In situ chemical formation of iron phthalocyanine (FePc) monolayer on the surface of magnetite nanoparticles†

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The surface of magnetic nanoparticles (Fe_3O_4) has been modified chemically with iron phthalocyanine monolayer. The under-coordinated Fe sites on the surface of SCFD-derived Fe_3O_4 nanoparticles (NPs) and phthalic nitrile acted as template ions and components, respectively, for the formation of FePc. The presence of chemical linkages between *in situ* formed FePc monolayer and the surface of Fe_3O_4 NPs has been characterized by TEM, FTIR, UV-Vis, MS and TG-DSC *etc*. As compared to the neat Fe_3O_4 nanoparticles, the FePc monolayer-protected Fe_3O_4 nanoparticles (FePc@Fe_3O_4 NPs) that resulted could be dissolved in common organic solvents and showed much higher antioxidativity to oxygen.

Introduction

Phthalocyanines (Pcs) are one of the most extensively studied of functional materials.[1] As functional materials, the immobilization of Pcs on some supports (*e.g.*, metal oxides) is essential for fully exploiting their functionalities. For example, Pcs or its analogous-modified silica gel, TiO_2, magnetic iron oxide, and gold nanoparticles have potential applications in HPLC materials, catalysis, dye-sensitized solar cells, photocatalysis and photodynamic therapy.[2] Usually, the methods that can offer chemical linkage between Pcs and supports will provide high stability and effective electron relays for these composites.[2d,f] One of the important features of nanoparticles is the presence of active sites on the surface, the reactions that occur between these sites and other substances may lead to the formation of chemically linked monolayer. Rajh's study[3] revealed the existence of under-coordinated metal sites on the surface of metal oxide nanoparticles (including iron oxide). Upon binding of enediol ligands, these under-coordinated surface sites can be converted back to a octahedral bulk-like lattice structure. The surface reactivity of iron oxide nanoparticles toward enediol ligands (*e.g.*, dopamine) has been employed by several research groups recently to further anchor functional molecules chemically.[2g,4] However, no other further investigations on nitrogen ligands have been reported so far.

Both Fe_3O_4 nanoparticles (NPs) and Pcs are important functional materials, they are complementary in both properties and functions. The effective combinations of these two kinds of materials have potential application in catalysis, photocatalysis and anticancer therapy. Shaikhutdinov[5] suggested that one could obtain iron-terminated or oxygen-terminated iron oxide surfaces by altering the preparation conditions, and dissociative chemisorption of water or other small molecule on all iron oxides that expose metal cations in their topmost layers was observed. Usually, supercritical fluid drying (SCFD)-derived aerogel nanoparticles show high surface reactivity owing to their large surface area and low density.[6] Based on the ideas mentioned above, we chose SCFD-derived Fe_3O_4 nanoparticles as substrate to react with phthalic nitrile ($Ph(CN)_2$) superficially to form FePc monolayer in the present work. Using these two simple starting materials, we obtained Fe_3O_4 NPs which were chemically coated by FePc monolayer just in one step. To the best of our knowledge, it is a totally new strategy to functionalize iron oxides with FePc. Also this method may be extended to other metal oxide (*e.g.*, TiO_2[3a] and Fe_2O_3) nanoparticles and other phthalic nitrile derivatives. Scheme 1 illustrates the pathway of *in situ* formation of MPc-coated metal oxide NPs.[7]

Experimental

Equipments and materials

All chemicals were of analytical reagent grade and used directly without further purification. TEM images were obtained by a JEOL JEM-200CX transmission electron microscope with an accelerating voltage of 200 kV. Infrared spectra were recorded in the wavenumber range 4000–400 cm^{-1} using a Perkin-Elmer 2000 spectrometer and KBr pellets. UV-Vis absorption spectra were recorded in transmission mode using a PE UV-λ 900 spectrophotometer. Thermogravimetric and differential scanning calorimetry (TG-DSC) were recorded on a NETZSCH simultaneously for the samples of *ca.* 10 mg under an air atmosphere in the temperature range from 20 °C to 800 °C, with a heating rate of 10 °C min^{-1}.

Preparation of the Fe_3O_4 nanoparticles

The Fe_3O_4 nanoparticles in present work were obtained by treating iron oxide gel with supercritical ethanol for 45 min.

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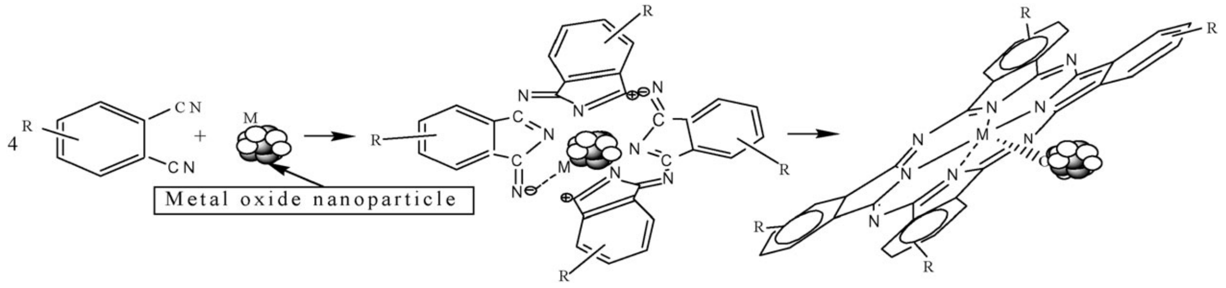

Scheme 1 Pathway of *in situ* formation of MPc@metal oxides NPs, here R = H, M = Fe.

$Fe(NO_3)_3 \cdot 9H_2O$ and NH_4OH were applied as iron oxide gel precursors. Deionized water was applied as medium of reaction. The Fe_3O_4 aerogel was prepared in three steps:

(1) Gel preparation: to a 200 mL of 0.5 M $Fe(NO_3)_3 \cdot 9H_2O$ solution, NH_4OH was added slowly under strong stirring until a brown gel was formed. Then the gel was washed repeatedly with deionized water to remove the soluble ions.

(2) Solvent replacement: the water-containing gel was washed with ethanol by repeated centrifugation at 8000 rpm and ultrasonication to ensure the thorough exchange of water with ethanol before being treated by supercritical ethanol. The last centrifugation-obtained ethanol-containing gel was the so-called alcogel.

(3) Supercritical drying: the alcogel was dried in a typical stainless reactor (500 mL) under supercritical conditions for ethanol (243.5 °C and 6.3 MP). Alcogel contained in glass tubes were transferred into a 500 mL autoclave that was pre-charged with 150 mL ethanol. In order to prevent the gels from collapse at the heating-up stage, the reactor was filled with nitrogen to a pressure of *ca.* 7 MP (above the critical parameters of EtOH). The excess pressure, a result of solvent vaporization, was carefully reduced during the heating stage. The rate of heating was *ca.* 100 $^{\circ}C\ h^{-1}$. The aerogel samples were kept in the reactor for 45 min after reaching the pre-determined conditions. Then the pressure was reduced to atmospheric pressure. At this stage, the reactor's temperature must be kept above the EtOH critical temperature. After reaching atmospheric pressure, N_2 was used to flush the autoclave to drive off the absorbed EtOH. When ambient pressure and temperature were reached, a porous dried black powder with low density was obtained.

Surprisingly, during the SCFD process in EtOH, partial reduction of Fe^{3+} to Fe^{2+} occurred, and Fe_3O_4 was obtained (XRD, see ESI†). Further investigation is needed to explain this observation. A similar result was also reported in ref. 8.

Formation of core–shell FePc/Fe_3O_4 NPs

The SCFD-derived Fe_3O_4 NPs showed high surface reactivity towards $Ph(CN)_2$. The reaction between Fe_3O_4 NPs and $Ph(CN)_2$ (mass ratio 10 : 1) was carried out in a sealed glass tube at 200 °C for 2.5 h in the absence of air. The unreacted $Ph(CN)_2$ in the resulting solid mixture was washed with ethanol several times, then the unbound FePc was washed off with hot *N*,*N*-dimethylformamide (DMF) under strong sonication and alternately centrifuged 5–7 times, until the blue washings turned colorless and the characteristic Q-band of Pcs disappeared under UV-Vis spectroscopic checking (see Fig. 3c). Then the DMF-containing wet powder was dried in vacuum at 80 °C. A dark green powder was obtained finally (named as FePc@Fe_3O_4 NPs in the present work).

Results and discussion

TEM characterization

Fig. 1 presents the TEM micrographs of neat Fe_3O_4 NPs (Fig. 1a) and FePc@Fe_3O_4 NPs (Fig. 1b). The size of the neat Fe_3O_4 NPs varies between 19 and 23 nm, while the FePc@-Fe_3O_4 NPs were in the 16–18 nm regime. This implies that the reaction between Fe_3O_4 NPs and $Ph(CN)_2$ had occurred, and some of the Fe atoms were lost in the form of FePc resulting in a decrease in the size of Fe_3O_4 NPs.

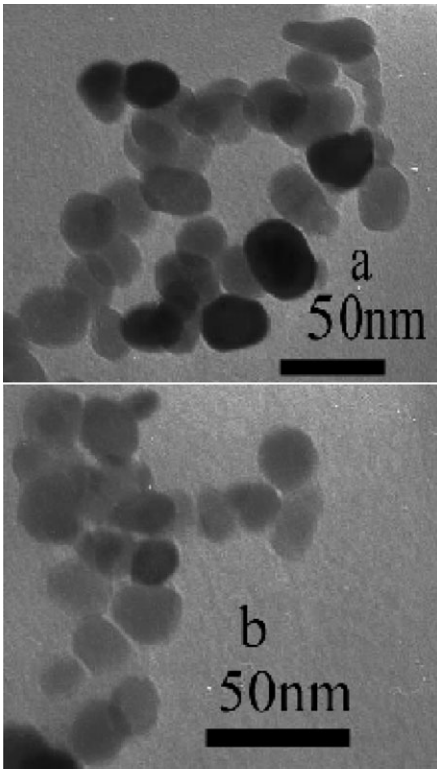

Fig. 1 Transmission electron microscopy micrographs of neat Fe_3O_4 NPs (a) and FePc@Fe_3O_4 NPs.

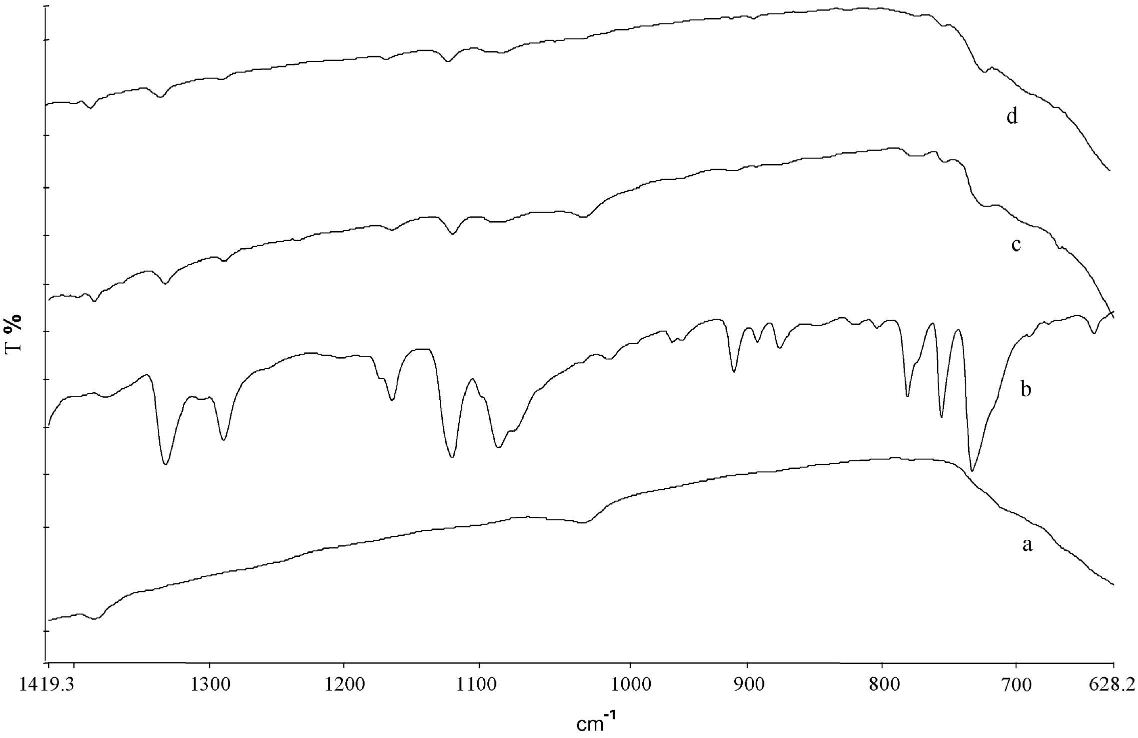

Fig. 2 FTIR spectra of (a) the neat Fe_3O_4, (b) the neat FePc and the FePc@Fe_3O_4 NPs before (c) or after (d) being washed by DMF under ultrasonication.

FT-IR measurements

Fig. 2 presents the Fourier Transform Infrared (FTIR) spectra of (a) the neat Fe_3O_4 NPs, (b) neat FePc and FePc@Fe_3O_4 NPs before (c) or after (d) the DMF treatment ultrasonically. The main bands of FePc@Fe_3O_4 are quite consistent with the main bands of neat FePc except for the absorption of iron oxide (Fig. 2b and d). This indicates that the FePc was still present on the surface of Fe_3O_4 NPs even after being washed by DMF under sonication. The main bands of the FePc are assigned with wavenumbers in cm^{-1} as 756 (ring breathing, C–H wagging), 909 (Fe–Pc), 1084 (Pc C–H stretch vibration), 1164 (pyrrole C=C bending) and 1332 (isoindole C–N stretch vibration). Both neat Fe_3O_4 NPs and FePc@Fe_3O_4 NPs displayed absorption at 570 (not shown here) and 1384 cm^{-1}, these two bands can be assigned to the iron oxide Fe–O stretch and the remaining NO_3^- vibration, respectively. Almost no difference in FTIR between the samples before and after being washed by DMF was observed (Fig. c and d), this implies that most of the formed FePc was bound with Fe_3O_4 NPs. Direct observation of chemical linkage between FePc and Fe_3O_4 NPs through FTIR spectroscopy is still a challenge.

UV-Vis characterization

For further confirmation of the presence of FePc on the surface of Fe_3O_4 NPs after the washing of solvent under ultrasonication, we did the following experiments: concentrated HCl was used to decompose the core (*i.e.*, Fe_3O_4) of FePc@Fe_3O_4 NPs. After being decomposed, a certain amount of DMF was added, and obtained a blue solution. The UV-Vis spectrum of this blue solution showed the characteristic Q-band of FePc. Fig. 3 presents the UV-Vis spectra of (a) the pure FePc in DMF, (b) the DMF solution of HCl-decored FePc@Fe_3O_4 NPs and (c) the DMF washing of the mixture obtained from the reaction between Fe_3O_4 NPs and $Ph(CN)_2$.

Both DMF washings of as-prepared FePc@Fe_3O_4 and pure FePc exhibited the same Q band absorption (~660 nm) (Fig. 3a and c), this indicates that the reaction between Fe_3O_4 NPs and phthalic nitrile resulted in formation of FePc (MS, see ESI†). Furthermore, part of the formed FePc was bound with Fe_3O_4 NPs to form FePc@Fe_3O_4 NPs. However, due to the axial ligation of Cl^- to FePc, the DMF solution of HCl-decored FePc@Fe_3O_4 displayed a small red shift at Q band (Fig. 3b).

Thermal analysis

A thermogravimetric and differential scanning calorimetry study of the neat Fe_3O_4 NPs and FePc@Fe_3O_4 NPs were

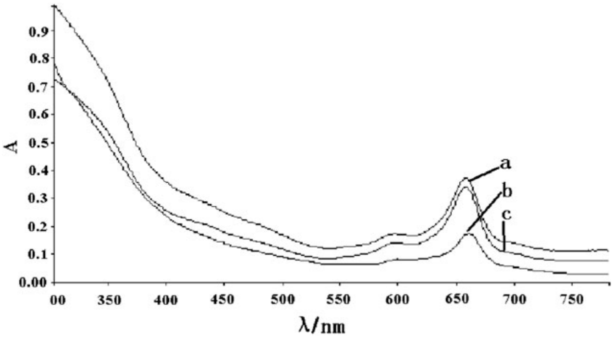

Fig. 3 UV-Vis spectra of (a) the pure FePc in DMF, (b) the DMF solution of decored FePc@Fe_3O_4 and (c) the DMF washing of the mixture obtained from the reaction between Fe_3O_4 NPs and $Ph(CN)_2$.

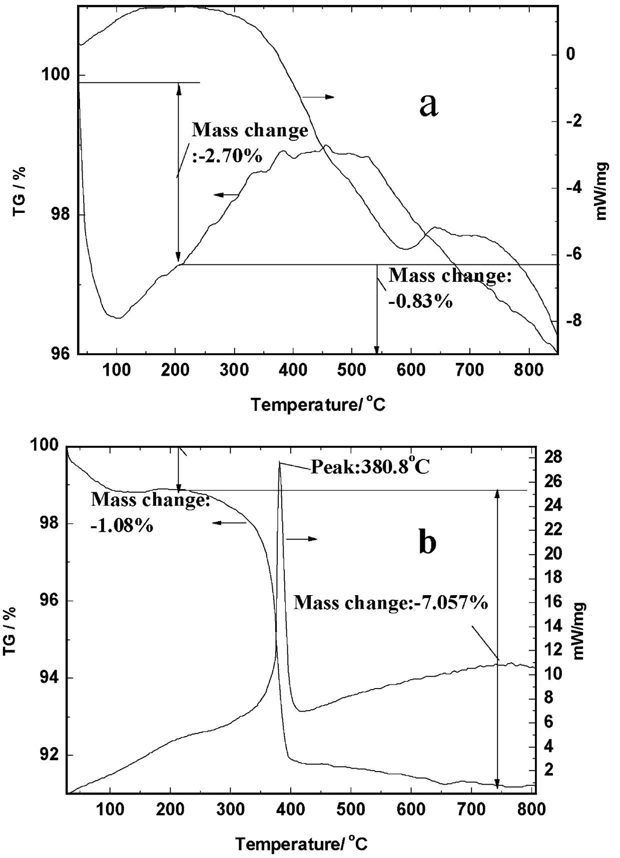

Fig. 4 TG–DSC curves for neat Fe_3O_4 NPs (a) and FePc@Fe_3O_4 NPs (b).

performed over the temperature range 20–800 °C in an atmosphere of air. As for neat Fe_3O_4 NPs (Fig. 4a), the first and brief event of weight loss occurs below 110 °C and is due to evaporation of the adsorbed ethanol. The TG curves corresponding to the runs in air show a weight gain effect between 120 and 340 °C. This weight gain is attributed to the oxidation of Fe_3O_4 to Fe_2O_3. The weight loss above 450 °C is due to the decomposition of the remaining NO_3^-.

As compared to neat Fe_3O_4 NPs, no clear weight gain below 300 °C was observed on FePc@Fe_3O_4 NPs (Fig. 4b). This means that FePc@Fe_3O_4 NPs was more antioxidative than neat Fe_3O_4 NPs. However, due to the decomposition of FePc in air atmosphere, a large weight loss as well as a sharp exothermic peak (380.8 °C) was observed between 300 and 400 °C for FePc@Fe_3O_4 NPs. The total weight loss for neat Fe_3O_4 NPs and FePc@Fe_3O_4 NPs was 3.53% and 8.14%, respectively, indicating the existence of FePc molecules on the surfaces of FePc@Fe_3O_4 NPs.

Comparison studies

For comparison purposes, we also tried a physical method to combine FePc and Fe_3O_4 NPs together. Tetrahydrofuran (THF) solutions containing an amount of FePc and Fe_3O_4 NPs were mixed together, the mixture was stirred and refluxed for 8 h, and the THF was then removed by vacuum evaporation. The dried green powder was thoroughly washed by DMF under sonication. FTIR spectrum (ESI†) showed that the characteristic absorptions of FePc vanished completely. This indicates that no chemical interactions exist between FePc and Fe_3O_4 NPs in this case. This can be explained as follows. The *in situ* formation of FePc@Fe_3O_4 NPs is a bottom-up process, *i.e.*, the iron in FePc complex (as shells) comes originally from the Fe_3O_4 NPs (as cores). The reaction between Fe atoms took place at the surface of Fe_3O_4 NPs, *i.e.*, $Ph(CN)_2$ just reacted with the Fe atoms located on the surface of Fe_3O_4 NPs. As a result, the formed shell of FePc monolayer was tightly bound with Fe_3O_4 NPs core (Scheme 1), which cannot be removed even under ultrasonication in hot solvent. However in the dipping process, FePc molecules were introduced externally. FePc and Fe_3O_4 were just combined physically, leading to the complete leaching of FePc in organic solvent.

Interestingly, further comparison studies showed that no reactions occurred between bulk Fe_3O_4 particles (~ 1 μm) and Ph $(CN)_2$ when using the same conditions as carried out on Fe_3O_4 NPs and Ph $(CN)_2$. This indicates that reaction of surface Fe atoms with Ph $(CN)_2$ is exclusively characteristic of small Fe_3O_4 nanoparticles.[3]

As compared to the neat Fe_3O_4 NPs, the FePc@Fe_3O_4 NPs can be dissolved in common organic solvents such as THF, ethyl acetate and DMF to form stable colloidal dispersions. Further, these dissolved FePc@Fe_3O_4 NPs could be recovered reversibly by means of an external static magnetic field.

Conclusion

In the present work, we provide a new idea for functionalization of metal oxide nanoparticles with MPc monolayer. Based on this idea, FePc@Fe_3O_4 NPs with high stability have been prepared successfully. The chemical interaction between FePc molecules and Fe_3O_4 NPs was evidenced by TEM, FTIR, UV-Vis, MS and TG-DSC analyses. As compared to the FePc/Fe_3O_4 nanocomposite obtained by the conventional method, the *in situ* formed FePc@Fe_3O_4 NPs showed total resistibility toward ultrasonic washing of organic solvent, implying the presence of chemical linkage between FePc and Fe_3O_4. Additionally, we found that the reaction of surface Fe atoms with $Ph(CN)_2$ is exclusively characteristic of small Fe_3O_4 nanoparticles (derived from SCFD process in this work). Further exploration of the reactivity between metal oxide NPs other than iron oxide NPs and phthalic nitrile derivatives is under way in our group.

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