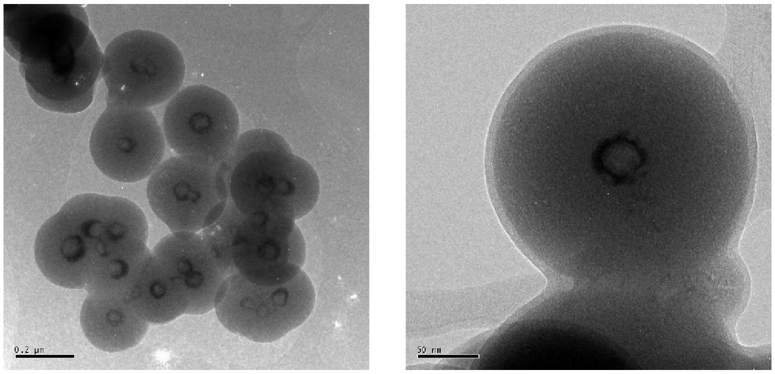
Communication

The Synthesis of Silica Nanospheres Doped with Polyoxometalates

Mark Green, Joanna Harries, Gareth Wakefield, and Robin Taylor

J. Am. Chem. Soc., **2005**, 127 (37), 12812-12813• DOI: 10.1021/ja0543200 • Publication Date (Web): 27 August 2005



Journal of the American Chemical Society is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

J|A|C|S
COMMUNICATIONS

The Synthesis of Silica Nanospheres Doped with Polyoxometalates

Mark Green,*,† Joanna Harries,‡ Gareth Wakefield,‡ and Robin Taylor‡

Department of Physics, King's College London, The Strand, London WC2R 2LS, U.K., and Oxonica Ltd., Begbroke Science and Business Park, Sandy Lane, Yarnton, Oxfordshire OX5 1PF, U.K.

Received June 30, 2005; E-mail: mark.a.green@kcl.ac.uk

Submicron silica spheres have been extensively studied, as they are easily prepared and simply modified to contain dopants, support surface decorations or functional groups. With the advent of the biological applications of nanomaterials, specifically, labeling technologies, silica spheres are prime candidates due to their historical use in imaging.[1] Of particular interest is the preparation of silica spheres containing light emitting compounds, as the surface of these spheres can easily be altered to accommodate biological interactions. The inclusion of organic dyes, however, is not ideal, as they often photobleach, and a more stable alternative is desirable.

Polyoxometalates (POMs) are a class of stable metal-oxide-based clusters ideally suited for biological applications. Polyoxometalates have been investigated as anti-viral agents, antibiotics, and HIV inhibitors and have a high efficacy and low toxicity.[2,3] Despite the enormous potential in biological applications, there have been, to date, no examples of biological labeling using POMs, which can be attributed in part to the quenching of rare-earth emission by water.[4]

Peacock and Weakley reported the seminal rare-earth POM, europium decatungstate, $Na_9EuW_{10}O_{36}\cdot 18H_2O$.[5] Numerous POM materials have been reported, including a related material, $K_{13}[Eu(SiW_{11}O_{39})_2]$, which was prepared using an adaptation of Peacock and Weakley's original method.[6] Here, we used a related compound, $Na_{13}[Eu(SiMoW_{10}O_{39})_2]$,[7−9] the optical properties of which closely match those of $K_{13}[Eu(SiW_{11}O_{39})_2]$, as shown in Figure 1.

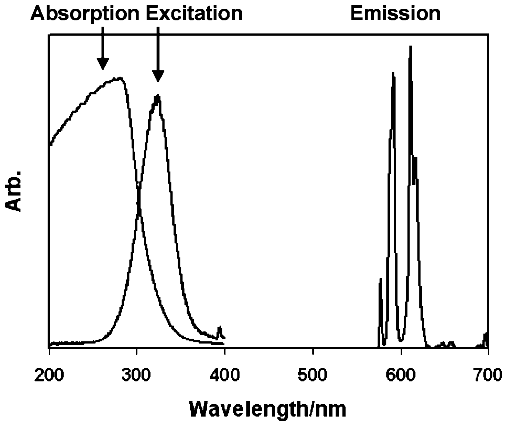


Figure 1. Optical properties of $Na_{13}[Eu(SiMoW_{10}O_{39})_2]$.

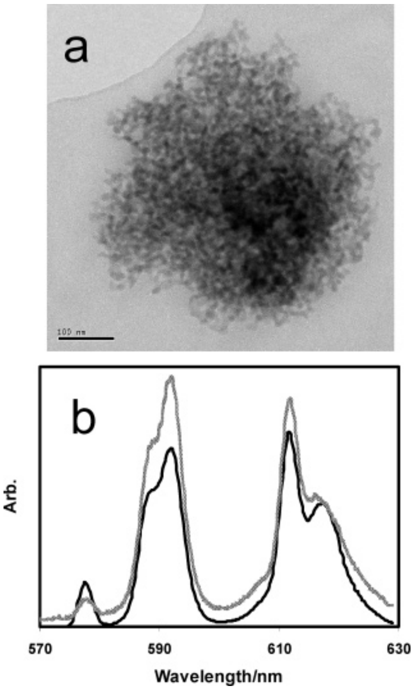


Figure 2. (a) Electron microscopy image of POM/poly-L-lysine conjugate. (b) Change in intensity of $^5D_0 \rightarrow {}^7F_1$ (592 nm) and $^5D_0 \rightarrow {}^7F_2$ (611 nm) peaks upon conjugation (dark lines = free POM, gray line = POM and poly-L-lysine).

The POM exhibited a solid-state quantum efficiency of 50%, which dropped to 2% when dissolved in water. The quantum efficiency of materials to be used as biotags needs to be significantly higher than 2%. There is, however, a tendency to confuse quantum efficiency with brightness. The brightness of an emitting material is the quantum yield multiplied by the extinction coefficient, hence the extinction coefficient is at least as important. In comparison, highly luminescent water-soluble emitting quantum dots can have minimum quantum efficiencies of ca. 5%[10] but have molecular extinction coefficients in the order of 10^5 cm^{-1} M^{-1}.[11,12] To date, the extinction coefficient of $Na_{13}[Eu(SiMoW_{10}O_{39})_2]$ has not been ascertained; however, a similar material ($K_{13}[Eu(SiW_{11}O_{39})_2]$) reportedly exhibited an extinction coefficient of up to 7.5×10^4 cm^{-1} M^{-1}, a realistic figure for use in biomarking.[6]

In an attempt to find a suitable agent that enhanced the luminescence while keeping the POM in solution, numerous compounds were screened for an encapsulation effect.[13,14] It was found that three compounds, poly-L-lysine, ethanolamine, and polyarginine, all increased the photoluminescence in water, not only overcoming the quenching of the emitting state but also, in fact, increasing the emission beyond that of the parent polyoxometalate in the solid state, with poly-L-lysine being the most effective. The quantum efficiency of $Na_{13}[Eu(SiMoW_{10}O_{39})_2]$ in a dilute (0.01%) aqueous solution of poly-L-lysine exceeded that of $Na_{13}[Eu(SiMoW_{10}O_{39})_2]$ in the solid state (quantum efficiency 50%) to a maximum of ca. 60%, depending upon the ratio of POM:poly-L-lysine and the molecular weight of poly-L-lysine used. Initially, it was hypothesized that the coordination of the various ligands to the central rare-earth ion displaced water molecules; however, this was ruled out as numerous ligands were screened that tightly bound to the structure yet did not enhance the emission.

---

† King's College London.
‡ Oxonica Ltd.

10.1021/ja0543200 CCC: $30.25

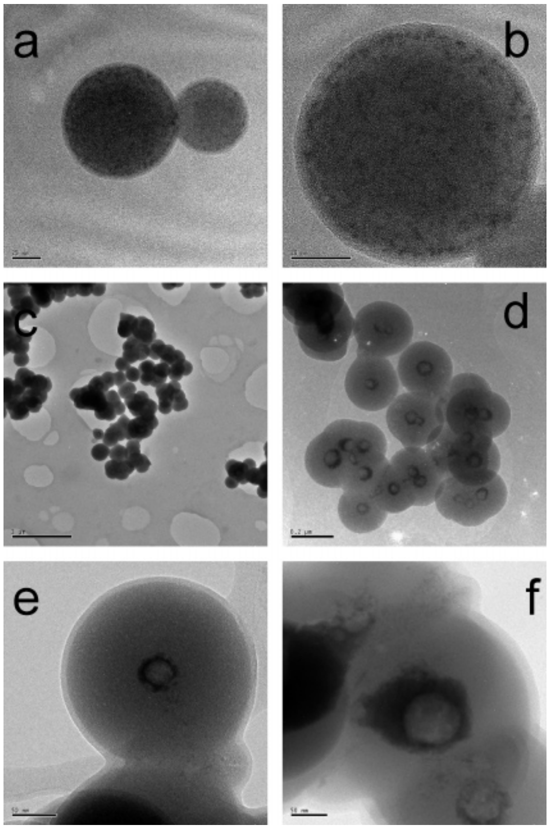


Figure 3. (a, b) Electron microscope image of evenly doped silica sphere, bars = 20 nm. (c−f) Electron microscope images of silica spheres with POMs confined to the core, bars = 1 μm, 0.2 μm, 50 nm, and 50 nm, respectively.

Similar results have been observed when using the polyoxometalates, $K_{15}\{M(W_5O_{18})[M(H_2O)_2(SbW_9O_{33})(W_5O_{18})]\}$ (M = Eu, Tb, Dy), with poly-L-lysine, although in this case, the use of high molecular weight polymers resulted in immediate precipitation from solution. The use of di- and tri-lysine resulted in the enhancement of emission, although the origin of the improvement has yet to been confirmed as an encapsulation related phenomena and not simple water displacement. The simple polyoxometalate $Na_9EuW_{10}O_{36}\cdot 18H_2O$ was found to be unaffected by dispersion in poly-L-lysine solution of any molecular weight and was not considered for further studies.

The poly-L-lysine/POM conjugates were relatively stable, although they precipitated out of an aqueous solution upon prolonged standing. The conjugate formed a polymeric network (Figure 2a), as shown by transmission electron microscopy, suggesting the amine groups of the poly-L-lysine bound to a metal ion.

The profile of the main peaks in the emission spectra changed upon conjugation, with the $^5D_0 \rightarrow {}^7F_1$ (592 nm) and $^5D_0 \rightarrow {}^7F_2$ (611 nm) peaks switching intensity (Figure 2b). This indicated a change in the coordination geometry around the Eu ion, a result of the attachment of the amine groups.[15]

Dilution of the POM/poly-L-lysine conjugate to the required concentration for biological applications resulted in dissociation into the free POM and polymer.

To counteract this, investigations were undertaken into the incorporation of POMs in silica spheres. Incorporating POMs into silica spheres prepared by an alcosol route[16] resulted in heavily doped spheres (Figure 3a,b), with the material spread evenly throughout the particle. The luminescence from the particle was quenched over 24 h, however, as water reached the rare-earth-containing material through the porous sphere. Ideally, the dopant should reside away from the surface, reducing contact with aqueous species. Fortuitously, incorporation of *both* poly-L-lysine and $Na_{13}[Eu(SiMoW_{10}O_{39})_2]$ during the preparation of silica spheres by the Stöber process[17] resulted in the POM binding to the polymer at the center of the particle (Figure 3c−f). Unusually, the POM/poly-L-lysine conjugates did not form a solid cluster inside the sphere, but appeared to favor a spherical hollow entity. The spheres with the POMs confined to the core showed enhanced stability toward water quenching.

In conclusion, we have observed enhanced emission from $Na_{13}[Eu(SiMoW_{10}O_{39})_2]$ when attached to amine-rich species, which circumvented problems encountered by water quenching of the rare-earth emitting state. We have also immobilized the POMs and the enhancing agent in silica spheres, which confines the POM to the core of the particle while increasing the emission of the material. The surface of the silica sphere lends itself to biofunctionalization, which is currently underway.

Supporting Information Available: The experimental details of the preparation of the doped silica spheres and the determination of quantum yields. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Peters, K. R.; Rutter, G.; Gschwender, H. H.; Haller, W. *J. Cell Biol.* **1978**, *78*, 309.
(2) Rhule, J. T.; Hill, C. L.; Judd, D. A. *Chem. Rev.* **1998**, *98*, 327.
(3) Judd, D. A.; Nettles, J. H.; Nevins, N.; Snyder, J. P.; Liotta, D. C.; Tang, J.; Ermolieff, J.; Shinazi, R. F.; Hill, C. L. *J. Am. Chem. Soc.* **2001**, *123*, 886.
(4) Kropp, J. L.; Windsor, M. W. *J. Chem. Phys.* **1965**, *42*, 1599.
(5) Peacock, R. D.; Weakley, T. J. R. *J. Chem. Soc. A* **1971**, *11*, 1836.
(6) Ballardini, R.; Chiorboli, E.; Balzani, V. *Inorg. Chim. Acta* **1984**, *95*, 323.
(7) Lis, S.; But, S. *Mater. Sci. Forum* **1999**, *315−317*, 431.
(8) Klemperer, W. G. *Inorg. Synth.* **1990**, *27*, 71.
(9) Lis, S.; But, S. *J. Inclusion Phenom. Macrocycl. Chem.* **1999**, *35*, 225.
(10) Gerion, D.; Pinaud, F.; Williams, S. C.; Parak, W. J.; Zanchet, D.; Weisse, S.; Alivisatos, A. P. *J. Phys. Chem. B.* **2001**, *105*, 8861.
(11) Yu, W. W.; Qu, L.; Guo, W.; Peng, X. *Chem. Mater.* **2003**, *15*, 2854.
(12) Stiolo, A.; Ward, J.; Prausnitz, J. M.; Parak, W. J.; Zanchet, D.; Gerion, D.; Milliron, D.; Alivisatos, A. P. *J. Phys. Chem. B* **2002**, *106*, 5500.
(13) Bu, W.; Li, H.; Li, W.; Wu, L.; Zhai, C.; Wu, Y. *J. Phys. Chem. B* **2004**, *108*, 12776.
(14) Zhang, T.; Spitz, C.; Antonietti, M.; Faul, C. F. J. *Chem.*−*Eur. J.* **2005**, *11*, 1001.
(15) Gudgin Dickson, E. F.; Pollak, A.; Diamandis, E. P. *J. Photochem. Photobiol. B: Biol.* **1995**, *27*, 3.
(16) Buining, P. A.; Liz-Marzan, L. M.; Philipse, A. P. *J. Colloid Interface Sci.* **1996**, *179*, 318.
(17) Stöber, W.; Fink, A.; Bohn, E. *J. Colloid Interface Sci.* **1968**, *26*, 62.

JA0543200