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Hard Proof of the $NaYF_4$/$NaGdF_4$ Nanocrystal Core/Shell Structure

Keith A. Abel, John-Christopher Boyer, and Frank C. J. M. van Veggel*

Department of Chemistry, University of Victoria, P.O. Box 3065, Victoria, British Columbia, Canada, V8W 3V6

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Inorganic nanocrystals (NCs) of various compositions have become an increasingly studied research topic in recent years owing to their novel electrical, optical, and magnetic properties. In particular, lanthanide doped inorganic crystals have been studied for their potential use in a variety of applications, such as bioimaging.[1] Fundamental to the understanding and development of nanomaterials is the accurate determination of their internal structure and composition. The growth of a shell surrounding the core is a common way to improve luminescence efficiency, but to date, core/shell structures based on lanthanides have only been inferred from indirect measurements.[2−6] Furthermore, our recent work has shed some doubt on the formation of core/shell structured lanthanide-based NCs formed in aqueous media.[7] In this communication, we present the synthesis of $NaYF_4$/$NaGdF_4$ NCs and report on X-ray photoelectron spectroscopy (XPS) data measured with tunable synchrotron radiation that provides direct evidence of a $NaYF_4$/$NaGdF_4$ core/shell structure. The particles were then rendered water-soluble with poly(ethylene glycol) PEG-phosphate utilizing a procedure recently reported by our group.[8] These new NCs, because of their Gd^{3+} content, show potential to be used as contrast agents for magnetic resonance imaging (MRI) applications.[4,9,10]

Hexagonal-phase $NaYF_4$ (β-$NaYF_4$) core and β-$NaYF_4$/β-$NaGdF_4$ core/shell NCs were synthesized, for the first time, using a modification of a previously reported procedure used to grow β-$NaYF_4$/β-$NaYF_4$ core/shell NCs (see Supporting Information for synthetic details).[5] The $NaYF_4$ core NCs were grown first and then served as nuclei for shell growth leading to $NaYF_4$/$NaGdF_4$ core/shell NCs. The energy-dispersive X-ray spectroscopy (EDS) confirmed the presence of the elements for both the core and core/shell NCs, respectively (Figure S1). To date, β-$NaYF_4$ is the most efficient host material for upconverting lanthanide ions and is therefore an excellent material choice for the core.[11] Addition of a shell has been shown to further improve luminescence efficiency and passivate the core NCs.[2−6] We chose $NaGdF_4$ as the shell material because of its excellent lattice match with $NaYF_4$ and because Gd^{3+} in the shell can potentially act as an excellent contrast agent for MRI due to its large magnetic moment and nanosecond time-scale electronic relaxation time.[10] Gd^{3+} in close contact with the surroundings (i.e., Gd^{3+} in the shell) is thought to be the best way to observe spin−lattice relaxation (T_1) and spin−spin (T_2) effects.[9]

Figure 1 shows transmission electron microscopy (TEM) images of the synthesized NCs before and after shell growth. The TEM images of the core particles (Figure 1a) demonstrate that the NCs are monodisperse, uniform, and 16.2 ± 0.8 nm in diameter. The core NCs are single crystals, as seen in the high-resolution (HR) TEM image (Figure 1a, inset). The highly crystalline hexagonal-phase $NaYF_4$ crystals are further confirmed from the XRD pattern shown in Figure S2, with the diffraction peaks matching the standard pattern for β-$NaYF_4$.

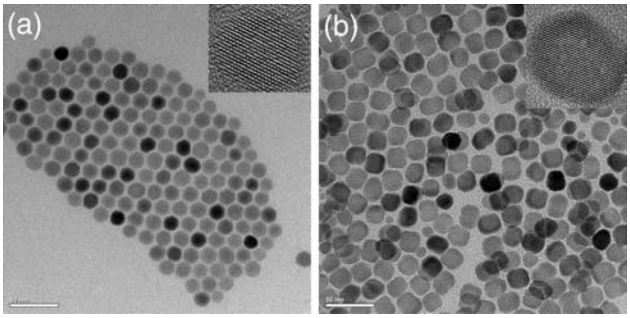

Figure 1. (a) TEM images of $NaYF_4$ core NCs and (b) $NaYF_4$/$NaGdF_4$ core/shell NCs. The insets show the HR-TEM image. Scale bars = 50 nm.

As shown in Figure 1b, the core/shell NCs are less uniform and have a larger size distribution when compared to the original core particles. The overall increase in size of the core/shell particles with an average diameter of 21 ± 1 nm suggests that $NaGdF_4$ was grown on the surface of the $NaYF_4$ core NCs. The XRD pattern of the core/shell particles also matches the standard bulk materials (Figure S2). The HR-TEM image (Figure 1b, inset) shows clear lattice fringes and good lattice match between the core and shell material.

Despite these results, the $NaYF_4$/$NaGdF_4$ NCs could in principle be alloy materials, rather than true core/shell structures. Commonly employed characterization methods are only able to infer that a core/shell structure has formed. TEM, for example, is useful when there is good contrast between the shell and core but fails when there is not, as is the case here between $NaYF_4$ and $NaGdF_4$. Elemental analysis techniques, such as EDS, fail to provide information regarding the location of the element inside the material. Optical data, such as previously observed enhanced luminescence efficiency attributed to shell growth (i.e., screening of the optical ions from the surroundings), is inadequate evidence for shell growth because larger particles also have improved efficiency.[6] XPS using tunable synchrotron radiation is one technique capable of surface elemental depth-profiling and has recently been applied successfully to other core/shell structured NC systems.[12−15] XPS spectra of the core/shell NCs were measured at varying photon energies (from 250 to 1050 eV) to determine the internal composition of the particles, following the previously reported methods. Experiments were performed at the Canadian Light Source, Inc. using the spherical grating monochromotor (SGM) undulator beamline, 11-1D.1, in Saskatoon, Saskatchewan.[16,17] $NaYF_4$/$NaGdF_4$ NCs in THF were deposited directly onto Au foil. After the solvent evaporated, the samples were quickly transferred to the experimental chamber. No charging effects were observed at low particle concentration. Experimental details of the XPS method are presented in the Supporting Information.

An example of a recorded XPS spectrum ($h\nu = 450$ eV), before background subtraction, is shown in Figure 2a. Photoelectron spectra of elements Y^{3+} 3d (core) and Gd^{3+} 4d (shell) were recorded at

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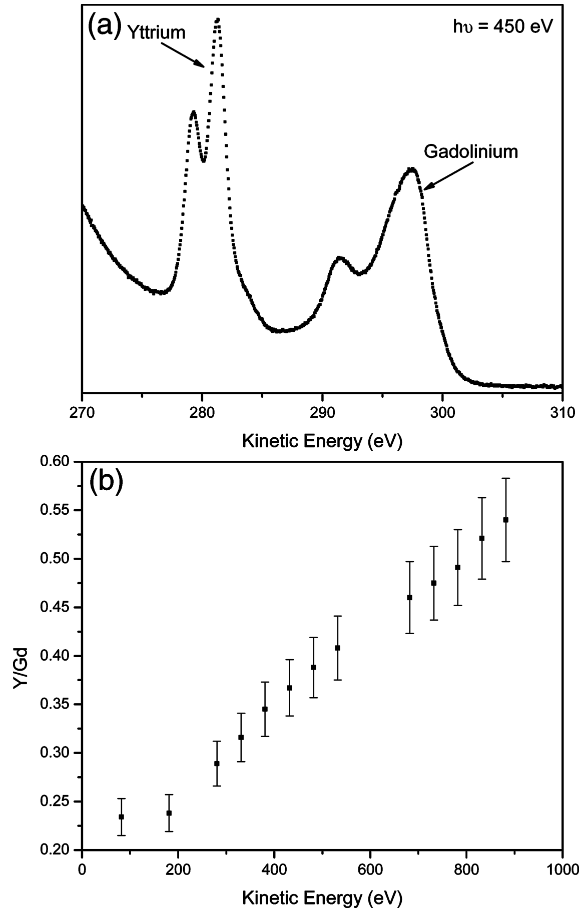

Figure 2. (a) Spectrum of the Y^{3+} 3d and Gd^{3+} 4d core levels before subtraction of a polynomial background, at a photon energy of ca. 450 eV. (b) Intensity ratio of the Y^{3+} 3d to Gd^{3+} 4d core levels as a function of photoelectron kinetic energy.

increasing excitation photon energies, thus gradually increasing the sampling depth. Each spectrum was subject to a polynomial background subtraction, and the peak areas were corrected for the photoionization cross sections. The error analysis and background subtraction are detailed in the Supporting Information.

The intensity ratio of Y^{3+} 3d to Gd^{3+} 4d core levels is shown in Figure 2b. Changing the photon energy changes the kinetic energy range. An increase in the ratio is observed at increasing kinetic energies, demonstrating that Gd^{3+} lies predominantly on the surface of the particles. The ratio increase is caused by the screening of the Y^{3+} intensity by the surrounding Gd^{3+} atoms at low kinetic energies. If the $NaYF_4$/$NaGdF_4$ NCs were alloys, the intensity ratio would remain constant. Whereas the TEM images do not show a clear interface between the core and shell materials, the increase in Y^{3+} 3d to Gd^{3+} 4d ratio is direct evidence for a core/shell structure. We note however that, without extensive simulations, further conclusions cannot be drawn on the sharpness of the interface between the core and shell materials. Furthermore, the XPS ratio does not level off at high kinetic energy because the particle size is still larger than the sampling depth (typically less than 10 nm).[18]

To evaluate the potential of the $NaYF_4$/$NaGdF_4$ core/shell NCs for MRI purposes, T_1 measurements at 1.5 and 3 T were performed as a function of nanoparticle concentration using a standard inversion recovery spin echo sequence. Prior to this, the particles were rendered water-soluble with PEG (2000)-phosphate.[8] The resulting mass relaxivities were on the order of 1 Hz mg^{-1} mL at both fields. Although this is lower than mass relaxivities reported for commercial MRI contrast agents such as Gd-DTPA or Gd-DOTA,[19] the core/shell NCs have two distinct advantages for future imaging applications: (1) as the NC diameters are on the order of 21 nm, their clearance times from tumors and leaky vasculature will be severely reduced in contrast to small molecules; (2) the core/shell structures can easily be functionalized with PEG and/or targeting moieties. Thus, high NC concentrations and corresponding higher relaxivities may be obtained.

In conclusion, hexagonal-phase $NaYF_4$/$NaGdF_4$ core/shell NCs were synthesized and characterized extensively with TEM, XRD, EDS, and XPS using synchrotron radiation. Although the former three are all suggestive that a core/shell structure had formed, XPS showed conclusively that Gd^{3+} is located on the surface of the NCs. This is the first time that such a material has been characterized and demonstrates that lanthanide based core/shell particles can be formed, despite recent reports.[7] Finally, preliminary MRI data show clear lengthening of T_1 times and the potential of this material as a contrast agent for MRI. Future work in our group will evaluate the effects of dopant ions on the core/shell structure and properties of the NCs.

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Supporting Information Available: Complete ref 4, experimental details, XRD patterns, EDS and XPS data. This material is available free of charge via the Internet at http://pubs.acs.org.

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