

Spectroscopic Probe of the Surface of Iron Oxide Nanocrystals

Nicholas J. Turro,^{*,†} P. H. Lakshminarasimhan,[†] Steffen Jockusch,[†]
Stephen P. O'Brien,[‡] Stephanie G. Grancharov,[‡] and Franz X. Redl[‡]

*Departments of Chemistry and of Applied Physics and Applied Mathematics,
Columbia University, New York, New York 10027*

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ABSTRACT

The surface of highly monodisperse nanocrystals of iron oxide (γ -Fe₂O₃) prepared via a non-hydrolytic controlled oxidation route were investigated using pyrene carboxylic acid and related derivatives (an ester and an alcohol) as spectroscopic probes of the nanocrystal surface.

Introduction. Nanocrystals¹ possess some similarities and some significant differences from molecules with respect to their interaction with light (UV–vis absorption and photoluminescence). It is commonly assumed that the interfacial features of nanocrystals are important in determining their interaction with light.² Nanocrystals have the potential to serve as constituents of novel optical devices if their interfacial chemistry and structure can be understood.^{1,3} We report an investigation of the photoluminescence of a spectroscopic probe, pyrene, which is bound through a short chain tether to the surface of iron oxide nanocrystals (γ -Fe₂O₃, maghemite). Objectives of this investigation are (a) to determine the feasibility of photoluminescence probe spectroscopy as a method for providing in situ information on ligand/interface structure and dynamics of nanocrystals that are capped with conventional ligands such as carboxylic acids and (b) to investigate the possibility of employing photoexcitable ligands bound to nanocrystal interfaces as a means of controlling the photooptical and photoelectric properties of nanocrystals.

Steady-state emission measurements of γ -Fe₂O₃ (maghemite) nanocrystals display a fast (picosec) overall decay and a weak fluorescence, resulting from very efficient nonradiative relaxation that may result from a dense band structure and a high density of trap states or strong coupling of the trap states.⁴ These results provide some insight into the poor efficiency of Fe₂O₃ as an electrode material. It is therefore a challenging problem to develop techniques that will convert Fe₂O₃ into a more efficient charge carrier. One such possibility is to use “a photosensitization method”, whereby a sensitizer ligand absorbs incident light and undergoes a charge-transfer interaction with the Fe₂O₃ nanocrystal. In this way it is conceivable that interactions

between the sensitizer and the nanocrystal may be detected directly or indirectly. An understanding of the structure and dynamics of ligand binding to the nanocrystal interface is essential for developing effective photosensitizers.

The strong size dependence of the optical properties of nanocrystals, an asset in many applications,² presents a difficulty in their quantitative evaluation. Thus, it is important to employ nanocrystals with as small a size distribution as possible when investigating their optical properties.² Accordingly, we have employed highly monodisperse γ -Fe₂O₃ nanocrystals in this investigation.

Pyrenebutyric acid, which is available commercially, was selected as a spectroscopic probe and potential photosensitizer because of the well-established photoluminescence of the pyrene lumophore⁵ and because the carboxylic acid group is well established as a good ligand for binding to the surface of metal oxides.⁶ The butyl chain is a convenient separator of the lumophore and the nanocrystal surface and is expected to assist in binding by reducing the repulsive steric effects of the surface and pyrene moiety in addition to serving to assist in the “blending” of the total probe with oleic acid, the ligand associated with the prepared γ -Fe₂O₃ (Scheme 1).

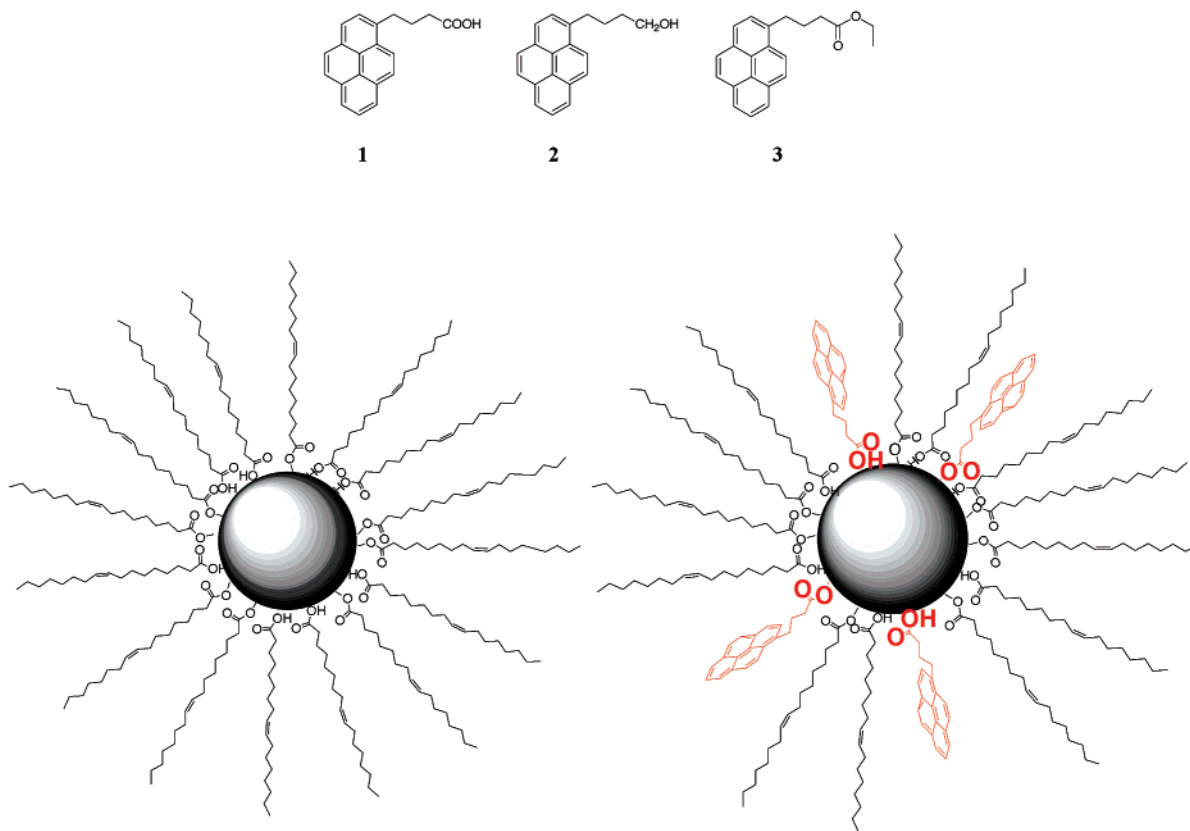
Results. The γ -Fe₂O₃ nanocrystals were prepared using a modified procedure.⁷ The particles are highly monodisperse with an average size of 12 nm and a size distribution of 3.3% (TEM and electron diffraction pattern in Figure 1). The synthesized nanocrystals were capped with oleic acid and were dispersed in hexane to form a transparent solution. The infrared spectrum of samples shows fine structured main peaks at 600 and 460 cm⁻¹, consistent with an ordered distribution of the ferric ions in the crystal lattice.⁸ The absorption spectrum of solutions of the nanocrystals showed a broad featureless spectrum extending from short wavelengths to around 650 nm (Figure 2), characteristic of γ -Fe₂O₃ nanocrystals.⁴ 1-Pyrenebutyric acid, **1** (Aldrich), was purified by crystallization from ethanol. The pyrene alcohol,

* Corresponding author. E-mail: turro@chem.columbia.edu. Tel: 212-854-2175. Fax: 212-932-1289.

[†] Department of Chemistry.

[‡] Department of Applied Physics and Applied Mathematics.

Scheme 1. Model Illustrating Two Different Types of Binding of the Probe Molecule^a



^a The chemisorbed and the physisorbed probe molecules are highlighted in red.

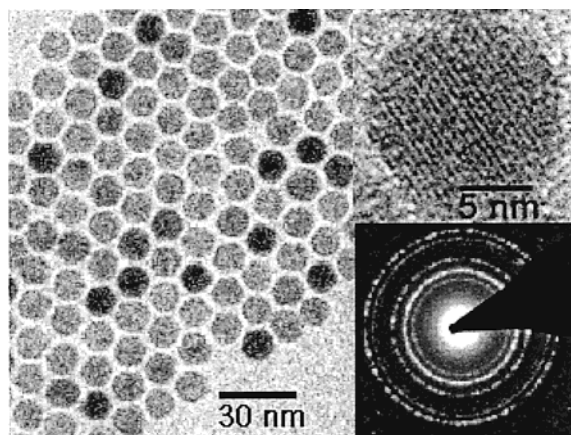


Figure 1. Transmission electron microscopy image of 12 nm diameter γ phase nanocrystals with (inset) HRTEM lattice image and electron diffraction pattern.

2, and the ethyl ester, 3, were prepared from the acid by reported procedures.^{9,10} A 10^{-5} M hexane solution of the probe molecules was titrated with the nanocrystal solution (10^{-7} M) under aerated conditions. Fluorescence from pyrene after excitation at 325 nm was monitored with increasing concentration of the nanocrystals. The lifetime of pyrene fluorescence is ca. 8–10 ns under aerated conditions.

To compare the results with each probe, the same solution of the iron oxide nanocrystals was used for titration with all the probe molecules. Although the fluorescence from pyrene was quenched in all three cases, the efficiency of quenching

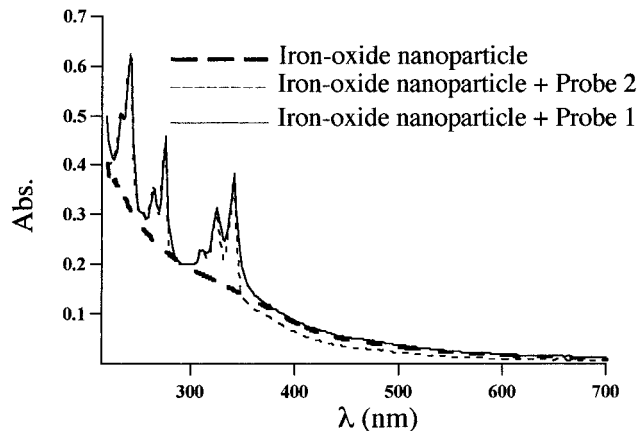


Figure 2. Absorption spectra of iron oxide nanocrystals in the absence and presence of probes 1 and 2.

strongly depended on the headgroup. As shown in Figure 3, the quenching efficiency was highest for 1 and was significantly lower in the case of 2 and 3. Although the intensity of probe photoluminescence was quenched upon addition of iron oxide, the probe lifetime (ca. 8.5 ns) did not change significantly upon addition of nanocrystals to the solution containing the probe molecules. A Stern–Volmer plot of the quenching data (Figure 4) clearly shows the largest difference in quenching efficiency for probe 1 compared to 2 and 3.

A reverse titration was carried out with oleic acid (10^{-3} M) to investigate the reversibility of this quenching process for the system containing 1 and the γ -Fe₂O₃ nanocrystals.

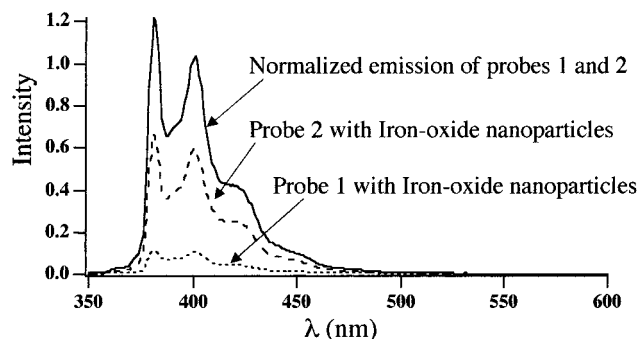


Figure 3. Fluorescence spectra of $\gamma\text{-Fe}_2\text{O}_3$ nanocrystals in the absence and in the presence of probes **1** and **2** ($\lambda_{\text{ex}} = 325$ nm in hexane).

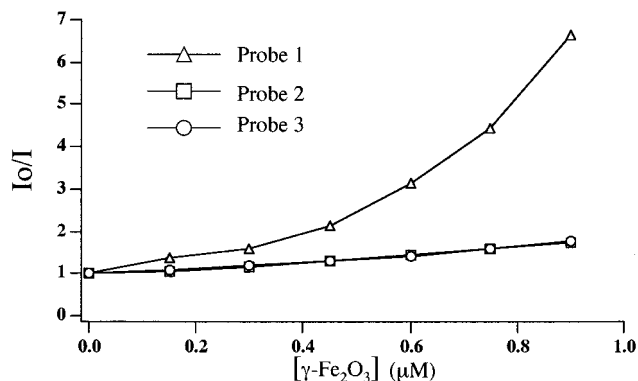


Figure 4. Stern–Volmer plots for quenching of the fluorescence of the probes by $\gamma\text{-Fe}_2\text{O}_3$ nanocrystals ($\lambda_{\text{ex}} = 325$ nm in hexane), where I_0 is the fluorescence intensity in the absence and I in the presence of nanocrystals.

The quenching was reversed significantly, but not completely, upon addition of small (ca. 10^{-6} M) initial amounts of oleic acid, but complete reversal was observed by adding a much larger amount (ca. 10^{-3} M) of oleic acid.

Laser flash photolysis studies were carried out on the $\gamma\text{-Fe}_2\text{O}_3$ nanocrystals in the presence and absence of **1** in hexane to investigate the mechanism for quenching of the probe photoluminescence. Excitation of the probe molecule at 355 nm (10 ns pulse, 10 mJ, Nd:YAG laser) produced a transient species possessing a featureless absorption spectrum that extended from 380 to 600 nm and possessing a lifetime of ca. 40 ns. The intensity of the transient absorption was strongly dependent on the power of the exciting laser pulse, suggesting a multiphoton process, which will be the subject of an upcoming paper. At the excitation wavelength (355 nm) the nanocrystals absorb strongly. Therefore, control experiments were performed with solutions containing only the nanocrystals. No transient absorption was observed. However, laser flash photolysis of **1** in the absence of nanocrystals did show clearly the triplet–triplet absorption of pyrene. These control experiments demonstrate that the broad transient absorption extending from 380 to 600 nm requires both **1** and the iron oxide nanocrystal, and the transient is not the pyrene triplet.

Discussion. The new procedure to synthesize iron oxide nanocrystals provides access to highly monodispersed samples. Hence it is possible to rule out size dependent effects as an

explanation of the results obtained with these nanocrystal–probe systems. Both TEM and electron diffraction results (Figure 1) combined with UV–vis results⁷ (Figure 2) clearly show that the nanocrystals are composed of $\gamma\text{-Fe}_2\text{O}_3$ (maghemite) with an average diameter of 12 nm. Oleic acid stabilizes the dispersion of these nanocrystals in hexane but does not possess significant photoluminescence, whereas the characteristic pyrene photoluminescence of the probe molecules **1–3** allows the direct investigation of the surface features of iron oxide nanocrystals in solution (in situ) as opposed to most other studies that involve depositing these nanocrystals on a surface, such as graphite or glass, before imaging.

The quenching studies with **1–3** (Figure 4) clearly demonstrate that the acid group binds more strongly to the iron oxide surface than do the alcohol or ester functional groups. This could be due to formation of a covalent bond to form an organometallic ester linkage with the hydroxyl groups of the acid to available sites on the surface of the nanocrystal. Moreover, the details of the reversal of quenching of **1** with added oleic acid suggests two modes of binding of the acid group to the iron oxide surface, a stronger binding and a weaker binding mode. The stronger mode is assigned to the chemical binding through formation of an ester linkage (Scheme 1, binding site in bold face) and the second mode is assigned to simple physical adsorption of the probe to the surface of these nanocrystals (Scheme 1, binding site in bold face). The more weakly bound physisorbed probe molecules should be readily displaced by added oleic acid molecules and would be responsible for the more efficient reversal of the fluorescence quenching of the probe molecule **1** by smaller amounts of oleic acid. Displacement of the chemically bound probe molecules is much more difficult and occurs only upon addition of a large excess of the oleic acid. The observation of this dual binding behavior is important, since this indicates that attempts to exchange the oleic acid for some other capping ligand should take into account the fact that some of these molecules might not be replaced completely and this could have important consequences in subsequent studies.

The less effective fluorescence quenching by the nanocrystals observed in the case of probes **2** and **3** can be mainly assigned to the weaker physisorption of these probe molecules to the surface of the nanocrystal, since this quenching is completely reversed by addition of oleic acid. The lifetime of the probe molecule (8.5 ns) does not change during the entire quenching process, indicating that there is no dynamic exchange between the probe molecules on the surface and those in solution during the lifetime of the emission. Although the fluorescence lifetime of pyrene is significantly longer in deoxygenated solutions,¹⁷ the reported experiments were performed under aerated conditions, which leads to reproducible results, maintains a good signal-to-noise, and simplifies the experimental procedure, all of which are desirable for a useful and general photoluminescence probe technique.

Although the iron oxide nanocrystals absorb strongly at 325 nm and show a weak photoluminescence, in the presence

of the probe molecules, **1–3**, the fluorescence from pyrene is orders of magnitudes stronger than that from the iron oxide nanocrystal at the concentrations of the systems analyzed. Therefore, the weak luminescence of the iron oxide nanocrystals does not interfere with the luminescence analysis.

Laser flash photolysis studies were undertaken in order to provide information concerning whether the quenching process involves electron transfer, which is expected to be related to the redox characteristics of the nanocrystal surface. Previous investigations have shown that the pyrene cation radical possesses a characteristic and distinct spectrum that is observable by time-resolved laser flash photolysis.^{11,12} The absence of a signal corresponding to the pyrene radical cation or anion on a time scale longer than 100 ns suggests that simple electron transfer from or to the pyrene singlet to the nanocrystal does not occur or that the radicals have a lifetime shorter than the time resolution of our instrument. It is also possible that signals corresponding to pyrene cation or anion radicals probably would be masked by the strong broad transient absorption from 380 to 650 nm mentioned above. The presence of oxygen in the system and the negligible amount of triplet pyrene signal even in the absence of nanocrystals suggests that the triplet energy transfer pathway is not a significant contributor to the quenching. Singlet energy transfer from excited pyrene to the nanocrystal is a possible quenching mechanism. However, if singlet–singlet energy transfer to the nanocrystals occurs, fluorescence from the nanocrystal should be observed. No fluorescence attributed to the nanocrystal was observed when the probe was quenched. This result could be because of the very low quantum efficiency of the nanocrystal fluorescence (see above) or because singlet energy transfer does not occur. Other possible quenching mechanisms include enhanced singlet–triplet intersystem crossing and electron transfer between the probe and the nanocrystal. The latter involves the free electrons on the nanocrystal surface to form some sort of “complex” of the excited surface and pyrene.¹³ Such a complex would explain the broad absorption observed from 380 to 650 nm, which has a much longer lifetime, 40 ns, than that of the bound pyrene in its singlet excited state. The laser power dependence on the transient can be attributed to the absorption of photons by the complex followed by interactions with the bound pyrene to form an additional complex.

Another possible application of the probe method for studying the surface of nanocrystals is its use in studying the uniformity of the nanocrystal surface on core–shell species for which iron is the core. For example, we have performed exploratory investigations of iron nanocrystals coated with Au.^{14,15} In these systems the Fe nanocrystals that were prepared were coated with gold using procedures described elsewhere.¹⁶ If either the coating is non-uniform or if there was a phase separation between the iron and the gold systems, the probe molecule would be quenched by the iron surface, but if the Au shell coating were uniform, then

the emission would remain constant. Preliminary investigations on Fe nanocrystals and Au shell/Fe core nanocrystals show that the gold-coated nanocrystals do not quench the photoluminescence of **1** significantly, whereas there was efficient quenching of the emission from probe **1** for Fe nanocrystals. Thus, the probe methodology provides a very sensitive and straightforward method to ascertain the surface coatings requiring only an emission spectrophotometer.

Conclusion. In conclusion, based on the quenching and reverse titration studies of the probes **1–3** in solutions of nanocrystals of γ -Fe₂O₃, a model is proposed in which the probe binds to the nanocrystal surface in a weak and strong binding mode (Scheme 1). The strong binding mode is a covalent binding of the carboxylic acid group to the γ -Fe₂O₃ surface, and the weak binding mode is a simple physisorption to the γ -Fe₂O₃ surface. The laser flash photolysis studies show a transient that could be due to a complex between the probe and the nanocrystal and further investigations are underway to understand the mechanism leading to its formation and its potential applications. The photoluminescence probe method can also be used to check the uniformity of a shell coating over the core of a nanocrystal.

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