Room-temperature ionic liquids (RTILs) have received growing attention for various applications such as catalysis, electrochemistry, extractions, and, owing to their unique physical and chemical properties, as support for nanoparticles.1–4 The physical properties of ILs strongly depend on the species of cation and anion and on the length of the alkyl groups on the heterocyclic rings. Furthermore, the desired structures are easily synthesized and controlled. In particular, imidazolium-based ILs are favorable because of their air, water, and electrochemical stability and wide liquid range.

Nanoparticles have been extensively investigated owing to their unique physical properties, chemical reactivity, and potential applications with high academic and industrial impacts.5 The potentialities of metal nanoparticles are mainly due to the quantum size effect,6 which is derived from a dramatic reduction of the number of free electrons in nanoparticles smaller than 5 nm, as exemplified by specific size-dependent catalytic, optical, electronic, and magnetic properties. Therefore, the precise control of nanoparticle size and a better understanding of their chemical behavior have been recognized as key research tasks. Polymer, micelles, and coordinative ligands have been widely used as stabilizers in order to generate certain characteristic properties of nanoparticles. Brust and colleagues developed a method for facile synthesis of alkanethiol-stabilized gold nanoparticles.7,8 The study on metal nanoparticles stabilized by alkanethiol groups has contributed to the development of size-selective nanoparticle synthesis.

The stable dispersion of nanoparticles in water is important to many applications.8 However, the water-based synthesis of nanoparticles is fraught with inherent problems such as ionic interaction, low reactant concentration, and difficulty in removing the residue of stabilizers after synthesis.9 Particles synthesized in organic solvents can be made at relatively high concentrations10 with predefined size and shape and with improved monodispersity11 when compared with those prepared in aqueous media.

In the present study, we devised a novel strategy for the water-phase synthesis of monodisperse Au and Pt nanoparticles based on newly synthesized thiol-functionalized imidazolium ILs. Thiol-functionalized ionic liquids (TFILs) are potentially good candidates for stabilizers based on the following background: (1) TFILs are easily manufactured to be hydrophobic or hydrophilic according to the design of their structure, and the cation or anion in the IL can be tailored by thiol substitutes. (2) TFILs are liquids that consist of ions, and therefore the solvation and stabilization of transition metal ionic species...
The dispersion of gold and ionic liquid turned into a clear dark-brown in water was added dropwise under vigorous stirring. The turbid hexahydroxyplatinate (Na₂Pt(OH)₆) in 10 mL of water, respectively. The reaction mixture became a slightly turbid dispersion was added dropwise under vigorous stirring to a solution of 0.1 sample of TFIL (TFIL-3, TFIL-5, and TFIL-6) in 10 mL of water because of the formation of metal nanoparticles. The TFILs were prepared from 1-methylimidazole, sodium 3-mercapto-1-propanesulfonic acid, and 1-chloro-2,3-propanediol. Then, the cationic dithiol ligands in both the cation and the anion and one-pot metathesis reaction, reagents were prepared by esterification of the corresponding imidazole, and 1-chloro-2,3-propanediol. Then, the cationic dithiol ligands in either symmetrical or unsymmetrical positions in the cation and anion were so broadened that the anion substitution by the thiol group is also an important contribution to the stabilization of metal nanoparticles. At these higher magnifications, the crystalline nature of gold cores is visible by the appearance of lattice fringes. Electron diffraction reveals that all Au and Pt nanoparticles are crystalline with face-centered cubic (fcc) packing arrangements of bulk metals. The resulting histograms are presented in Figures 2 and 3. The overall analysis showed that TFILs (TFIL-3, TFIL-5, and TFIL-6) stabilized Au and Pt nanoparticles to a very small (average diameter (Åv) = 3.5, 3.1, and 2.0 nm for Au; 3.2, 2.2, and 2.0 nm for Pt) and uniform (standard deviation (SD) = 0.7, 0.5, and 0.1 nm for Au; 1.1, 0.2, and 0.1 nm for Pt) state. The average diameters and size distribution decreased with increases in the number of thiol groups in the IL. These values also were changed according to the symmetrical or unsymmetrical positions of thiol groups in the cation. The nanoparticle solutions in water were drop cast onto a 300 mesh carbon supported film copper grid. Bright field images and normal incidence selected area electron diffraction (SAED) patterns were obtained using a Phillips CM-120 high-resolution transmission electron microscope at 200 keV beam energy to determine the average particle size and distribution, as presented in Figures 1 and 2. A representative detailed section of the image in Figures 2 and 3 further corroborates the crystalline nature of these metal nanoparticles. These ILs were designed to have one, two, or more thiol groups in order to understand the effects of the number and position of thiol groups in the IL on the size and distribution of nanoparticles. Herein, we report the preliminary results on the synthesis of novel ILs terminated with thiol ligands in either symmetrical or unsymmetrical positions only in the cation and terminated with thiol ligands in both the cation and the anion and one-pot preparation of Au and Pt nanoparticles stabilized by these ligands in water.

**Experimental Section**

**The Synthesis of TFILs.** Three TFILs (TFIL-3, TFIL-5, and TFIL-6) were selected for preparing metal nanoparticles as shown in Figure 1. Scheme 1 shows the synthesis mechanism of the various TFILs. The TFILs were prepared from 1-methylimidazole, imidazole, and 1-chloro-2,3-propanediol. Then, the cationic dithiol reagents were prepared by esterification of the corresponding chlorides with mercaptoaetoxypropyl chloride. For the metathesis reaction, sodium 3-mercaptopropyl sulfonic acid was used.

**The Preparation of Metal Nanoparticles.** The one-phase preparation of Au and Pt nanoparticles in water using TFILs was straightforward, and purification of nanoparticles was carried out in ambient conditions. A 0.1 mmol portion of each sample of TFIL (TFIL-3, TFIL-5, and TFIL-6) in 10 mL of water was added dropwise under vigorous stirring to a solution of 0.1 mmol of hydrogen tetrachloroaurate (HAuCl₄) or disodium hexahydroxyplatinate (Na₂Pt(OH)₆) in 10 mL of water, respectively. The reaction mixture became a slightly turbid dispersion because of the formation of metal–sulfide group bonding. After stirring for approximately 30 min at room temperature, a freshly prepared 0.1 mmol aqueous solution of sodium borohydride (NaBH₄) in water was added dropwise under vigorous stirring. The turbid dispersion of gold and ionic liquid turned into a clear dark-brown solution immediately. In the case of the mixture of platinum salt and ionic liquid, after a few minutes, it became darker and finally a dark-green solution was obtained. The addition of a reducing agent was continued until no further gas evolution could be observed, thus making completion of the reduction. No precipitates were found in the dispersions, and they remained stable for several weeks. The stabilized Au and Pt nanoparticles could be purified by removing excess unbound ionic liquid with ethanol. The nanoparticles were precipitated, and the supernatant liquid was removed by ethanol. The nanoparticles were dried in a vacuum oven (0.04 Torr) at room temperature. The purified powder of Au and Pt nanoparticles could be kept in powder form or dispersed into water.

**Results and Discussion**

Transmission electron microscopy (TEM) images for Au and Pt nanoparticles are shown in Figures 2 and 3, which display a representative selection of the nearly spherical nanoparticles. Thin films of Au and Pt nanoparticle solutions in water were drop cast onto a 300 mesh carbon supported film copper grid. Bright field images and normal incidence selected area electron diffraction (SAED) patterns were obtained using a Phillips CM-120 high-resolution transmission electron microscope at 200 keV beam energy to determine the average particle size and distribution, as presented in Figures 1 and 2. A representative detailed section of the image in Figures 2 and 3 further corroborates the crystalline nature of these metal nanoparticles. These ILs were designed to have one, two, or more thiol groups in order to understand the effects of the number and position of thiol groups in the IL on the size and distribution of nanoparticles.
Figure 2. TEM images, size distributions, and electron diffractions of the TFIL-stabilized Au nanoparticles. Stabilizer: (a) TFIL-3; (b) TFIL-5; (c) TFIL-6.
Figure 3. TEM images, size distributions, and electron diffractions of the TFIL-stabilized Pt nanoparticles. Stabilizer: (a) TFIL-3; (b) TFIL-5; (c) TFIL-6.
The results indicate that the thiol groups in the IL are in close contact with the metal surface. Also, the treatment of Au and Pt salt with TFIL at room temperature yielded diaminocarbene. This reaction was expected to produce Au-carbene and Pt-carbene adducts at the surface of the nanoparticles. Free diaminocarbenes have been described as better donors than phosphine donors and are strongly coordinated with metals. The $^1$H NMR spectrum of Pt nanoparticles displayed no signal for H$^2$ in position 2 in the imidazolium ring, indicating deprotonation by metals in this position. The long-range coupling between the H$^4$ and H$^5$ ring protons in the nanoparticles was also no longer visible.

TFILs surrounding the nanoparticle surface can act as the most effective stabilizers of Au and Pt nanoparticles, thus becoming highly dispersible in aqueous media. The nanoparticle size and stability were affected by the position and number of thiol groups in the cation and anion of the TFILs, and therefore the chemical and physical interaction between the ILs and metals plays a decisive role in determining the nanoparticle structure. Moreover, the nanoparticle size could be tunable depending on the cation and anion structure of the stabilizer ILs. The diameter of the nanoparticles was observed to decrease as the number of thiol groups increased in the cation. Interestingly, the diameter also decreased when a sulfite anion with a thiol group was adopted. Furthermore, nanoparticles were encapsulated by TFILs, which acted to prevent agglomeration. Accordingly, the IL's functional groups in the cation and anion can be used as selective gates to control the size and uniformity of the encapsulated nanoparticles. The anion of the ILs can also be tailored to control the growth and solubility of nanoparticles in organic solvents or aqueous media.

In summary, we have demonstrated for the first time that TFILs can act as a highly effective medium for the preparation and stabilization of gold and platinum metal nanoparticles. The nanoparticle size and uniformity depend on the number of thiol groups and their position in ILs. The structural tuning of IL stabilizers provides a powerful strategy for preparing metal nanomaterials.

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**Supporting Information Available:** Synthetic mechanism of TFILs, $^1$H NMR results, and $^1$H NMR spectrum of the Pt nanoparticle. This material is available free of charge via the Internet at http://pubs.acs.org.

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