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Remarkably stable gold nanoparticles functionalized with a zwitterionic liquid based on imidazolium sulfonate in a high concentration of aqueous electrolyte and ionic liquid†

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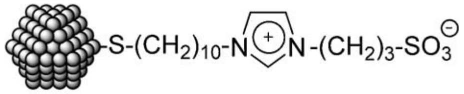
A new type of gold nanoparticle with a zwitterionic liquid function (zwitter-Au) has been prepared using an imidazolium sulfonate-terminated thiol as a capping agent. Zwitter-Au was found to be remarkably stable in high concentrations of aqueous electrolytes, ionic liquids, and protein.

Ionic liquids have received much attention as environmentally benign solvents for organic chemical reactions, catalysis, separations, and electrochemical applications.[1] Their ability to undergo multiple solvation interactions with many molecules places them among the most complex solvents.[2] Many common ionic liquids consist of nitrogen-containing organic cations and inorganic anions. Their chemical and physical properties can be tuned for a range of potential applications by varying the cations and anions. Generally, the anion has a greater influence on the property of ionic liquids. More recently, a new type of ionic liquid, like a zwitterionic liquid composed of covalently tethered cations and anions, has been developed in which the ions do not migrate along a potential gradient.[3] Ionic liquids have been used as a new type of highly efficient electrolyte.

Metal nanoparticles are of great interest because of their interesting optical, electrical, and other properties and potential applications in optics, electronics, and catalysis.[4,5] The surface properties of metal nanoparticles can be controlled by the organic functional molecules of capping reagents for metal nanoparticles. Most recently, we reported that the surface of palladium nanoparticles was activated by chiral bisphosphine as a protecting agent.[6] A limited number of syntheses and properties of metal nanoparticles in ionic liquids,[7,8] and of gold nanoparticles with imidazolium ionic liquid moieties have been reported.[9] As an example, gold nanoparticles modified with a thiol-linked imidazolium chloride as a capping group were aggregated by the addition of an electrolyte such as HPF_6 (very low concentration).[9b]

Significantly, however, we have found that gold nonoparticles stabilized by a zwitterionic imidazolium sulfonate-terminated thiol (zwitter-Au) were remarkably stable in high concentrations of an aqueous electrolyte such as NaCl, $NaNO_3$, $NaPF_6$, CF_3SO_3Na, and HCl.[10] Generally, metal nanoparticles were unstable and aggregated in electrolyte solutions.[4] Herein we report the synthesis of new gold nanoparticles (zwitter-Au) and their properties in inorganic and organic electrolytes, ionic liquids, and protein. Alkanethiol-protected gold nanoparticles are usually insoluble in water; most biological applications require that the gold nanoparticles readily dissolve in aqueous media and do not aggregate non-specifically due to electrostatic interactions. The stable dispersion of metal nanoparticles in an aqueous electrolyte is important to many applications.



Zwitter-Au

A new zwitter-disulfide **1** was prepared by a general method (see ESI†). The synthesis of zwitter-Au nanoparticles is as follows: to a vigorously stirred solution of $HAuCl_4 \cdot 4H_2O$ (157 mg, 0.38 mmol) in 50 mL of MeOH was added **1** (137 mg, 0.2 mmol) in 25 mL of MeOH at room temperature. $NaBH_4$ (227 mg, 6 mmol) in 15 mL of MeOH was then added. The mixture was stirred for 1 h at room temperature. The resulting precipitate was collected by filtration and washed periodically with MeOH. The FT-IR spectrum of zwitter-Au showed the O=S=O stretching vibrations at 1197 and 1043 cm^{-1} and the C=C stretch vibration of the imidazolium ring at 1652 cm^{-1}. The proton signals in the ^1H NMR spectrum of zwitter-Au, though significantly broadened, appeared at positions that are almost identical to those of free zwitter-disulfide **1**.[11] The X-ray photoelectron spectroscopy (XPS) spectrum of zwitter-Au showed the Au 4f binding energies at 84.2 and 87.9 eV.

Zwitter-Au was found to be insoluble in organic solvents such as *n*-hexane, benzene, $CHCl_3$, THF, ethyl acetate, MeOH, acetone, DMF, DMSO, and water. Interestingly, however, zwitter-Au was soluble in an aqueous electrolyte such as NaCl (0.2 M). Zwitter-Au was quite stable in the solid state. Lyophilized particles could be readily redissolved in aqueous electrolyte to form a clear red solution. After one month of storage in aqueous NaCl, no agglomeration was seen. It has been known that gold nanoparticles are aggregated in an aqueous solution of an electrolyte such as NaCl.[4] Aqueous solutions of the soluble zwitter-Au particles were prepared using various salts (0.2 M NaCl, $NaNO_3$, $NaPF_6$ and CF_3SO_3Na, 6 M NaCl and 2 M HCl). The stability of zwitter-Au in aqueous solutions was examined by UV–vis spectroscopy. Fig. 1(a) indicates that the UV–vis spectrum of a zwitter-Au nanoparticle solution in 0.2 M aqueous NaCl exhibited a surface plasmon resonance at 524 nm. The surface plasmon resonance of zwitter-Au in several electrolytes is as follows: 522 nm for $NaNO_3$, 526 nm for $NaPF_6$ [Fig. 1(b)], 523 nm for CF_3SO_3Na, 527 nm for 6 M NaCl [Fig. 1(c)], and 526 nm for 2 M HCl

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† Electronic supplementary information (ESI) available: experimental details and analytical data for **1**. See http://www.rsc.org/suppdata/cc/b4/b413385d/

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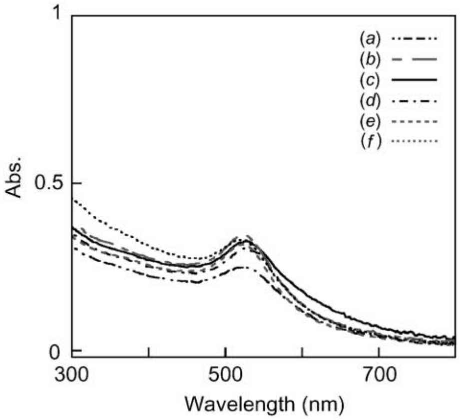

Fig. 1 UV–vis spectra of zwitter-Au in (a) 0.2 M NaCl, (b) 0.2 M $NaPF_6$, (c) 6 M NaCl, (d) 2 M HCl, (e) EMIM-BF_4, and (f) BSA.

[Fig. 1(d)]. Significantly, zwitter-Au was stable even in a high concentration of 6 M NaCl and acidic HCl for at least one month. In contrast to zwitter-Au, the gold nanoparticles modified with imidazolium chloride were aggregated due to anion exchange by the addition of a HPF_6 aqueous solution at a very low concentration (4.0×10^{-3} mmol), *i.e.*, the presence of HPF_6 induced a red shift (λ = 682 nm).[9b] Thus, the interfacial property between zwitter-Au and the gold nanoparticles modified with imidazolium chloride is quite different.

The size, shape, and dispersity of zwitter-Au were determined with transmission electron microscopy (TEM). Zwitter-Au was redissolved in 0.2 M aqueous NaCl (1 mg mL^{-1}) and a drop of the resulting dispersion was placed on a carbon coated copper grid; its micrograph reveals the formation of dispersed particles with diameters of 2.5 ± 0.4 nm (Fig. 2). The particle size of zwitter-Au in several aqueous electrolytes is as follows: 2.4 ± 0.4 nm for $NaNO_3$, 2.7 ± 0.5 nm for $NaPF_6$, and 2.4 ± 0.6 nm for CF_3SO_3Na. These results suggest that the surface property of zwitter-Au does not change with the addition of the electrolyte, because the zwitterionic liquid is composed of a covalently tethered cation and anion.

Thus, zwitter-Au was found to be soluble and stable in aqueous electrolyte solutions. Although it was reported that citrate-capped gold nanoparticles were aggregated to precipitate in a 1-*n*-butyl-3-methylimidazolium hexafluorophosphate (BMIM-PF_6) ionic liquid,[8] very few properties of metal nanoparticles in ionic liquids are known. Accordingly, we have investigated the behavior of zwitter-Au in a new type of electrolyte such as ionic liquids, *i.e.*, a water-soluble ionic liquid, 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIM-BF_4) and a water-immiscible ionic liquid, BMIM-PF_6. We have found that gold nanoparticles modified with octanethiol or octylsulfonatethiol, $HS–(CH_2)_8–O–C_6H_4–SO_3^-\ Na^+$, cannot be dissolved in both ionic liquids, EMIM-BF_4 and BMIM-PF_6.

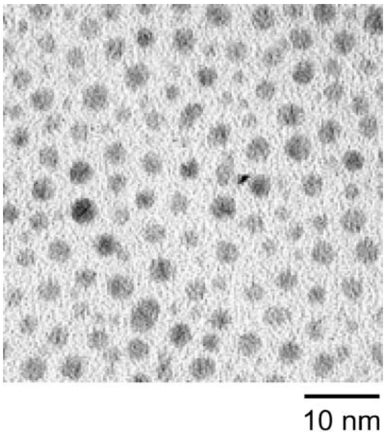

Fig. 2 TEM micrograph of zwitter-Au.

Interestingly, zwitter-Au was soluble and stable in the EMIM-BF_4 ionic liquid; its UV–vis spectrum showed a plasmon peak at 522 nm (clear red solution) [Fig. 1(e)]. The particle size of zwitter-Au in the EMIM-BF_4 ionic liquid was obtained using small angle X-ray scattering (SAXS).[12] From the SAXS analysis of zwitter-Au, an average particle size of 3.6 nm was determined. In contrast to EMIM-BF_4, the BMIM-PF_6 ionic liquid did not dissolve zwitter-Au. However, zwitter-Au was readily soluble in a 1 : 1 MeOH–BMIM-PF_6 mixture, and in aqueous BMIM-PF_6 (1–10 mmol L^{-1} in H_2O);[13] the UV–vis spectrum exhibited the plasmon absorption band at 524 nm (clear red solution), whereas zwitter-Au cannot be dissolved in only MeOH. The TEM image of the zwitter-Au in aqueous BMIM-PF_6 showed a core size of 2.8 ± 0.9 nm. These findings demonstrate that EMIM-BF_4 and BMIM-PF_6 can behave differently toward zwitter-Au. Experiments are under way to study the properties and reactions of zwitter-Au in ionic liquids.

We have further examined the property of zwitter-Au in organic electrolytes, with calix[8]arene *p*-sulfonic acid octasodium salt as an inclusion host molecule, with poly(sodium 4-styrenesulfonate) as a polymer, with a carboxylate-terminated PAMAM dendrimer (G1.5-$COO^-\ Na^+$) as a nanoscale host molecule, and with bovine serum albumin (BSA) as a protein. The UV–vis spectrum of zwitter-Au in these electrolyte solutions did not show any color changes due to aggregation; surface plasmon resonance was at 522 nm for the calix[8]arene, 523 nm for the polystyrene and 526 nm for the dendrimer. Fig. 1(f) displays the plasmon peak (λ = 522 nm) of zwitter-Au in an aqueous solution of BSA. Essentially no red shift of zwitter-Au was observed with BSA, indicating no interaction between the zwitter-Au and BSA. Such a feature is most attractive for biological applications.

In summary, we have successfully prepared a series of novel gold nanoparticles modified with a zwitterionic liquid consisting of an imidazolium cation and a sulfonate anion. Zwitter-Au has great stability in aqueous solutions with high concentrations of electrolytes, ionic liquids, and protein. These first examples of zwitter-Au open up interesting perspectives in the fields of reaction and catalysis using water- and ionic liquid-soluble metal nanoparticles based on green chemistry, and electronic and bio-analytical applications. Further studies on zwitterionic liquid-functionalized metal nanoparticles are in progress.

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11 The broadening effects of ^{1}H NMR signals in alkanethiolate-stabilized gold nanoparticles have been discussed[5b].

12 Measurements were performed on a Rigaku RINT-2500.

13 Most ionic liquids have been characterized to have polarities which are close to those of alcohols.