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# Preparation and electrochemical polymerization of new multifunctional pyrrolethiolate-stabilized gold and palladium nanoparticles

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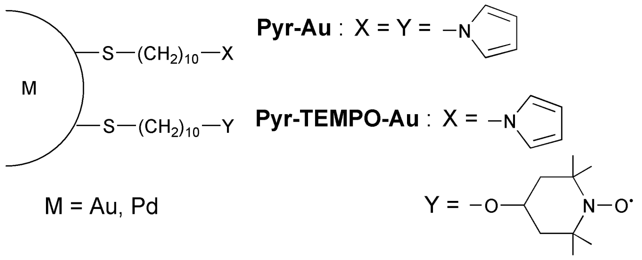
**New pyrrolylalkanethiolate-stabilized gold and palladium nanoparticles have been prepared: electrochemical polymerization of their metal nanoparticles and their TEMPO-derivatized metal nanoparticles gave the remarkably stable poly(pyrrole metal nanoparticle) films on metal electrodes.**

The study of noble metal nanoparticles has been an extremely active area in recent years because of their unique electronic, optical, and catalytic properties.[1–3] Specifically, the modification of flat solid surfaces with colloidal gold nanoparticles has received considerable interest, *e.g.*, the assembly of gold nanoparticles on glass or conductive glass substrates has been accomplished by either the adsorption of the metal nanoparticles on the substrates coated with bifunctional aminosiloxane and mercaptosiloxane as terminal ligand[4a–d] or dithiols as cross-linkers of metal nanoparticles.[4e] An intriguing further development in this area involves the attachment of electropolymerizable groups at the periphery of metal nanoparticles taking advantage of the electropolymerization process to prepare electrodes modified by electroactive poly(metal nanoparticles). Electrochemical polymerization is an elegant strategy for the immobilization of redox-active groups on the surface of electrodes. The surface modification of electrodes with electroactive polymer films has been performed from the electrochemical polymerization of pyrrole-based monomers which are the most commonly used materials.[5] Although a number of studies for functionalization of gold nanoparticles have been reported,[6–9] there is no clear-cut example of the preparation and electrochemical polymerization of ω-(*N*-pyrrolyl)alkanethiolate-stabilized metal nanoparticles and their corresponding metal nanoparticles with a redox-active functional group which shows reversible redox property. We have now synthesized ω-(*N*-pyrrolyl)decanethiolate-stabilized gold and palladium nanoparticles (Pyr-Au and Pyr-Pd nanoparticles), and new electroactive multifunctional gold nanoparticles (Pyr-TEMPO-Au nanoparticles) containing pyrrole and 2,2,6,6-tetramethylpiperidinyloxyl (TEMPO) radical groups. TEMPO derivatives show reversible redox waves in the cyclic voltammograms and are regarded as stable free radicals, excellent catalysts for the oxidation of alchohols, and organomagnetic materials.[10] This communication presents the synthesis, properties, and electrochemical polymerization of their pyrrole-functionalized metal nanoparticles.



The synthesis of Pyr-Au nanoparticles is as follows: to a vigorously stirred solution of tetraoctylammonium bromide (1.09 g, 2 mmol) in 40 mL of toluene was added $HAuCl_4 \cdot 4H_2O$ (165 mg, 0.4 mmol) in 15 mL of deionized water. A solution of ω-(*N*-pyrrolyl)decanethiol (Pyr-SH: 96 mg, 0.4 mmol)[11] in 18 mL of toluene was added, and the resulting solution was stirred for 20 min at room temperature. $NaBH_4$ (189 mg, 5 mmol) in 13 mL of deionized water was then added. The mixture was stirred for 3 h at room temperature. After stirring, the organic phase was evaporated to 5 mL *in vacuo* and mixed with EtOH (200 mL). The resulting precipitate was collected by filtration and washed serially with EtOH. The nanoparticles were redissolved in toluene to purify and precipitated with EtOH, and then the particles were isolated by filtration. These processes were repeated until no free thiol or phase transfer catalyst remained, as detected by TLC and $^1H$ and $^{13}C$ NMR spectroscopy. Analogously, Pyr-Pd nanoparticles were prepared by the same procedures as Pyr-Au nanoparticles using $K_2PdCl_4$ instead of $HAuCl_4$.

The UV-Vis spectrum of the Pyr-Au nanoparticle solution in toluene exhibited significant plasmon resonance at ~520 nm. The proton signals in the $^1H$ NMR spectra of the Pyr-Au nanoparticles and Pyr-Pd nanoparticles, though significantly broadened, appeared at positions that are almost identical to those of free Pyr-SH.[12] Transmission electron microscopy (TEM) indicated a particle size of 2.7 ± 0.3 nm for Pyr-Au nanoparticles (Fig. 1) and of 2.0 ± 0.3 nm for Pyr-Pd nanoparticles.

The electrochemical properties of Pyr-Au nanoparticles were studied by cyclic voltammetry (CV). The cyclic voltammogram of Pyr-Au nanoparticles in $CH_2Cl_2$–0.1 M $Bu_4NPF_6$ at a gold electrode showed one irreversible oxidation peak at $E_p = +0.97$ V (*vs.* Ag/0.1 M $AgNO_3$) due to oxidation of the pyrrole group (Fig. 2). In the following scans, an increase in the anodic/cathodic peaks of Pyr-Au nanoparticles is noticed as indication of the polymer growth. Similar results were also obtained with Pyr-Pd nanoparticles. Furthermore, in order to confirm the surface immobilization of the electrode with the pyrrole-functionalized gold nanoparticles by electropolymerization, new redox-active multifunctional gold nanopaticles (Pyr-TEMPO-Au nanoparticles: 2.5 ± 0.6 nm) containing pyrrole and TEMPO groups were prepared by ligand-exchange reaction of Pyr-Au nanoparticles with TEMPO-substituted decanethiol.[13,14]

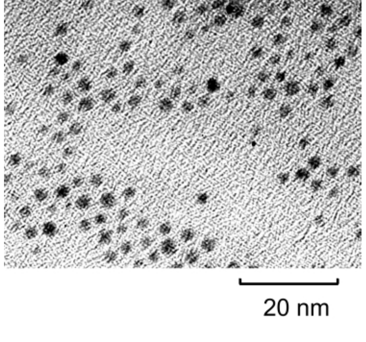


**Fig. 1** TEM micrograph of Pyr-Au nanoparticles.

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The first scan of the cyclic voltammogram of Pyr-TEMPO-Au nanoparticles in $CH_2Cl_2$–0.1 M $Bu_4NPF_6$ at a gold electrode exhibited a single reversible oxidation wave corresponding to the oxidation of the nitroxyl radical groups at $E_{1/2}$ = +0.53 V (*vs.* Ag/0.1 M $AgNO_3$), followed at higher potential by the irreversible oxidation of the pyrrole group, $E_p$ = +0.94 V [Fig. 3(a)]. Significantly, repeated scans over the 0.00 to +1.20 V range showed an increase in the redox-peak-currents of TEMPO units. After ten scans, the electrode was rinsed copiously with solvent and dipped into fresh $CH_2Cl_2$–0.1 M $Bu_4NPF_6$ solution. Fig. 3(b) indicates the cyclic voltammogram of poly(Pyr-TEMPO-Au nanoparticle) films-modified gold electrode which displayed one reversible redox peak at $E_{1/2}$ = +0.51 V. Many scans of the poly(Pyr-TEMPO-Au nanoparticle) films-modified electrode can be repeated without any change of the voltammetric wave. Thus, poly(pyrrole metal nanoparticles) bearing functional groups are readily formed as stable films on a metal electrode surface.

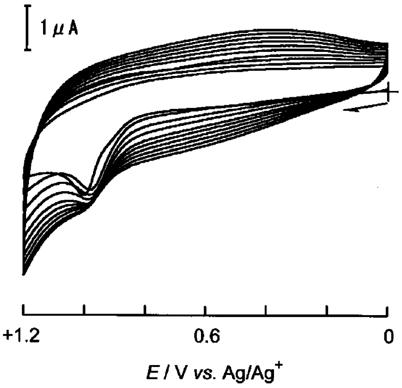

**Fig. 2** Electrochemical oxidation of Pyr-Au nanoparticles by repeated potential scans on a gold electrode in 0.1 M $Bu_4NPF_6$–$CH_2Cl_2$; scan rate 100 mV $s^{-1}$.

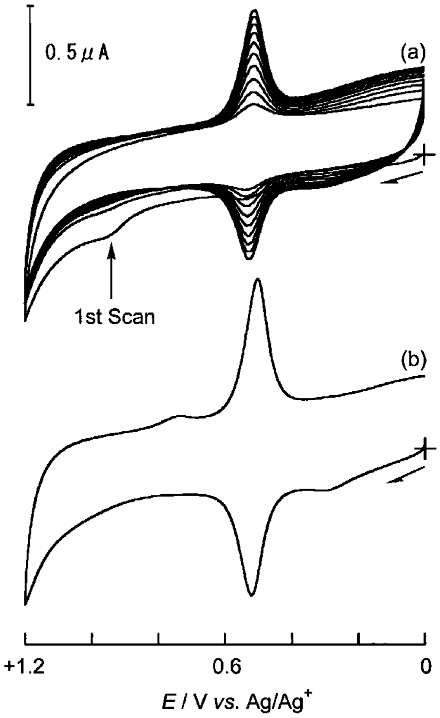

**Fig. 3** (a) Oxidative electropolymerization of Pyr-TEMPO-Au nanoparticles by repeated potential scans on a gold electrode in 0.1 M $Bu_4NPF_6$–$CH_2Cl_2$; scan rate 100 mV $s^{-1}$. (b) Cyclic voltammogram of poly(Pyr-TEMPO-Au nanoparticle) films-modified gold electrode in 0.1 M $Bu_4NPF_6$–$CH_2Cl_2$; scan rate 100 mV $s^{-1}$.

In summary, new electroactive multifunctional gold and palladium nanoparticles possessing electropolymerization sites such as pyrrole were prepared. The ligand-exchange reaction of pyrrolethiolate-stabilized gold nanoparticles with a thiol terminated functional group (*e.g.*, TEMPO) gave the corresponding multifunctional gold nanoparticles which can be immobilized on metal electrode surfaces by electrochemical polymerization. These first examples of electrogenerated poly(pyrrole metal nanoparticles) open interesting perspectives in the field of modified electrodes for electrocatalysis and electroanalysis. Further studies on the immobilization of pyrrolylthiolate-stabilized metal nanoparticles on electrodes are in progress.

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11 Pyr-SH was prepared by the general methods. **Pyr-SH**: FT-IR 2554 $cm^{-1}$ (SH); $^1H$ NMR ($CDCl_3$) $\delta$ 6.64 (t, 2H, $J$ = 2 Hz, 2,5-pyrrole), 6.13 (t, 2H, $J$ = 2 Hz, 3,4-pyrrole), 3.85 (t, 2H, $J$ = 7 Hz, $NCH_2$), 2.51 (dt, 2H, $J$ = 8, 7 Hz, C$H_2$SH), 1.75 (q, 2H, $J$ = 7 Hz, $NCH_2CH_2$), 1.59 (q, 2H, $J$ = 7 Hz, $SCH_2CH_2$), 1.42–1.23 (m, 12H, $CH_2$) and 1.32 (t, 1H, $J$ = 8 Hz, SH); $^{13}C$ NMR ($CDCl_3$) $\delta$ 120.4, 107.7, 49.7, 49.6, 33.9, 31.5, 29.3, 29.1, 28.9, 28.3, 26.7, 24.5. MS, *m*/*z* 239 ($M^+$).

12 The broadening effects of $^1H$ NMR signals in alkanethiolate-stabilized gold nanoparticles have been discussed.[7]

13 The TEMPO radical was chosen for the following reasons. (1) The oxidation peak of the TEMPO derivative does not overlap with that of the pyrrole group in Pyr-Au nanoparticles. (2) The electrochemical redox behavior of the TEMPO derivative is reversible. (3) The gold and palladium nanoparticles (TEMPO-Au and TEMPO-Pd nanoparticles) stabilized directly by the TEMPO-decanethiol were prepared by our groups: unpublished results.

14 Electron paramagnetic resonance (EPR) of Pyr-TEMPO-Au nanoparticles showed three signals (*g*-value of 2.00644) due to the TEMPO radical, which is identical to that of 4-hydroxy-TEMPO (*g*-value of 2.00642). The CV of TEMPO-Au nanoparticles showed one reversible oxidation peak at +0.53 V (*vs.* Ag/0.1 M $AgNO_3$).