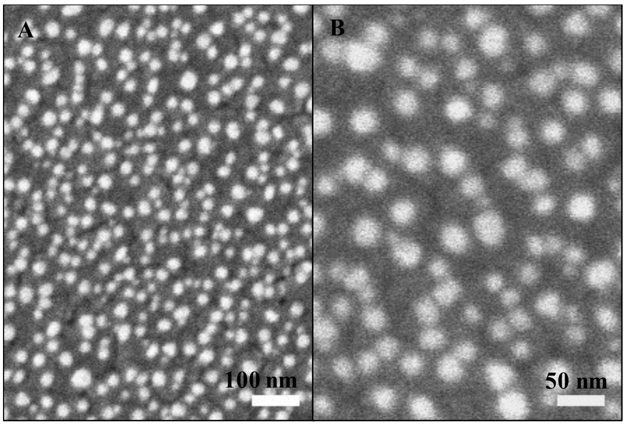

Fig. 7 FESEM image of gold nanosphericals obtained by grown using gold seed at magnification (a) 50K and (b) 100K.

In this study, we found that introduction of silver nanoseeds leading the formation of gold nanoparticles with nanorices structures. It is presumed that when silver nanoseeds introduced in the growth process, it allowing for easier growth access in a certain direction, especially in the tip end and resulting shape changes from spherical nanoseeds to gold nanorices. Here, silver nanoseeds play an important role as a sacrificial template to generate the gold nanorices. This result agrees with prior studies that introducing silver ions could control the geometry of cylindrical gold nanoparticles such as gold nanorods and nanobipyramids [19], [20]. However, the underpotential deposition of silver nanoseeds on control growth mechanism that leads to the formation shape of nanorices is a complex mechanism because it is a combination of multiple growth factors such as metal precursor, surfactant, reducing agent, surface molecules, pH of growth solution and so on. Therefore, a systematic study is necessary to isolate the effect of each factor and further may offer some clues. Meanwhile, when gold nanoseeds is used, the rate of growth process occurs same in every direction, resulting in gold nanoparticles with sphericals shape in end of the growth process.

4. Summary

The gold nanorices with long axis size of 55.54±3.30 nm, shot axis size of 28.71±2.30 nm, and aspect ratio 1.98±0.09 has been successfully synthesized on ITO substrate using seed-mediated growth method (SMGM) by modifying the reaction condition for gold nanoparticles. In this work, gold nanorices was grown from citrate-stabilized silver nanoseeds. The results from UV-Vis absorbance show that gold nanorices exhibit two distinct localized surface plasmon resonance (LSPR) at wavelength 541 nm and 730 nm peak which has very potential application for plasmonic sensing.

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References

[1] V. G. Yarzhemskii, M. A. Kazaryan, and E. N. Murav, "Electronic Structure and Optical Properties of Gold Nanoparticles," *Bull. Lebedev Phys. Inst.*, vol. 39, no. 9, pp. 254–255, 2012.

[2] A. A. Odintsov, A. A. Revina, K. N. Zhavoronkova, and O. A. Boeva, "Catalytic Properties of Gold Nanoparticles Prepared in Reverse Micelles," *Prot. Met. Phys. Chem. Surfaces*, vol. 52, no. 2, pp. 223–224, 2016.

[3] J. Lee, "Recent progress in gold nanoparticle-based non-volatile memory devices," *Gold Bull.*, vol. 43, no. 3, pp. 189–199, 2010.

[4] A. A. Umar and M. Oyama, "Growth of High-Density Gold Nanoparticles on an Indium Tin Oxide Surface Prepared Using a ' Touch ' Seed-Mediated Growth Technique 2005," *Cryst. Growth Des.*, vol. 5, no. 2, pp. 599–607, 2005.

[5] N. Sri, A. A. Umar, and M. M. Salleh, "The Effect of Nanoseed Concentration on the Aspect Ratio of

Gold Nanorod," *Adv. Mater. Res.*, vol. 364, pp. 254–259, 2012.

[6] A. A. Umar and M. Oyama, "High-Yield Synthesis of Tetrahedral-Like Gold Nanotripods Using an Aqueous Binary Mixture of Cetyltrimethylammonium Bromide and Hexamethylenetetramine & DESIGN 2009," *Cryst. Growth Des.*, vol. 9, no. 2, pp. 1146–1152, 2009.

[7] J. H. M. Maurer, B. Reiser, I. Kanelidis, and T. Kraus, "Templated Self-Assembly of Ultrathin Gold Nanowires by Nanoimprinting for Transparent Flexible Electronics," *Nano Lett.*, vol. 16, no. 5, pp. 2921–2925, 2016.

[8] C. Chiu, P. Chung, K. Lao, C. Liao, and M. H. Huang, "Facet-Dependent Catalytic Activity of Gold Nanocubes, Octahedra, and Rhombic Dodecahedra toward 4 ‑ Nitroaniline Reduction," *J. Phys. Chem. C*, vol. 116, no. 44, pp. 23757–23763, 2012.

[9] M. Morsin, M. M. Salleh, A. A. Umar, and M. Z. Sahdan, "Gold Nanoplates for a Localized Surface Plasmon Resonance-Based Boric Acid Sensor," *Sensors*, vol. 17, no. 5, p. 947, 2017.

[10] E. Cao, W. Lin, M. Sun, W. Liang, Y. Song, and O. Access, "Exciton-plasmon coupling interactions : from principle to applications," *Nanophotonics*, vol. 4, p. 472, 2017.

[11] H. Wang, D. W. Brandl, F. Le, and P. Nordlander, "Nanorice : A Hybrid Plasmonic Nanostructure," *Nano Lett.*, vol. 6, no. 4, pp. 827–832, 2006.

[12] M. Morsin, M. Mat, and M. Zainizan, "Investigation on the Growth Process of Gold Nanoplates Formed by Seed Mediated Growth Method," *Procedia Eng.*, vol. 184, pp. 637–642, 2017.

[13] G. Chang, J. Zhang, M. Oyama, and K. Hirao, "Silver-Nanoparticle-Attached Indium Tin Oxide Surfaces Fabricated by a Seed-Mediated Growth Approach," *J. Phys. Chem. B*, vol. 109, no. 3, pp. 1204–1209, 2005.

[14] Y. Y. Yu, S. S. Chang, C. L. Lee, and C. R. C. Wang, "Gold nanorods: electrochemical synthesis and optical properties," *J. Phys. Chem.*, vol. 101, no. 34, pp. 6661–6664, 1997.

[15] P. Jorge, I. Pastoriza-santos, L. M. Liz-marz, and P. Mulvaney, "Gold nanorods: Synthesis, characterization and applications," *Coord. Chem. Rev.*, vol. 249, pp. 1870–1901, 2005.

[16] M. Morsin, M. M. Salleh, M. Z. Sahdan, and F. Mahmud, "Effect of Seeding Time on the Formation of Gold Nanoplates," *Int. J. Integr. Eng.*, vol. 9, no. 2, pp. 27–30, 2017.

[17] X. Huang, I. H. El-sayed, and M. A. El-sayed, "Gold nanoparticles: interesting optical properties and recent applications in cancer diagnostics and therapy," *Nanomedicine*, vol. 2, no. 5, pp. 681–693, 2007.

[18] M. Treguer-Delapierre, J. Majimel, S. Mornet, E. Duguet, and S. Ravaine, "Synthesis of non-spherical gold nanoparticles," *Gold Bull.*, vol. 41, no. 2, pp. 195–207, 2008.

[19] S. S. Chang, C. W. Shih, C. D. Chen, W. C. Lai, and C. R. C. Wang, "The shape transition of gold nanorods," *Langmuir*, vol. 15, no. 3, pp. 701–709, 1999.

[20] M. Liu and P. Guyot-sionnest, "Mechanism of Silver (I)-Assisted Growth of Gold Nanorods and Bipyramids," *J. Phys. Chem. B*, vol. 109, pp. 22192–22200, 2005.