# Coordination Driving Self-assembly of Gold Nanoparticles and Tetrapyridylporphine into Hollow Spheres

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We report a facile method for self-assembling Au nanoparticles and tetrapyridylporphine into composite hollow spheres at the water/oil interface driven by coordination interaction between them. The interaction was studied by X-ray photoelectron spectroscopy, FT-IR spectroscopy, UV–vis spectroscopy, and fluorescence spectroscopy.

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Hollow spheres are an appealing structural design for many applications such as drug delivery, chemical storage, and catalysts.[1] Researches on metal hollow spheres are increasing recently because the properties of the superstructures composed of metal nanoparticles are mostly different from those of individual nanoparticles (NPs). These hollow nanostructures can be achieved by using a template[2] (such as polymer beads, $SiO_2$ spheres, metal cores, micelles, and ceramic hollow spheres) or by self-assembly method.[3] Stucky obtained $Au_{NP}$–poly(l-lysine)–$SiO_2$ composite hollow spheres through a charge-driven self-assembly route.[4] To the best of our knowledge, there is no report on fabricating photoelectrically active organic compound/metal nanocomposite hollow spheres in the literature. Here, we report a facile method for self-assembling Au NPs and tetrapyridylporphine (TPyP) into composite hollow spheres at the water/oil interface of the emulsion drops, which were composed of $H_2O$/$CHCl_3$ with tetrabutyl ammonium bromide, driven by coordination interaction between them. Because porphyrins have unique electronic, optical, and catalytic properties,[5] the composite structures might find new applications other than in photoelectric fields and offer a model to learn about the collective optic and electric properties between metal cores and organic molecules.

The novel hollow sphere composed of TPyP and Au NPs was prepared via reduction of $HAuCl_4$ by $NaBH_4$ under weak acidic conditions and the presence of TPyP (Supporting Information). The size of these spheres ranges from 50 to 200 nm. TEM image of the hollow spheres (Figure 1a) showed a striking contrast between the dark edges and the pale center, which indicates a hollow structure. The inset of Figure 1a shows the hollow structure clearly. HRTEM (Figures 1b and 1c) shows that these hollow spheres are composed of small nanoparticles with nearly uniform size (ca. 5 nm). The figures also show the shell fairly, and its thickness is about 20 nm. The corresponding selected area electron diffraction (SAED) (see the inset of Figure 1b) indicates a polycrystalline structure. The structure of the hollow gold spheres was also investigated by X-ray diffraction. All the peaks of XRD pattern in Figure S4 (S is referred to Supporting Information) can be indexed to the (111), (200), (220), (222), and (311) of cubic phase Au. The most frequent interparticle spacing in the hollow spheres was about 2.0–2.5 nm (Figure 1d). There presents two different coordination and stack modes shown in Scheme 1. In Scheme 1a, each of two opposite pyridyl group in TPyP coordinates to a gold nanoparticle and the distance $L_1$ between two Au NPs ($\approx$1.9 nm) is equal to the sum of the diagonal dimension of porphyrin molecule (1.5 nm) and two Au–N bonds (pyridine) ($\approx$0.2 nm for each).[6] In Scheme 1b, only one of the opposite pyridyl groups of TPyP coordinates to a Au nanoparticle and the other is still free. There has some extent $\pi$-stacking between two moieties of TPyP. In this case, the distance $L_2$ between two Au nanoparticles is $L_1 < L_2 < 2L_1$, in which $2L_1$ corresponds to the side-by-side arrangement of TPyP. All the above indicated that TPyP mediated these Au NPs. FT-IR spectra (Figure 2a) of the obtained hollow spheres display almost all the characteristic vibration bands of TPyP with obvious shifts. The shifts may imply that there exists coordination interaction between Au NPs and N atom in TPyP. XPS showed that the binding energy of $Au4f_{7/2}$ was 83.5 eV (Figure 3a). It is different from thiol monolayer-protected gold nanoparticles (83.8–

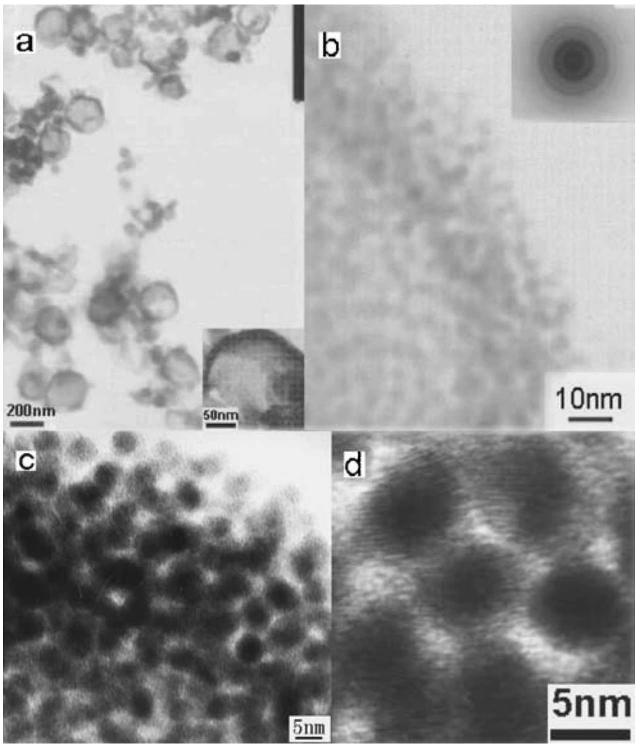
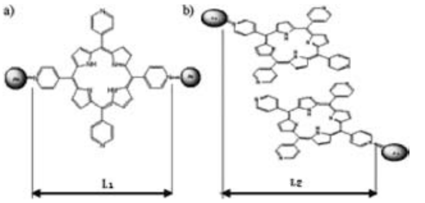


**Figure 1.** TEM of gold hollow spheres: (a) low magnification, (b) high magnification of the shell of the hollow spheres and the inset shows the corresponding SAED, (c) HRTEM of the hollow spheres, and (d) a high magnification of the part of the spherical shell.



**Scheme 1.** Two different coordination and stack modes of TPyP in the hollow spheres.

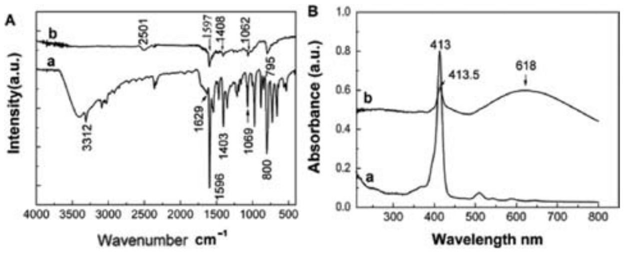


**Figure 2.** A. FT-IR spectra of (a) pure TPyP (b) gold hollow spheres. B. UV–vis spectra of (a) free TPyP (b) gold hollow spheres.

84.4 eV).[7] The negative shift was attributed to electron in the negative pyridyl group in porphyrins donating to the 5d orbital of gold in the hollow spheres.[8] UV–vis spectra of the gold hollow spheres as well as TPyP are shown in Figure 2b for comparison. There present two bands for the gold hollow spheres. The first band at 413 nm is attributed to the Soret band of TPyP. Surface Plasmon (SP) extinction band of hydrosol of 5 nm gold nanoparticles located at 512 nm,[8] but it shifted to around 618 nm for hollow gold spheres because of enhanced interaction between nanoparticles[2] and changes in the dielectric medium surrounding the gold nanoparticles,[9] which was induced by TPyP coordinating to the gold NPs. The direct coordination on gold nanoparticles of the TPyP induced special fluorescent properties. The fluorescence of TPyP in the gold hollow spheres is significantly quenched as compared to that of free TPyP (Figure 3b). This indicated that energy transfer (ET) from the porphyrin excited singlet state ($^1P^*$) to the gold is faster in the hollow gold spheres than in alkyl-chain linked porphyrin gold MPCs.[10]

We found that the pH value of the reaction system is a crucial factor to determine the product structure. In neutral and basic conditions ($\mathrm{pH} > 7.0$ or $\mathrm{pH} = 7.0$), irregular gold aggregates were obtained (Figure S5). Hollow spheres began to form when the pH value decreased ($\mathrm{pH} < 7.0$). High yield of gold hollow spheres was obtained at an optimum pH value of 4.4. Based on the above results, the formation process of gold hollow spheres is proposed. $[AuCl_4]^-$ ions in the aqueous solution were transferred into chloroform through phase transfer agent, tetrabutylammonium bromide. When TPyP was added to the above weak acidic chloroform solution, it was partly protonated immediately. Protonated TPyP has a strengthen affinity to water. When an aqueous solution of reducing agent $NaBH_4$ was added, the surfactant $Bu_4NBr$ instantaneously emulsified the solution to water-in-oil (W/O) system. $[H_nTPyP]^{n+}$ ($n = 1$–4) and $[AuCl_4]^-$ in $CHCl_3$ phase were concentrated on the water/oil interface, and reacted with $NaBH_4$ there. The formed gold nanoparticles were instantly coordinated with the surrounding porphyrin and arranged on the surface of emulsion drops to form gold–TPyP hollow spheres. When the solution is neutral or basic, TPyP can't gather on the water/oil interface because it's not hydrophilic enough. Therefore, the small Au NPs aggregated rapidly and turned into large irregular aggregates. The hollow sphere cannot be formed.

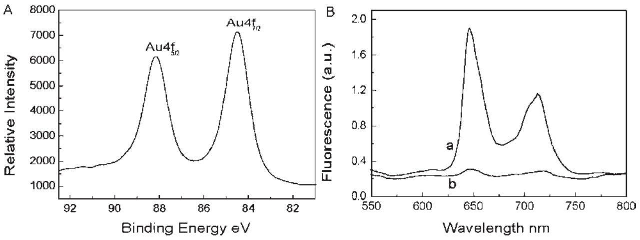


**Figure 3.** A. XPS spectrum of Au4f region. Samples were calibrated by assigning the C1s peak at a value of 284.6 eV. B. Fluorescence spectra of (a) free TPyP (b) gold hollow spheres. Excitation wavelength was taken at the intersection point of curves a and b in the UV–vis spectra (417 nm) to ensure the same absorbance of TPyP in two samples.

In conclusion, gold nanoparticles were successfully assembled into hollow spheres utilizing a multidentate compound tetrapyridylporphine. TPyP directly coordinated to gold nanoparticles led to significantly quenched fluorescence of TPyP. This Au–TPyP complex hollow structure may find potential applications in photoelectric conversion, catalysts, drug delivery, and especially in biology. This approach could be extended to prepare other functional inorganic–organic composite hollow spheres.

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