Green synthesis of 1–2 nm gold nanoparticles stabilized by amine-terminated ionic liquid and their electrocatalytic activity in oxygen reduction†

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Stable gold nanoparticles with average size 1.7 nm synthesized by an amine-terminated ionic liquid showed enhanced electrocatalytic activity and high stability.

Electrocatalytically active gold nanoparticles are enjoying increasing applications in electrochemistry, electroanalysis and bioelectronics. Catalytic activity has been shown to depend strongly on the gold oxidation state, nanoparticle size and surface properties. For example, 1.3 nm gold nanoparticles exhibited superior activity in catalysis of aerobic alcohol, relative to larger (9.5 nm) particles. An established method for generating 1–3 nm gold nanoparticles is reduction of AuCl₄⁻ by sodium borohydride in the presence of an alkanethiol in water–toluene biphasic reaction systems. While the resulting nanoparticles are very stable, the reagents are hazardous. A “greener” route, reduction by citrate in water, yields particles of only limited stability. In general, preparation of gold particles with narrow size distribution in the 1–3 nm range and long-term electrocatalytic activity is difficult, and reports of suitable novel syntheses are few.

Room-temperature ionic liquids (RTILs) seem well positioned to address the challenge of preparing stable, active gold nanoparticles, due to their high chemical and thermal stability, negligible vapor pressure, recyclability, high conductivity and wide electrochemical window. Moreover, low interfacial tensions result in high nucleation rates, allowing formation of very small particles because Ostwald ripening occurs only weakly. RTILs have been successfully employed in “green” preparations of Cu₂O crystals, gold nanosheets, and nanoparticles of silver, gold or platinum. In this work, a functionalized RTIL, 1-(3-aminopropyl)-3-methylimidazolium bromide (IL-NH₂), was applied to simultaneously reduce aqueous HAuCl₄ and stabilize the resulting gold nanoparticles, which had an average diameter 1.7 nm and retained long-term stability without special protection. These IL-stabilized gold nanoparticles (Au-IL) showed better electrocatalytic activity in reduction of oxygen than similarly prepared gold nanoparticles stabilized by thiol or citrate.

The resulting orange gold suspension did not show a plasmon band in the range of 500–550 nm (Fig. 1A), qualitatively indicating average particle size less than 2 nm. The UV-vis analysis is verified easily by TEM (Fig. 1B) and HRTEM (Fig. 1C) measurements. The TEM image revealed well-dispersed gold nanoparticles with average diameter ~1.7 nm. Several particles with diameter > 2.0 nm are also present, but it was suspected that these particles arise from overlapping of two or more small particles. The formation of 1–2 nm gold nanoparticles resulted from two factors. Firstly, in the presence of ILs, gold nanoparticles undergo weak Ostwald ripening and easily formed very small gold nanoparticles. Further, the chemical and physical interaction between the ionic liquid and the metal plays a decisive role in controlling the size and structure of the nanoparticles. Fig. 1C shows a representative HRTEM image of a gold nanoparticle. Clear lattice fringes indicate high crystallinity, and d-spacing of 2.4 Å corresponds to the (111) lattice planes of gold. The selective-area-electron-diffraction (SAED) pattern (Fig. S1, ESI†) and XRD results (Fig. S2, ESI†) indicate the small Au nanoparticles possess (111) facets. Fig. 1D shows a typical XPS spectrum of Au-IL particles. While
the line shape and peak-to-peak distance of the Au 4f doublet is consistent with the Au⁰ state, the binding energies 84.3 (Au 4f⁷/₂) and 87.9 (Au 4f⁵/₂) were slightly higher than expected for bulk Au (Au 4f⁷/₂ 84.0 eV and Au 4f⁵/₂ 87.6 eV). This difference might be a consequence of the small size of these nanoparticles¹⁸e and the presence of the IL-NH₂ ligands.¹⁸f The increase in values of the binding energy with the decrease in the size is consistent with the previous reports.¹⁸a,b However, other opposite results showed that the binding energy of small gold nanoparticles decreased compared to the bulk Au.¹⁸c,d

To investigate the role of the IL-NH₂ terminal amine group, IL-NH₂ was replaced by [C₄mim]⁺BF₄⁻ (Fig. S3, ESI†) in a control reaction. Here, no change happened even after two days stirring, indicating that the terminal amine reduces [AuCl₄]⁻. At the same time, the disappearance of the primary amine peak in the control reaction’s NMR spectrum (inset of Fig. S4, ESI†), compared with the NMR spectra of IL-NH₂ (Fig. S5, ESI†) and Au-IL (Fig. S4, ESI†), confirms the reaction of the amine group.

After dialysis of Au-IL solution, the originally ca. 1.7 nm Au nanoparticles evolved into larger particles (ca. 9 nm) and hexagonal gold sheets (Fig. S6, ESI†). Removal of IL units by dialysis destabilized the nanoparticles by exposing surface area for further crystallization. This observation also confirms that IL-NH₂ plays an active role in stabilizing the gold nanoparticles, by the weak interaction of Au⁰/N.¹⁹

In addition, the ζ potential of aqueous Au-IL suspensions were as high as 35 ± 0.5 mV, which further indicated that imidazole positive termini are exposed to the outside of gold nanoparticles, illustrated in Scheme 1.

Fig. 2A shows typical cyclic voltammograms (CV) for the reduction of oxygen at electrodes functionalized with Au-IL (Au-IL f-electrode) in O₂- and N₂-saturated acidic electrolyte solutions. A well-defined peak for oxygen reduction is present at 0.28 V, while in the nitrogen-saturated systems no peak is apparent. Oxygen reduction at a naked GC electrode gave a peak at −0.50 V (inset of Fig. 2A). The 780 mV positive peak shift achieved with the functionalized electrode indicates the significant electrocatalytic effect of the Au-IL nanoparticle coating.

For comparison, CV in the same system was also conducted using Au-SH and Au-cit f-electrodes. Fig. 2B shows that oxygen reduction at the Au-SH f-electrode began at a potential of −0.51 V, approximately the same as at the naked electrode, while the Au-cit f-electrode showed a reduction peak at −0.26 V. These results indicate that the electrocatalytic activity of Au-IL nanoparticles is higher than that of thiol- and citrate-stabilized gold. Since the particle sizes of Au-IL, Au-SH and Au-cit were all quite similar, the clear difference in their voltammograms suggests that the type of the stabilizing group contributes strongly to the catalytic activity. The too strong interaction between Au and –SH reduced the catalytic activity of gold nanoparticles greatly,²⁰ the presence of –SH even prevents oxygen from reacting on the f-GC electrode surface. However, the good electrocatalysis might be attributed to the unique properties of IL, such as the high conductivity²¹ and the weak interaction of Au⁰/N.

Samples of the stabilized-gold products were kept in air without any special protection, and UV-vis absorbance was monitored over a period of more than eight months (Fig. 3). At no point did the absorbance spectrum of Au-IL change significantly, indicating that aggregation did not occur. However, in Au-cit suspensions, peak shifting was apparent after only 2.5 h (Fig. S7, ESI†) due to significant aggregation.

In conclusion, Au nanoparticles (1.7 nm average diameter) were synthesized and stabilized by 1-(3-aminopropyl)-3-methylimidazolium bromide through a one-step green method. Despite their small size, the obtained nanoparticles are very stable in air, compared to similarly prepared Au-cit particles.

Scheme 1 Structure illustration of the resulting Au-IL nanoparticles.

Fig. 3 UV-vis spectra of Au-IL nanoparticles kept at room temperature over time.

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908 | Green Chem., 2008, 10, 907–909 This journal is © The Royal Society of Chemistry 2008
of comparable size. Moreover, Au-IL nanoparticles showed significant electrocatalytic activity towards O\textsubscript{2} reduction (780 mV positive peak shift in cyclic voltammetry). Control experiments with Au-cit and Au-SH indicated that the presence of 1-(3-aminopropyl)-3-methylimidazolium bromide plays a unique role in improving the electrocatalysis of the gold nanoparticles.

**Materials**

Methylimidazole (≥98%) was distilled under a nitrogen atmosphere at reduced pressure prior to use. HAuCl\textsubscript{4}·H\textsubscript{2}O (99.9+%, Aldrich), 3-bromopropylamine hydrobromide (98%, Aldrich), 1-buty1-3-methylimidazolium tetrafluoroborate, [C\textsubscript{4}mim]\textsuperscript{+}BF\textsubscript{4}⁻ (99%, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences), ethanol (99.8%, Beijing Chemicals Company) and ethyl acetate (99.7%, Beijing Chemicals Company) were used as received. All aqueous solutions were prepared with ultra-pure water (>18 MΩ) from a Milli-Q Plus system (Millipore). All experiments were carried out at room temperature.

**Preparation of IL-NH\textsubscript{2}**

IL-NH\textsubscript{2} was prepared following our previous report.\textsuperscript{15} Briefly, 3-bromopropylamine hydrobromide (1.1000 g, 5 mmol) and 1-methylimidazole (0.395 mL, 5 mmol) were added to 12.5 mL ethanol, forming a colourless solution which was refluxed under nitrogen for 24 h. The resulting turbid mixture was purified by recrystallization from ethanol, with ethyl acetate as anti-solvent. Finally, the resulting white powder was dried overnight at 60 °C under vacuum and purity verified by \textsuperscript{1}H NMR (Fig. S5, ESI†).

**Preparation of Au-IL**

Ionic-liquid stabilized gold nanoparticles (Au-IL) were typically prepared by dissolving 0.2096 g IL-NH\textsubscript{2} (0.95 mmol) in 5.000 mL ultra-pure water, followed by dropwise addition of 1.000 mL of aqueous HAuCl\textsubscript{4}·H\textsubscript{2}O (containing 0.0080 g, 0.02 mmol) over several minutes. During addition, the colour of the resulting solution changed from yellow to orange to deep red, indicating formation of gold nanostructures. After stirring for an additional 8 h, the colour remained deep red, and some precipitate was evident, which was collected by centrifugation, washed several times with ultra-pure water and dried overnight at 60 °C under vacuum. After the re-suspension into distilled water, the colour was orange.

Preparation of gold nanoparticles stabilized by thiol (Au-SH) and citrate (Au-cit):

Au-SH (Fig. S8, 1–3 nm, ESI†) and Au-cit (3.5 nm) were prepared following Brust\textsuperscript{4} and Gao,\textsuperscript{16} respectively.

Preparation of Au-IL, Au-SH and Au-cit-functionalized glassy carbon electrode:

Au-IL, Au-SH and Au-cit samples were suspended in ethanol, respectively. And then, these suspensions were dropped onto separate 3 mm-diameter glassy carbon electrodes. After ethanol evaporated, these functionalized-Au-nanoparticle electrodes (f-electrodes) were applied in reduction of molecular oxygen.

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**Notes and references**