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Synthesis and characterization of terpyridine-type ligand-protected gold-coated Fe_3O_4 nanoparticles

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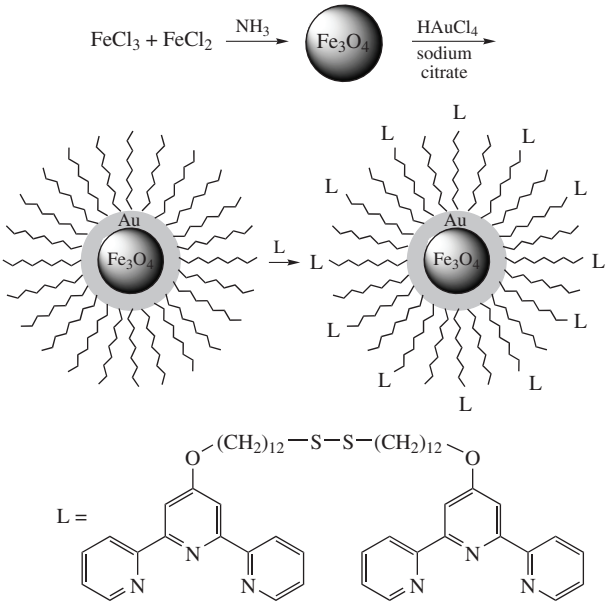
The three-step synthesis of new magnetic terpyridine-type ligand-protected gold-coated iron oxide nanoparticles (Fe_3O_4@Au-L) with an average size of 30 nm has been proposed, and their properties have been investigated.

Nanoparticles are of considerable current interest because they display fascinating electronic, optical and sensing properties as a consequence of their dimensions.[1–5] Among metal nanoparticles, gold nanoparticles have been widely used since their facile and robust interaction with thiol and disulfide groups enables functionalization of gold particles with various molecules due to their exceptional optical properties that are influenced remarkably by their chemical environment, their agglomeration, their kinds, or even their conformational differences.[6–8] Gold represents an excellent candidate by virtue of its easy reductive preparation, high chemical stability and biocompatibility. Meanwhile, magnetic nanoparticles are also attractive since they find applications in medical diagnostics, therapeutics, magnetic resonance imaging for detections, high-density magnetic recording, controlled drug delivery, biological targeting or separation and catalysis.[9–12] Iron oxide nanoparticles have attracted much interest due to their strong magnetic properties.[13] The biomedical applicability of Fe_3O_4 nanoparticles depends on their degree of surface modification and stability in physiological solutions.[14] The use of magnetic particles is connected with new synthetic methods with better control of size distribution and particle surface properties.[15] However, the applicability of Fe_3O_4 nanoparticles is often hindered by their own spontaneous oxidation surfaces. Chemical methods to predictably tune the surface functionality of Fe_3O_4 nanoparticle are still being explored.[16,17]



Scheme 1 Synthesis of the Fe_3O_4, Fe_3O_4@Au and Fe_3O_4@Au-L nanoparticles.

In order to extend the applicability of Fe_3O_4 nanoparticles, Au-coated Fe_3O_4 nanoparticles have been fabricated to open wider possibilities of surface functionality and to reduce surface oxidation.[18–20] Gold coating over magnetic nanoparticles is an even more appropriate composite system: with Au coating, the magnetic nanoparticles, especially high moment metallic magnetic nanoparticles, can be stabilized more efficiently under corrosive biological conditions and readily functionalized through the well-developed Au-S chemistry; the coating also renders the magnetic nanoparticles with plasmonic properties.[21,22] Such core-shell nanostructures could find applications that explore the electronic, magnetic, catalytic, sensing, and chemical or biological properties of the nanocomposite materials.

Here, we report the synthesis of new terpyridine-type ligand-protected gold-coated iron oxide nanoparticles (Fe_3O_4@Au-L) in an aqueous state from Fe_3O_4 by a simple three-step reaction (Scheme 1).[†] Citrate-protected gold-coated iron oxide nanopar-

[†] *Synthesis of Fe_3O_4 nanoparticles*. The iron oxide (Fe_3O_4) nanoparticles were synthesized according to the published procedure.[23] An aqueous solution of iron(III) chloride ($FeCl_3$, anhydrous, 98%, 4 cm^3, 1 mol dm^{-3}) and iron(II) chloride ($FeCl_2 \cdot 4H_2O$, 98%, 1 cm^3, 2 mol dm^{-3}) in 2 M hydrochloric acid (HCl, 37%) was mixed and added to diluted ammonium solution (NH_3, 25%, 50 cm^3, 0.7 mol dm^{-3}). The reaction mixture was stirred for 30 min. Then, the precipitate was isolated by magnetic decantation. The precipitate was stirred with diluted perchloric acid ($HClO_4$, 70%, 50 cm^3, 2 mol dm^{-3}) and then isolated by centrifugation. The residue was finally made up to 50 cm^3 with deionised distilled (DI) water prepared from a Milli-Q-RO4 system (Millipore).

Synthesis of Fe_3O_4@Au-cit. An aqueous solution of hydrogen tetrachloroaurate(III) trihydrate ($HAuCl_4$, 99.9%, 15 cm^3, 2.0 mg cm^{-3}) was added to 105 cm^3 of DI water and then heated to boiling. Then, 8 cm^3 of as-prepared Fe_3O_4 nanoparticle solution was added to the reaction mixture followed by the addition of sodium citrate (sodium citrate·5.5H_2O, 5 cm^3, 80 mmol dm^{-3}) under stirring. The colour of the solution gradually changed from brown to burgundy. The reaction mixture was boiled under stirring for 15 min.

Synthesis of Fe_3O_4@Au-L. L (terpyridine-type ligand[24]) (0.36 g) was added to a boiling solution of Fe_3O_4@Au-cit (130 cm^3) under stirring and the colour of the solution changed from burgundy to deep blue. The reaction mixture was boiled under stirring for 30 min. Then, the L-Au-Fe_3O_4 nanoparticles were isolated by centrifugation. The gold-coated magnetic nanoparticles were washed three times with water and isolated by magnetic decantation.

All the reactions were carried out under N_2 atmosphere to minimize oxidation. Ulterior washing, drying, storage and analysis by superconducting quantum interference device (SQUID), TEM and UV-VIS were carried out in an ambient air atmosphere. The samples were stored in a desiccator.

ticles (Fe_3O_4@Au-cit) were prepared by the simple citrate reduction of Au^{3+}. Afterwards, Fe_3O_4@Au-L was synthesized by a fast ligand place-exchange reaction between the citrate and ligand molecules on the Fe_3O_4@Au nanoparticles. Then, these Fe_3O_4@Au-L nanoparticles were fully characterized by visible absorption spectroscopy, magnetic susceptibility measurements and transmission electron microscopy (TEM). The Fe_3O_4@Au-L nanoparticles showed good paramagnetic properties, they are well-dispersed in water and stable.

As compared with the synthesis of magnetic nanoparticles,[25–27] the proposed method is a simple three-step reaction to synthesize water-soluble new ligand-protected Au-coated iron oxide nanoparticles. The advantages of this method are simplicity, short reaction time, low reaction temperature and high reproducibility of results. Furthermore, another important characteristic of our as-prepared L-Au-Fe_3O_4 nanoparticles is that they are well dispersed in water and alcohols. An important aspect of our synthesis of the Fe_3O_4@Au nanoparticles is the formation of a gold shell at the iron oxide nanocrystal cores with high monodispersity and controllable surface capping properties, which facilitates the subsequent control and manipulation of the interparticle interactions and reactivities. The introduction of thiol molecules on the surface of the Fe_3O_4@Au nanoparticles does not induce the extensive assembly of nanoparticles, as reported by Wang.[20]

The size of magnetic nanoparticles was characterized by TEM (LEO 912 AB OMEGA). The samples for TEM analysis were prepared as follows: a drop of magnetic nanoparticles was dispersed in Nanopure water. The resulting solution was sonicated for 5 min to obtain better particle dispersion characteristics. A drop of the dispersed solution was then deposited onto a substrate and dried for 20 min at room temperature. The TEM images of Fe_3O_4@Au-L nanoparticles are presented in Figure 1(*a*) and the bar diagram in Figure 1(*b*) shows the size distribution and the average particle sizes (30 nm). Fe_3O_4@Au-L nanoparticles are spherical, and the size changes from 20 to 40 nm. Figure 1(*c*) depicts the electron diffraction pattern of the Fe_3O_4@Au-L nanoparticles, which is consistent with published data[23] on the core-shell structure of the Fe_3O_4@Au-L nanoparticles.

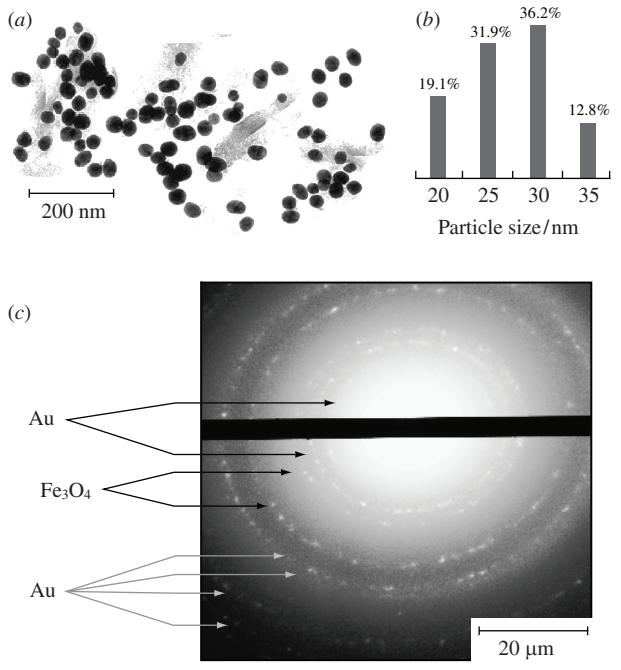


Figure 1 (*a*) TEM images, (*b*) size distributions and (*c*) electron diffraction pattern of Fe_3O_4@Au-L nanoparticles.

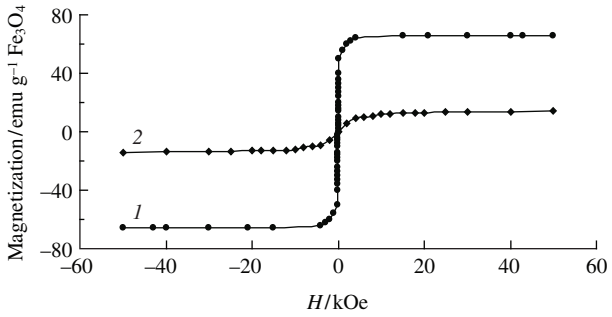


Figure 2 Magnetization hysteresis at 273 K for (*1*) Fe_3O_4 and (*2*) Fe_3O_4@Au nanoparticles.

Magnetic measurements were performed using a Faraday balance magnetometer. The samples of Fe_3O_4@Au-L nanoparticles were isolated from the aqueous solution by centrifugation and dried in a vacuum.

It has been reported[20] that overlaying iron oxide nanoparticle surfaces with a gold shell has a negligible effect on the magnetic behaviour. All the nanoparticles are concentrated at the bottom and right-hand side of the bottle when the magnet is placed at the corresponding positions. Our results demonstrate that the Fe_3O_4@Au-L nanoparticle solution is paramagnetic and the Au atoms are successfully coated on the Fe_3O_4 nanoparticles since a blue colour and paramagnetic properties originate from the gold nanostructure and Fe_3O_4 nanoparticle, respectively. On the other hand, the magnet only attracts the Fe_3O_4@Au-L nanoparticles to the corresponding positions, but it does not promote any precipitation effect. When the permanent magnet is removed, the L-Au-Fe_3O_4 nanoparticles can be re-dispersed in water again. This important characteristic allows the tracking of such particles in a magnetic gradient without loosing the advantage of a stable colloidal suspension.

The magnetic properties of the core-shell Fe_3O_4@Au nanoparticles were examined and compared with the magnetic properties of Fe_3O_4.[20] The saturation magnetization and blocking temperature were determined from magnetometer Faraday balance measurements. Figure 2 represents the magnetization *versus* magnetic field at 273 K by cycling the field from –50 kOe to 50 kOe. The magnetic data display major differences between Fe_3O_4 and Fe_3O_4@Au nanoparticles. First, the magnetization of Fe_3O_4@Au is smaller than that of Fe_3O_4. The maximum magnetization values are 66 and 10 emu g^{-1} Fe_3O_4 for Fe_3O_4 and Fe_3O_4@Au, respectively. The mass of Fe_3O_4 was determined from the loading of magnetic particles in the plastic capsules (0.001 g in this case). Second, the saturation magnetization of Fe_3O_4@Au is higher than that of Fe_3O_4.

To demonstrate the formation of a gold layer around the magnetic nanoparticles, colloidal gold and Fe_3O_4@Au solutions were prepared by dissolving Au nanoparticles and Fe_3O_4@Au, respectively, in 4 ml of water and the absorbance was measured. The visible absorption spectra of the solutions were acquired with a Hitachi U-2900 UV/visible spectrophotometer over the wavelength range of 400–800 nm. Figure 3 displays a typical set of the spectra of Fe_3O_4 (curve *1*) and Fe_3O_4@Au (curves *2* and *3*) nanoparticles dispersed in aqueous solution. In contrast to the largely silent feature in the visible region for Fe_3O_4 particles, Fe_3O_4@Au particles exhibit bands at 525 and 540 nm for the ligands (citrate and L).

In conclusion, we have proposed a simple three-step reaction to synthesize a new type of ligand-protected water-soluble terpyridine-type Fe_3O_4@Au-L nanoparticles. The attachment of gold atoms by the citrate reduction of Au^{3+} in aqueous solutions finally results in the formation of a very thin gold layer on the surface of the Fe_3O_4 magnetic nanoparticles. This report demon-

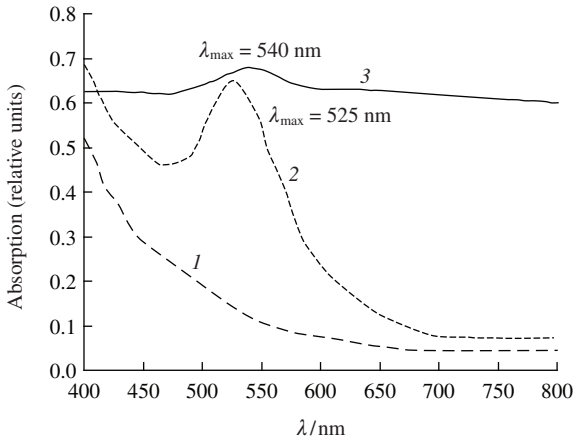


Figure 3 UV-VIS spectra of (*1*) Fe_3O_4, (*2*) Fe_3O_4@Au and(*3*) Fe_3O_4@Au-L.

strates the place-exchange reaction on gold-coated iron oxide nanoparticles in aqueous solution without the assembly of nanoparticles. The paramagnetic properties, blue colour and TEM data confirm that the Fe_3O_4 nanoparticles are successfully coated with a thin layer of Au atoms. Finally, the TEM data determine the composition and size of the Fe_3O_4@Au-L nanoparticles. The attached gold shell provides chemically active sites on the surface of the magnetic nanoparticles, enabling their potential derivatisation with multifunctional organic molecules. In addition, the ligand on the surface of the nanoparticles allows further surface modifications of water-soluble gold-coated magnetic nanoparticles to be carried out for wider applications. Moreover, the characteristics (small particle size, thin layer of Au, good dispersion in water and paramagnetic properties) of the Fe_3O_4@Au-L nanoparticles facilitate their catalytic, analytical and biomedical applications.

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