Synthesis of Gold Nanoparticles Modified with Ionic Liquid Based on the Imidazolium Cation

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The synthesis and processing of nanoparticles consisting of metallic nanocrystal cores and organic monolayer shells promise interesting technological applications.[1] In recent years, optical nanoprobes have been developed by modifying the surface of gold nanoparticles with various functional molecules. Gold nanoparticles have tremendously high molar absorptivity in the visible region. Particle aggregation results in further color changes of gold nanoparticle solutions due to mutually induced dipoles that depend on interparticle distance and aggregate size.[2] Gold nanoparticle aggregation-induced analytes have been demonstrated for DNA,[3] several metal ions,[4] and so on.[5]

Room-temperature ionic liquids are attracting much interest in many fields of chemistry and industry, due to their potential as a "green" recyclable alternative to the traditional organic solvents.[6] They are nonvolatile and provide an ultimately polar environment for chemical synthesis. Some ionic liquids are immiscible with water and organic solvents, giving biphasic ionic liquid systems, which enables easy extraction of products from the ionic liquid.[7] The miscibility with organic solvents or water is mostly dependent on the appropriate anions.[8]

Here, we report the synthesis and functions of gold nanoparticles modified with ionic liquids based on the imidazolium cation (Scheme 1). Hydrophilic and hydrophobic properties will be tuned by anion exchange of the ionic liquid moiety. We found the use of the aggregation-induced color changes of the gold nanoparticles in aqueous solutions as an optical sensor for anions via anion exchange of the ionic liquid moiety. We also demonstrated the phase transfer of the gold nanoparticles from aqueous media to ionic liquid. A few papers have reported the synthesis and catalytic application of composites of metal nanoparticles and ionic liquid.[9] However, to our knowledge, this is the first report of control of the surface properties of gold nanoparticles with ionic liquids based on the imidazolium cation.

An excess amount of NaBH$_4$ (2.0 mg, 0.054 mmol) was added dropwise to 10 mL of an aqueous solution of HAuCl$_4$ (5.0 mg, 0.012 mmol) in the presence of 3.3′-[disulfanylbis(hexane-1,6-diyl)]-bis(1-methyl-1H-imidazol-3-ium)dichloride (**1**) (5.5 mg, 0.012 mmol). The solution color immediately changed from yellow to dark red, indicating the formation of gold nanoparticles. The mixture was filtered through an ultrafiltration membrane (ADVANTEC USY-5, MW cutoff 50 000) to remove free **1** and ions. The UV−vis absorption spectrum of the red solution showed the surface plasmon band derived from the gold nanoparticles at around 526 nm. Figure 1a shows the transmission electron microscopy (TEM) image. The average diameter of the **1**-modified gold nanoparticles was 5.00 nm as measured by TEM. A FT-IR measurement of the **1**-modified gold nanoparticles showed that the C=C stretch vibration of the imidazolium ring was observed at 1589 cm^{-1},[10] demonstrating the surface binding of **1** to the gold nanoparticles. Thermogravimetric analysis (TGA) and elemental analysis estab-

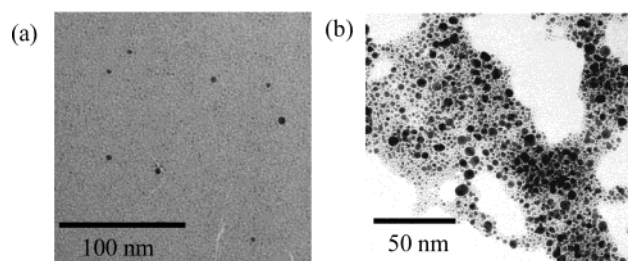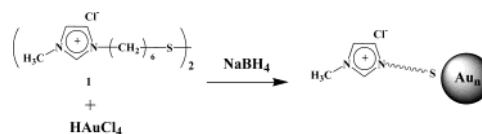**Figure 1.** TEM image of the **1**-modified gold nanoparticles (a) before and (b) after addition of HPF$_6$.

Scheme 1

lished that the content of **1** in the gold nanoparticles was 10 wt %. Based on the fact that the average particle size was 5.00 nm, the number of **1** adsorbed on the surface of each gold nanoparticle was 380.

We set out to investigate the effects that the particle-immobilized ionic liquid exerts on the properties of the gold nanoparticle. The aqueous solution (5 mL) of the **1**-modified gold nanoparticles (0.5 mg, containing 2.1×10^{-4} mmol of **1** calculated from the TGA and elemental analysis results) was prepared. The reaction of the **1**-modified gold nanoparticles with various anions was followed as a function of time through optical changes in the surface plasmon resonance in the UV−vis absorption spectrum. It is well-known that the addition of HX (X = BF$_4^-$, PF$_6^-$, and so on) to ionic liquids based on methylimidazolium chloride results in the anion exchange from Cl$^-$ to BF$_4^-$ or PF$_6^-$, respectively.[11] The same UV−vis spectrum was observed upon addition of 4.0×10^{-3} mmol of HCl, HBr, and HBF$_4$ to the solution. The presence of HPF$_6$ and HI induced a red shift ($\lambda_{max} = 539$ nm for HI and 682 nm for HPF$_6$) (Figure 2B). In the case of HI and HPF$_6$, the solution color changed dramatically from red to purple and blue, respectively (Figure 2A).

This red shift is attributed to the coupled plasmon absorbance of the gold nanoparticles in close contact, demonstrating the formation of the particle aggregates. The TEM image of the obtained solution after addition of HI and HPF$_6$ clearly indicated the particle aggregates (Figure 1b). In contrast, the TEM image indicated well-isolated homogeneous nanoparticles without any aggregates in the case of HCl, HBr, and HBF$_4$. These aggregations are due to the change of water miscibility by the anion exchange of the ionic liquid based on the imidazolium cation on the nanoparticle surface. That is, the surface property of the gold nanoparticles changed from hydrophilic to hydrophobic by the anion exchange of the ionic liquid, which led to the nanoparticle aggregation in water. In fact, **1** containing Cl$^-$ is soluble in water.
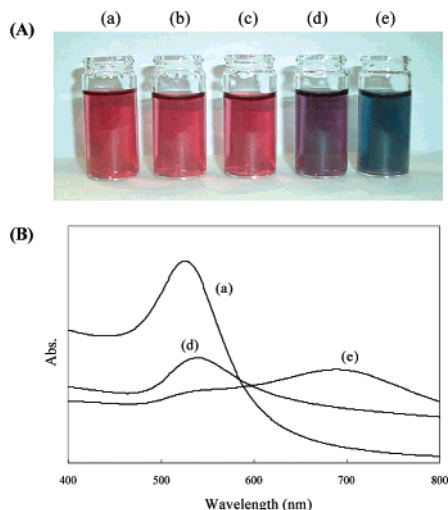
Figure 2. (A) Photographs of the obtained solutions of the **1**-modified gold nanoparticles after addition of (a) HCl, (b) HBr, (c) HBF$_4$, (d) HI, and (e) HPF$_6$. (B) UV−vis absorption spectra corresponding to (a), (d), and (e) in photograph A.

On the other hand, **1** containing PF$_6^-$ is immiscible with water. The strength of hydrogen bonding between water molecules and anions in ionic liquids increases in the order of PF$_6^-$ < BF$_4^-$.[12] The larger red shift will be expected by the addition of HPF$_6$. The described experimental results are in accordance with the expectation. Element analysis of the **1**-modified gold nanoparticles after the addition of HPF$_6$ showed that 30% of **1** immobilized on the nanoparticle surface changed from Cl$^-$ to PF$_6^-$ by the anion exchange.

The larger red shift of wavelength maximum was observed with an increase in the amount of HPF$_6$ (see Supporting Information). A similar behavior of the wavelength maximum was observed in the case of HBF$_4$ and HI (see Supporting Information). The larger red shift was observed in the order of HPF$_6$ > HI > HBF$_4$. Based on the TEM and element analysis results, the spectral changes were dominantly induced by the anion exchange under the present conditions, demonstrating that this system can be applied for optical anion sensing.

Among various known ionic liquids, ionic liquids containing imidazolium cation and PF$_6^-$ have a particularly useful set of properties, being virtually insoluble in water.[8,12] Such biphasic ionic liquid systems have been used to enable simple extraction of products. We investigate the transfer of the gold nanoparticles across a phase boundary (water to ionic liquid) via the anion exchange of the ionic liquid by addition of HPF$_6$ to an aqueous solution of the **1**-modified gold nanoparticles.

When HPF$_6$ was added to the aqueous solution containing the **1**-modified gold nanoparticles with stirring, the ionic liquid phase (1-methyl-3-hexylimidazolium hexafluorophosphate) quickly became colored, drawing from the original deep red color of the aqueous nanoparticle solution. The complete phase transfer of the gold nanoparticles was achieved. Figure 3 shows the UV−vis absorption spectrum of the aqueous solution before and after addition of HPF$_6$. Before addition of HPF$_6$, the surface plasmon absorbance of the gold nanoparticles was observed around 526 nm. In contrast, the absorption disappeared completely after addition of HPF$_6$. A TEM image of the resulting ionic liquid phase indicated the presence of the gold nanoparticles. The transferred nanoparticles displayed no signs of degradation or aggregation (see Supporting
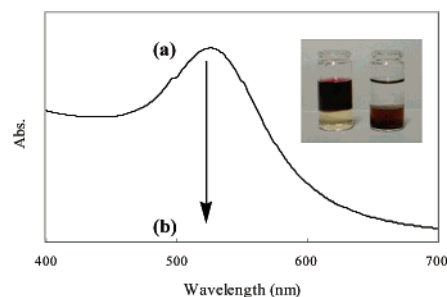

Figure 3. UV−vis absorption spectrum of the **1**-modified gold nanoparticle solution (a) before and (b) after addition of HPF$_6$. The inset shows the photograph of the solution (a) before (sample glass on the left) and (b) after (sample glass on the right) addition of HPF$_6$.

Information). These results clearly indicate that HPF$_6$ acts as an efficient phase transfer agent for the **1**-modified gold nanoparticles and allows their solubilization in the ionic liquid phase through the solubility change by the anion exchange from Cl$^-$ to PF$_6^-$.

In conclusion, we have demonstrated the synthesis of the imidazolium ionic liquid modified gold nanoparticles. This gold nanoparticle can be used as exceptionally high extinction dyes for colorimetric sensing of anions in water via a particle aggregation process. In this system, a new method to efficiently transfer gold nanoparticles from aqueous solution to ionic liquid via anion exchange has been described. Ionic liquid containing the transferred metal nanoparticles has potential for the recyclable biphasic catalysis process.

Supporting Information Available: Experimental details and characterization data of **1**. Figures of wavelength maximum versus time for the solution after addition of HI, HBF$_4$, and HPF$_6$. TEM image of the resulting ionic liquid phase (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Templeton, A. C.; Wuelfing, W. P.; Murray, R. W. *Acc. Chem. Res.* **2000**, *33*, 27.
(2) (a) Storhoff, J. J.; Lazarides, A. A.; Mirkin, C. A.; Letsinger, R. L.; Mucic, R. C.; Schatz, G. C. *J. Am. Chem. Soc.* **2000**, *122*, 4640. (b) Lazarides, A. A.; Schatz, G. C. *J. Phys. Chem. B* **2000**, *104*, 460.
(3) (a) Storhoff, J. J.; Mirkin, C. A. *Chem. Rev.* **1999**, *99*, 1849. (b) Mirkin, C. A.; Letsinger, R. L.; Mucic, C. A.; Storhoff, J. J. *Nature* **1996**, *382*, 607.
(4) (a) Kim, Y.; Johnson, R. C.; Hupp, J. T. *Nano Lett.* **2001**, *1*, 165. (b) Lin, S.-Y.; Liu, S.-W.; Lin, C.-M.; Chen, C.-h. *Anal. Chem.* **2002**, *74*, 330.
(5) (a) Thanh, N. T. K.; Rosenzweig, Z. *Anal. Chem.* **2002**, *74*, 1624. (b) Otsuka, H.; Akiyama, Y.; Nagasaki, Y.; Kataoka, K. *J. Am. Chem. Soc.* **2001**, *123*, 8226.
(6) (a) Welton, T. *Chem. Rev.* **1999**, *99*, 2071. (b) Dupont, J.; de Souza, R. F.; Suarez, P. A. Z. *Chem. Rev.* **2002**, *102*, 3667. (c) Wasserscheid, P.; Keim, W. *Angew. Chem., Int. Ed.* **2000**, *39*, 3772.
(7) (a) Fustero, S.; Pina, B.; Garcia de la Torre, M.; Navarro, A.; Ramirez de Arellano, C.; Simon, A. *Org. Lett.* **1999**, *1*, 977. (b) Blanchard, L. A.; Hancu, D.; Beckman, E. J.; Brennecke, J. F. *Nature* **1999**, *399*, 28.
(8) Anderson, J. L.; Ding, J.; Welton, T.; Armstrong, D. W. *J. Am. Chem. Soc.* **2002**, *124*, 14247.
(9) (a) Dupont, J.; Fonseca, G. S.; Umpierre, A. P.; Fichtner, P. F. P.; Teixeira, S. R. *J. Am. Chem. Soc.* **2002**, *124*, 4228. (b) Scheeren, C. W.; Machado, G.; Dupont, J.; Fichtner, P. F. P.; Texeira, S. R. *Inorg. Chem.* **2003**, *42*, 4738.
(10) Suarez, P. A. Z.; Dullius, J. E. L.; Einloft, S.; De Souza, R. F.; Dupont, J. *Polyhedron* **1996**, *15*, 1217.
(11) (a) Huddleston, J. G.; Willauer, H. D.; Swatloski, R. P.; Visser, A. E.; Rogers, R. D. *Chem. Commun.* **1998**, 1765. (b) Mathews, C. J.; Smith, P. J.; Welton, T.; White, A. J. P.; Williams, D. J. *Organometallics* **2001**, *20*, 3848.
(12) (a) Cammarata, L.; Kazarian, S. G.; Salter, P. A.; Welton, T. *Phys. Chem. Chem. Phys.* **2001**, *3*, 5192. (b) Carda-Broch, S.; Berthod, A.; Armstrong, D. W. *Anal. Bioanal. Chem.* **2003**, *375*, 191.

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