

Practical Synthesis of Au Nanowires via a Simple Photochemical Route

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The synthesis and characterization of nanosized materials is an important issue in basic science research as well as in technological applications, since their optical, electronic, magnetic, and catalytic properties differ greatly from the bulk materials. The properties of nanomaterials are critically dependent not only on particle size but on particle shape as well.^{1,4} Therefore, considerable effort has focused on size and shape selective nanocrystal growth using a variety of synthetic methods, including electrochemistry,^{5,6} templating,⁷⁻¹⁰ photochemistry,¹¹⁻¹³ and seeding.¹⁴⁻¹⁷

Anisotropic gold nanoparticles have been synthesized by several wet chemical routes. Fairly uniform gold nanorods with a controlled aspect ratio have been prepared by electrochemical reduction in the presence of rod-shaped concentrated cationic surfactants and cosurfactants, namely soft templates.⁶ Rod-like or thread-like surfactant micelles can be utilized to prepare gold nanorods by chemical and photochemical reduction methods.¹²⁻¹⁶ Several groups have shown that the addition of silver ions to the gold growth solution is an important factor in controlling the aspect ratio of Au nanorods.^{11,16} Polycrystalline rod-shaped gold particles have been prepared by electrochemical reduction in hard templates such as mesoporous aluminum oxide or polycarbonate membranes.⁷⁻⁹ More recently, seed-mediated crystal growth has been used in the synthesis of uniform Au nanorods, in which the seed concentration appears to be critical for shape-selective gold nanowire formation.¹⁴⁻¹⁶

In this communication, we describe a simple photochemical synthetic route for the production of Au nanowires. Long, freestanding, and continuous Au nanowires were prepared without the addition of spherical seeds or silver ions at ambient conditions. The ratio of AuCl₄⁻ to cationic surfactant, hexadecyltrimethylammonium bromide (CTAB), and the pH of the solution used for the growth play important roles in Au nanowire formation.

In a typical preparation, 1.5 mL of 0.5 mM aqueous HAuCl₄, 0.9-1.5 mL of 2 mM aqueous CTAB, 6-33 mL of 0.5 M aqueous NaOH, and 0.0-0.6 mL of deionized water were added to a quartz cuvette to give a total volume of 3 mL. The solution was mixed gently for 10 sec and then irradiated with a 365 nm UV light for about 9 h at a distance of 10 cm from the light source, at room temperature. The color of the resulting solution was bluish-violet. Absorbance spectra of the Au nanowire dispersions were obtained using a Cary 3 UV-Vis spectrophotometer. Low magnification and high resolution TEM studies were carried out on a JEM-

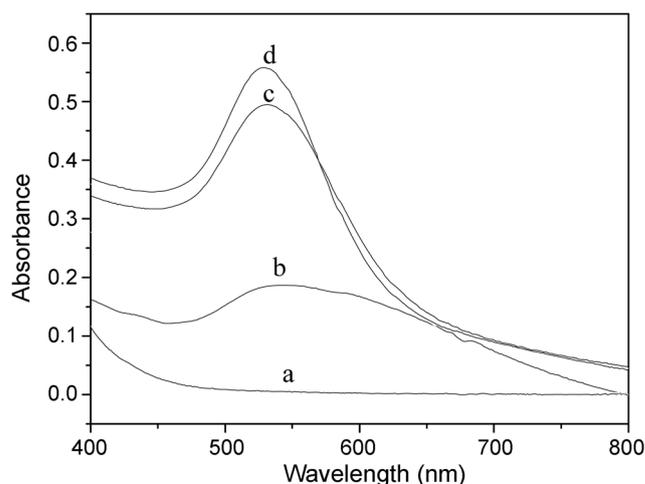


Figure 1. UV-Vis Spectra of (a) mixed solution containing HAuCl₄, CTAB, and NaOH before UV irradiation and Au nanocrystals produced during the course of UV irradiation for (b) 3 h, (c) 6 h, (d) 9 h.

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Figure 1a shows the UV-Vis spectrum of the solution before irradiation, which contained HAuCl₄, CTAB, and NaOH. Figures 1b-d show the UV-Vis spectra of Au nanocrystals that were produced in the course of UV irradiation. The color of the pure HAuCl₄ solution was light yellow, while the solution containing HAuCl₄ and CTAB appeared dark yellow in color. The color of the solution changed to a very light yellow or almost clear after the addition of different amounts of NaOH. As the UV irradiation time increased, the solution changed to a violet color with a blue tint, and a new absorption band appeared at around 530 nm, which corresponds to the known surface plasmon absorption band of Au nanocrystals.

One drop of the reaction mixture was placed on a carbon-coated copper grid for transmission electron microscopy (TEM) analysis. TEM images were obtained from samples prepared with different UV irradiation times. The TEM images were taken without any further separation procedure like centrifugation. Figures 2a-c show TEM images that correspond to the evolution of Au nanowires that probably originated from Au nanoparticles. Numerous gold nanoparticles, the diameters of which were not uniform, were observed during UV irradiation. After 3 h of irradiation, numerous tadpole-shaped Au nanoparticles were observed, indicated by arrows in Figure 2a. We assume that in the current preparation conditions, irregular Au nanoparticles

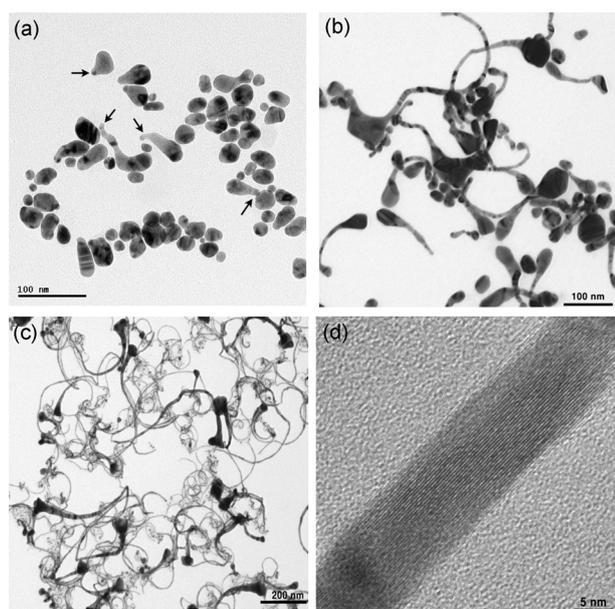


Figure 2. TEM images of the gradual evolution of Au nanowires during UV irradiation for (a) 3 h, (b) 6 h, (c) 9 h. Tadpole-shaped Au nanoparticles are indicated with arrows in (a). (d) High-resolution TEM image of a gold nanowire.

are produced at the beginning of UV irradiation and that the Au nanoparticles subsequently serve as seeds for their growth, which ultimately promotes growth of a 1-dimensional nanostructure. This was confirmed by TEM analysis. Longer UV irradiation resulted in further elongation of the tails of the gold nanoparticles, as shown in Figures 2b-c. High yields of well-defined Au nanowires were produced, which were continuous as can be seen in Figure 2c. Figure 2d shows a high resolution TEM image of a highly crystalline gold nanowire with a diameter of ~ 10 nm. The diameters of photochemically synthesized Au nanowires were in the range of 10-20 nm, and the lengths were several hundred nanometers to several micrometers.

Energy dispersive X-ray (EDX) spectrum recorded on photochemically synthesized Au nanowires was obtained and this data indicates that the synthesized Au nanowires are single phase gold. (see Supplementary Information)

Several control experiments were performed in order to identify the mechanism of deposition. When the photochemical reaction was carried with gold nanospheres added as seeds, the yield of nanowire increased slightly. This indicates that nanoparticles, either produced photochemically at the beginning of the process or added externally, could be used as seeds to promote 1-dimensional nanostructure growth in the presence of surfactants under the photochemical conditions used herein. In addition, the effect of CTAB concentration was investigated at a constant AuCl_4^- concentration (2.5×10^{-4} M). Au nanowires were formed in a CTAB concentration range of $0.6 \times 10^{-3} \sim 1 \times 10^{-3}$ M. When the concentration of CTAB was less than 0.6×10^{-3} M, only Au nanoparticles were produced. (see Supplementary Information) It has been reported that hexadecyltrimethylammonium chloride (CTAC) promotes

the formation of rod-shaped micelles at a concentration of ~ 30 wt %, ¹² which is a higher concentration than that used in our surfactant system. The critical micellar concentration (CMC) of CTAB is known to be 0.001 M at temperatures below 301 K and it has also been reported that the CMC for CTAB is decreased significantly by the addition of a salt, such as sodium salicylate or sodium chloride.¹⁸ At this point, it is not clear how gold nanowires were produced at this low surfactant concentration under our photochemical reduction conditions, but our preliminary results suggest that the addition of HAuCl_4 to the low concentration of CTAB solution might induce the formation of micelle shapes, threadlike or rod-shaped, for the formation of Au nanowires.

When the pH of the initially mixed solution (acidic, pH ~ 5) was not adjusted to a basic pH > 9 , the major products under the same photochemical conditions were irregular Au nanoparticles, indicating that pH is an important factor in the formation of Au nanowires. This is consistent with previous reports on the chemical synthesis of Au nanorods and fibrous nanoparticles.¹⁵

In conclusion, freestanding and continuous Au nanowires with aspect ratios > 100 were prepared without the addition of seeds or silver ions *via* a simple photochemical process at ambient conditions. The concentration of cationic surfactant, hexadecyltrimethylammonium bromide (CTAB), and the pH of gold growth solution play important roles in Au nanowire formation. Our ongoing project is currently directed to the synthesis of other metal systems including Ag and Pd.

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References

- Creighton, J. A.; Eadon, D. G. *J. Chem. Soc., Faraday Trans.* **1991**, 87, 3881.
- Cao, Y. W.; Jin, R.; Mirkin, C. A. *J. Am. Chem. Soc.* **2001**, 123, 7961.
- Link, S.; El-Sayed, M. A. *J. Phys. Chem. B* **1999**, 103, 8410.
- Wang, Z. L. *J. Phys. Chem. B* **2000**, 104, 1153.
- Chang, S.; Shih, C.; Chen, C.; Lai, W.; Wang, C. R. *C. Langmuir* **1999**, 15, 701.
- Yu, Y.; Chang, S.; Lee, C.; Wang, C. R. *C. J. Phys. Chem. B* **1997**, 101, 6661.
- Yu, J.; Kim, J. Y.; Lee, S.; Mbindyo, J. K. N.; Martin, B. R.; Mallouk, T. E. *Chem. Comm.* **2000**, 24, 2445.
- Wirtz, M.; Martin, C. R. *Adv. Mater.* **2003**, 15, 455.
- Han, Y.; Kim, J. M.; Stucky, G. D. *Chem. Mater.* **2000**, 12, 2068.
- Nicewamer-Pena, S. R.; Freeman, R. G.; Reiss, B. D.; He, L.; Pena, D. J.; Walton, I. D.; Cromer, R.; Keating, C. D.; Natan, M. J. *Science* **2001**, 294, 137.
- Kim, F.; Song, J. H.; Yang, P. *J. Am. Chem. Soc.* **2002**, 124, 14316.
- Esumi, K.; Matsuhisa, K.; Torigoe, K. *Langmuir* **1995**, 11, 3285.
- Esumi, K.; Hara, J.; Aihara, N.; Usui, K.; Torigoe, K. *J. Colloid Interface Sci.* **1998**, 208, 578.
- Murphy, C. J.; Jana, N. R. *Adv. Mater.* **2002**, 14, 80.
- Busbee, B. D.; Obare, S. O.; Murphy, C. J. *Adv. Mater.* **2003**, 15, 414.
- Nikoobakht, B.; El-Sayed, M. A. *Chem. Mater.* **2003**, 15, 1957.
- Sun, Y. G.; Xia, Y. N. *Adv. Mater.* **2002**, 14, 833.
- Goyal, P. S.; Dasannacharya, B. A.; Kelkar, V. K.; Monohar, C.; Rao, S.; Valaulikar, B. S. *Phys. B* **1991**, 174, 196.