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Synthesis of Gold Nanorods/Nanobelts and Their Potent Electrocatalytic Properties toward Ethanol Oxidation

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This paper describes surfactant-free and template-free synthesis of gold nanorods/nanobelts (Au-NRBs) using ciprofloxacin (CF) as a reducing/stabilizing agent (a fluoroquinolone antibiotic). Synthesized Au-NRBs were stable and easily soluble in water. Scanning electron microscopy, energy-dispersive X-ray spectroscopy (EDS), transmission electron microscopy (TEM), and UV–visible spectroscopy are used for characterization of synthesized Au-NRBs. Indeed, synthesized Au-NRB-modified electrodes show high electrocatalytic properties toward oxidation of ethanol in alkaline solution (0.1 M NaOH).

Gold nanoparticles (Au-NPs) have attracted much attention in emerging nanoscience and nanotechnology. Au-NPs are highly active catalysts for many important catalytic reactions.[1] The physical properties of Au-NPs are neither those of bulk metal nor those of molecular compounds, but they strongly depend on the particle size, interparticle distance, nature of the protecting organic shell, and shape of the nanoparticles.[2] Recently, Au-NPs have profound applications in nanomedicine, catalysis, biosensing, etc.[3–5] Nonspherical gold nanoparticles such as rods (short and long),[6,7] wires, cubes,[8] nanocages,[9] (multi-)concentric shells,[10] triangular prisms,[11,12] as well as hollow tubes, capsules,[11] even branched nanocrystals[13,14] and gold nanopeanuts[15] have garnered significant research attention in the past few years. They exhibit unique and fine-tuned properties which either strongly differ or are more pronounced from those of symmetric, spherical Au-NPs. These Au nanostructures with nonspherical shapes have unusual optical and electronic properties; improved mechanical properties and specific surface-enhanced Raman spectroscopy makes them ideal structures for emerging applications in photonics, electronics, optical sensing and imaging, biomedical labeling and sensing, catalysis, and electronic devices among others.[16] Generally, additional surfactants or other capping agents were employed to control the growth of the Au nanostructures in most of these cases. Further, surface coverage of surfactant or capping agent on the Au nanostructures limits their applications in surface-enhanced Raman scattering and catalysis.[15] In particular, the introduction of templates or catalysts to the reaction system tends to make the synthetic process much more complicated. Therefore, a simple and effective methodology for the synthesis of low-dimensional Au nanomaterials would be much preferred by nanoscience researchers.

In this paper, Au-nanorods/nanobelts (Au-NRBs) were successfully synthesized by using ciprofloxacin (CF) as reducing/stabilizing agent. CF is a fluoroquinolone, a familiy synthetic antibiotics which are extremely useful for the treatment of a variety of infections, including urinary tract infections.[17] Recently, CF was reported as a capping agent for Au-NPs.[18] Here, for the first time, we demonstrate CF as an effective reducing/stabilizing agent for synthesis of Au-NRBs. The as-synthesized Au-NRBs were soluble and highly stable in water. SEM, EDS, TEM, and UV–vis spectroscopy were used for characterization. These studies proved that Au-NRBs were successfully prepared. Interestingly, synthesized Au-NRBs have used as a potent electrocatalyst of oxidation of ethanol in alkaline solution.

Au-NRBs were prepared in the following manner. A 10 mL portion of 5 mM $HAuCl_4 \cdot 3H_2O$ was stirred using a magnetic bar and the bath temperature kept at 60 °C. Next, a 10 mL portion of 5 mM CF solution (dissolved in 0.1 M HCl) was added dropwise into $HAuCl_4 \cdot 3H_2O$ solution, which resulted in a color change to intense yellow. The pH of the solution mixture was adjusted with 0.5 M NaOH from 2 to 6 with continuous stirring. During this process an orange color solution was obtained. Subsequently, the color solution was centrifuged and washed with 0.1 M HCl and deionized water to remove unreacted reagents.

The synthesized Au-NRBs can be easily dispersed in deionized water by sonication. A 20 µL portion of Au-NRB solution was cast onto a cleaned indium tin oxide glass electrode and dried at 60 °C for 30 min. Figures 1a and 1b show the representative SEM images of synthesized Au-NRBs. The size and morphology of the Au-NRBs were examined by FE-SEM. Uniformly distributed Au-NRBs were observed as in Figures 1a and 1b. The Au-NRBs with the dimension of 25–750 nm in width and 1–5 µm in length are straight and have rectangular flat tips with somewhat sharp corners. It was further confirmed by SEM analysis as shown in Supporting Information, Figure 1[24] and these results were reproducible. EDS is precisely used for qualitative and quantitative estimation of gold particles.[19] In this study, the presence of Au nanostructures was confirmed by performing EDS. The EDS spectrum revealed major peaks of Au (Supporting Information, Figure 2[24]). The UV–vis spectrum of the synthesized Au-NRBs exhibits a surface plasmon absorption band maxima at ca. 530 nm (Figure 2b). The longitudinal surface plasmon of the Au-NRBs was observed at ca. 743 nm

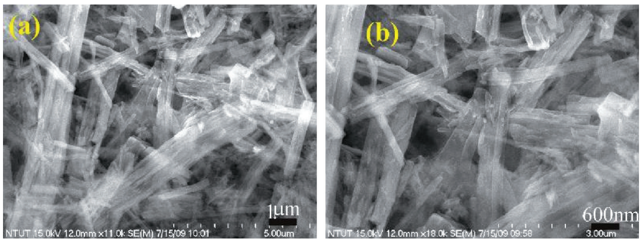

Figure 1. Representative SEM images of Au-NRBs (a, b).

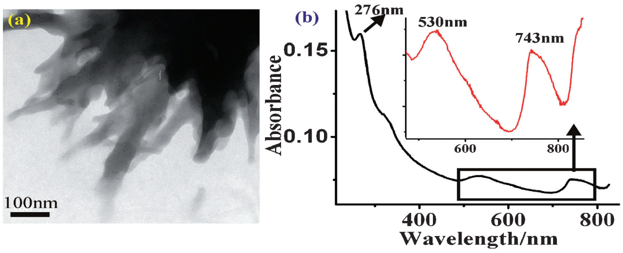

Figure 2. (a) TEM image of Au-NRBs and (b) UV–vis spectra of Au-NRB solution (0.5 mM).

(Figure 2b inset), confirming that nanorods were synthesized.[20] The sizes of the nanorods/nanobelts measured from TEM analysis were similar to the SEM measurements, as shown in Figure 2a (Supporting Information, Figure 1[24]). Under these experimental conditions, Au nanorods and nanobelts were obtained as a mixture with the approximate ratio of 10:2.

An aqueous solution of CF exhibits a UV absorption band at 276 nm due to the carboxylic group of CF.[21] The addition of $HAuCl_4$ with CF leads to the instantaneous formation of the CF–Au(III) complex (yellow color solution). This complex is more stable in acidic solution. However, when adding 0.5 M NaOH slowly into the CF–Au(III) complex solution, the color of the solution turns orange with continuous stirring. Resulting Au-NRBs were separated and used for investigation of SEM and TEM. Addition of NaOH is crucial in the formation of Au-NRBs. This was confirmed by an SEM image of a CF–Au(III) complex which shows irregular block-like microparticles. This observation is consistent with the results of Zhou et al. where addition of NaOH played a major role in the formation of gold nanocrystals.[22] Further investigations are required to elucidate the reaction mechanism in the formation of NRBs in the presence of NaOH. The synthesized Au-NRBs were covered by CF molecules which is confirmed by an additional absorption peak observed at 276 nm (Figure 2b). Adsorbed CF molecules on the nanorods control aggregation and improve their stability in water.

To test the electrocatalytic properties of synthesized Au-NRBs, we used a glassy carbon electrode (GCE) modified with 10 µL of Au-NRBs and dried at 60 °C for 30 min. Cyclic voltammograms (CVs) were recorded in 0.1 M NaOH using an Au-NRB-modified GCE, an anodic and a cathodic peak of Au-NRBs were observed at 0.60 and 0.16 V, respectively (Figure 3a curve a). Interestingly, after addition of ethanol to a 0.1 M NaOH solution, an enhanced anodic peak was observed at 0.3 V, suggesting oxidation of ethanol at the Au-NRB-modified electrode. Further, cathodic peak current of Au-NRBs at 0.16 V decreased dramatically (Figure 3a curve b). This observation suggests that the surface oxides generated by the process of premonolayer oxidation are responsible for the observed catalytic effect. As expected, unmodified GCE did not show oxidation current of ethanol in the potential window studied (Supporting Information, Figure 3).[24] The effect of ethanol concentration on the anodic current was also studied (Figure 3b curves a–g), continuous decrease in the cathodic current corresponding to the reduction of surface oxide with increasing concentration of ethanol demonstrated that the observed catalytic effect is due to the surface oxides of Au nanorods.[23]

In this study, Au-NRBs were synthesized using CF as a reducing agent. Synthesized Au-NRBs were characterized by SEM, TEM, UV–vis spectroscopy, and cyclic voltammetry. In addition, we demonstrated potential application of nanorods/nanobelts for electrocatalytic oxidation of ethanol in alkaline solution. We believe that Au-NRBs can be easily prepared by this method and that potential application is expected in electrocatalysis and biosensors.

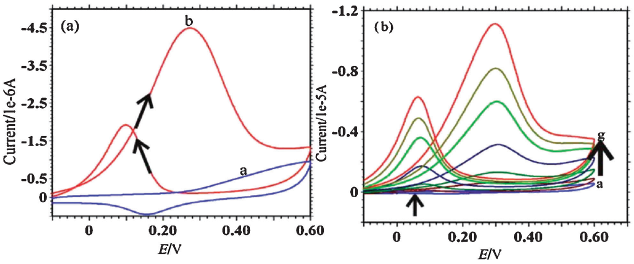

Figure 3. (a) CVs of Au-NRB-modified electrode in 0.1 M NaOH solution (curve a) and 0.5 M ethanol oxidation at Au-NRB-modified electrode (curve b). (b) CVs of different concentration of ethanol oxidation (from a to g; 0.0, 0.1, 0.2, 0.4, 0.6, 0.8, and 1.0 M) at Au-NRBs/GCE. Scan rate: 0.02 V s^{-1}.

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24 Supporting Information is available electronically on the CSJ-Journal Website, http://www.csj.jp/journals/chem-lett/index.html.