One-phase synthesis of small gold nanoparticles coated by a horizontal porphyrin monolayer†

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One-pot reduction of $HAuCl_4$ in a DMF solution containing a porphyrin-cored tetradentate passivant gives horizontal porphyrin monolayer-coated gold nanoparticles, whose particle size is significantly smaller than that made by using monodentate passivants under identical conditions.

Gold nanoparticles coated by an alkanethiol monolayer have attracted intense attention due to their unique optical and electronic properties that can be controlled by particle size as well as the nature of the protecting molecules.[1] Surface modification of gold nanoparticles with functional molecules has been utilized as a powerful method to create nanoscale devices such as memories, sensors and catalysts.[2,3] Introduction of functional molecules in well-defined orientation and alignment on the gold nanoparticle surface would bring about an appreciable improvement on this approach. Multipoint Au–S bond formation would be a straight way to fix functional molecules in the desired geometry. As a pioneering work, Beer and Davis's group reported that multidentate zinc porphyrin-modified gold nanoparticles exhibited enhanced anion binding ability thanks to the pre-organized structure of the zinc porphyrin receptor for anion sensing.[4] However, there are still only a few examples of multidentate ligands to passivate gold nanoparticles. Notably, Wei and co-workers first reported that tetrathiolated resorcinarene was able to stabilize large gold nanoparticles of up to 87 nm in diameter.[5] And very recently, Lee and co-workers proved that multidentate passivants can enhance the stability of large gold nanoparticles by testing a series of monodentate, bidentate and tridentate alkanethiols.[6] Not only to stabilize gold nanoparticles, multidentate ligands have also been utilized to control interparticle distances of gold nanoparticles.[7–9] Thus, the advantages of multidentate ligands to control the properties of gold nanoparticles have been demonstrated so far, but the above-mentioned gold nanoparticles were all obtained by ligand replacement from pre-made citrate-stabilized gold nanoparticles or through two-phase synthesis using phase transfer reagents like tetraoctylammonium bromide (TOAB), which is known as Brust's method.[10] In this study, we focused on a simple one-phase method; that is, the reduction of a $HAuCl_4$ solution containing multidentate passivant ligands in order to evaluate the intrinsic ability of the passivant to produce and stabilize gold nanoparticles without any assistance by other co-stabilizers such as citrate or TOAB.[6,11] Moreover, this simple system would avoid possible surface occupation by the co-stabilizers, which may block the fixation of the multidentate passivant on the gold surface.

In this study, we designed a porphyrin-based surface passivant ligand (**1**) that displays four sulfur atoms *via* rigid linkers in the same direction perpendicular to the porphyrin plane as shown in Fig. 1. Thus, we utilized the porphyrin molecule as a scaffold here, since it and its metal complexes are fascinating functional molecules exhibiting unique optical and electronic properties and high catalytic activities. The ligand **1** is expected to build up fast and tight connections with the gold surface *via* four Au–S bonds since all four S atoms are pre-oriented to form Au–S bonds and do not rotate away due to steric hindrance between the amide moiety and the porphyrin plane, as demonstrated with Collman's picket fence porphyrin.[12] Most importantly, this lunar-lander-like structure is supposed to be capable of fixing the porphyrin plane in a plane parallel with respect to the gold surface, and then enable to the gold nanoparticles to be coated with a horizontal porphyrin monolayer.[13–15]

Ligand **1** was prepared by treatment of an isolated α,α,α,α-atropisomer of 5,10,15,20-tetrakis(*o*-aminophenyl)porphyrin[16] with bromoacetyl bromide, followed by potassium thioacetate.

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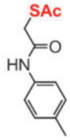

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Fig. 1 Structures of tetradentate and monodentate passivants, **1** and **2**.

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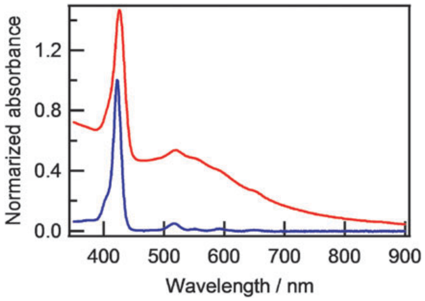

Fig. 2 UV-Vis spectra of **GN@1** (red) and **1** (blue) in DMF.

Gold nanoparticles coated by **1** (**GN@1**) were prepared by $NaBH_4$ reduction of $HAuCl_4$ in a DMF solution containing **1**. The resulting red-colored **GN@1** was then purified by repeated precipitation with methanol and chloroform to remove unbound ligand **1**. Fig. 2 shows UV-Vis spectrum of purified **GN@1** which was prepared at a molar ratio of 1 : 1 for **1** : $HAuCl_4$. The spectrum showed both features characteristic of porphyrin and gold nanoparticles: the Soret and Q bands at 426 nm and 500–670 nm, respectively, and the surface plasmon band at around 530 nm. The Soret band for **GN@1** was significantly broadened and red-shifted compared with that for **1** before reduction: 426 nm (FHW 13 nm) for **GN@1** *vs*. 422 nm (FHW 9.6 nm) for **1**, suggesting the electronic interactions between gold nanoparticles and the porphyrin and/or side-by-side alignment of **1** on the gold surface.[9,17] Although gold nanoparticles could be formed by $NaBH_4$ reduction of $HAuCl_4$ in DMF without **1**, the resultant gold nanoparticles were unstable and easily precipitated as gold chunks. In contrast, the gold nanoparticles **GN@1** did not change the surface plasmon band over weeks, apparently due to the surface coating with **1**.

Fig. 3(a) shows a representative TEM image of **GN@1**, where a crystal lattice of gold was observed. Particle analysis revealed that **GN@1** has a mean diameter of 3.5 ± 0.7 nm. The size of alkanethiol-protected gold nanoparticles has been demonstrated to be controlled by the initial thiol/gold ratio (ξ).[18] Therefore, we prepared **GN@1** at various ratios of **1** : $HAuCl_4$ from 0.025 to 4, which corresponded to ξ values from 0.1 to 16. Analyzed particles sizes are plotted against ξ values in Fig. 4, where the particle size decreased down to *ca*. 2 nm as ξ was increased to 16. To evaluate the capability of **1** to control the size of the formed gold nanoparticles, as a control we synthesized a monodentate surface passivant ligand (**2**) whose structure was taken from **1** (Fig. 1), and prepared monodentate-thiol-protected gold nanoparticles (**GN@2**) at different values of ξ from 0.1 to 16. The particle size of **GN@2** decreased as observed for **GN@1**, but was larger than those of **GN@1** when compared at the same value of ξ. We also prepared dodecanethiol-protected gold nanoparticles **GN@3** by the one-phase method, since dodecanethiol is known to stabilize gold nanoparticles by forming a closely packed self-assembled monolayer and would give smaller gold nanoparticles. In fact, however, the size of **GN@3** was larger than that of **GN@1** at every value of ξ, *i.e.* larger by 1.0 nm at $\xi = 16$. Thus, the passivant ligand **1** tends to produce smaller gold nanoparticles than monodentate passivant **2** and dodecanethiol. Although at this moment we cannot address exact mechanisms concerning how **1** determines the particle size, probably the relatively large porphyrin moiety of **1** may play a role in producing smaller gold nanoparticles.[19]

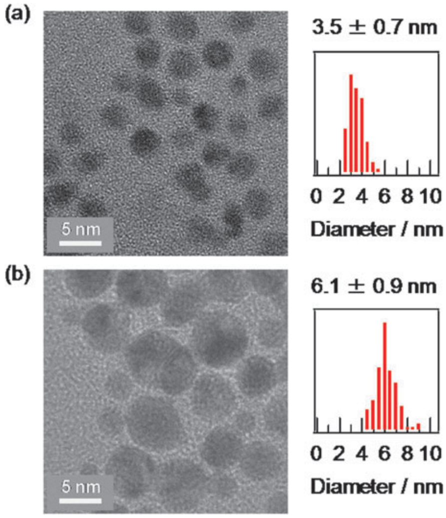

Fig. 3 TEM images of **GN@1** (a) and **GN@2** (b) with histograms of particle size to the right. The initial S to Au ratio = 1 for both cases.

To inspect the chemical status of the four S atoms of **GN@1**, X-ray photoelectron spectroscopy (XPS) measurements were carried out. Fig. 5(a) shows the S(2p) region of the XPS spectrum of **GN@1** prepared at $\xi = 1$, together with that for **1** for comparison. In the case of **GN@1**, S(2p) peaks were observed at the binding energy of 163 eV, together with a very weak peak at 170 eV. The latter peak is assignable to sulfur oxide (SO_x) of the impurities derived from **1**.[7,20] On the other hand, the main peak at 163 eV is ascribed to the alkanethiol bound to Au, judged from reported values for other alkanethiol-monolayer-protected gold nanoparticles.[7,21] Importantly, there was no peak at 164 eV that was observed for acetyl-protected S atoms of **1**. A similar spectrum was obtained with **GN@2**. Thus, these results indicate that **1** attached with the gold nanoparticle surface *via* four S–Au bonds, where the S atoms lack acetyl groups and exist as thiolate anions (Fig. 6). Therefore, it is conclusive that the porphyrin plane of **1** orients in a plane parallel to the gold surface, as we designed. Such a horizontal monolayer formation of **1** on the gold surface is in agreement with the red-shifted Soret band of **GN@1** (*vide supra*).

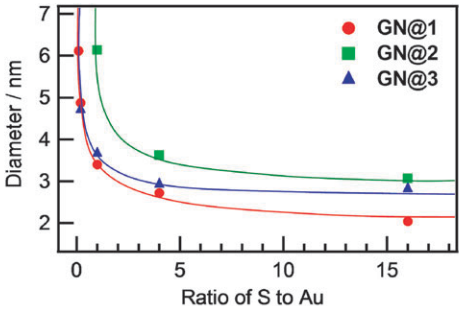

Fig. 4 Plots of the mean diameter of gold nanoparticles against the initial S to Au ratio.

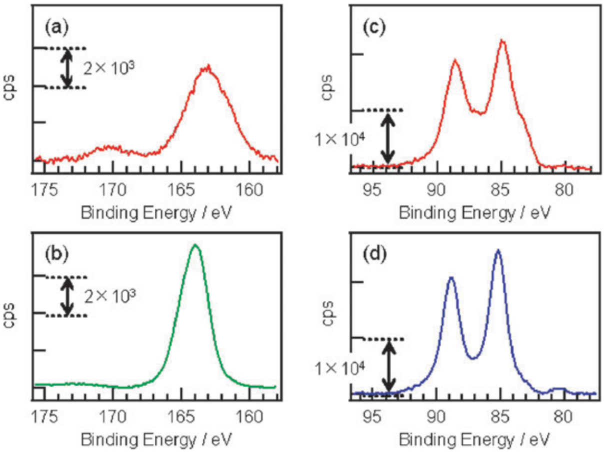

Fig. 5 XPS spectra of S(2p) core level of **GN@1** (a) and **1** (b) and Au(4f) core level of **GN@1** (c) and **GN@2** (d).

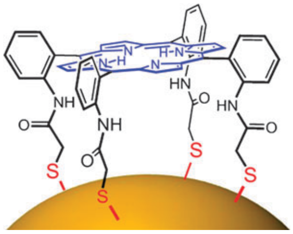

Fig. 6 Plausible structure of **GN@1**.

Fig. 5(c, d) shows XPS spectra of Au(4f) core levels. The XPS spectra exhibited an Au $4f_{7/2}$ level with a binding energy of 84.9 eV and 85.3 eV for **GN@1** and **GN@2**, respectively. These binding energies are higher than that observed for dodecanethiol-protected gold nanoparticles (83.8 eV)[10,21,22] and for bulk gold (84.0 eV). These results indicate that the gold cores of **GN@1** and **GN@2** were positively charged. In the case of **GN@1**, but not of **GN@2**, a shoulder peak was observed at around 84 eV that indicates the existence of neutrallt charged **GN@1** as a minor fraction. Although such positively charged thiol-protected gold nanoparticles are rarely known, Tsukuda and co-workers recently reported that chemical oxidation of $[Au_{25}(SC_6H_{13})_{18}]^0$ produced the corresponding positively charged gold nanoclusters.[23]

In conclusion, we have synthesized stable gold nanoparticles coated by a porphyrin monolayer by one-phase reduction of $HAuCl_4$ in DMF in the presence of a specially designed porphyrin-cored tetradentate passivant **1**. Our tetradentate passivant **1** reasonably affords a horizontal porphyrin monolayer on gold nanoparticles thanks to the four S atoms extending in the same direction. In addition, the systematic synthesis of gold nanoparticles at different values of ξ revealed that the new tetradentate passivant **1** gives smaller gold nanoparticles than monodentate ligands can. Thus, our studies demonstrated that highly functionalized multidentate passivants such as **1** are promising not only to control the size of gold nanoparticles, but also to introduce functional molecules onto the gold surface with well-defined orientation.

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