

# Core-shell NaHoF<sub>4</sub>@TiO<sub>2</sub> NPs: A Labelling Method to Trace Engineered Nanomaterials of Ubiquitous Elements in The Environment

*Xianjin Cui, <sup>†\*</sup> Benjamin Fryer, <sup>†</sup> Diwei Zhou, <sup>§</sup> Rhys W. Lodge, <sup>‡</sup> Andrei N. Khlobystov, <sup>‡</sup> Eugenia*

*Valsami-Jones <sup>†</sup> and Iseult Lynch <sup>†</sup>*

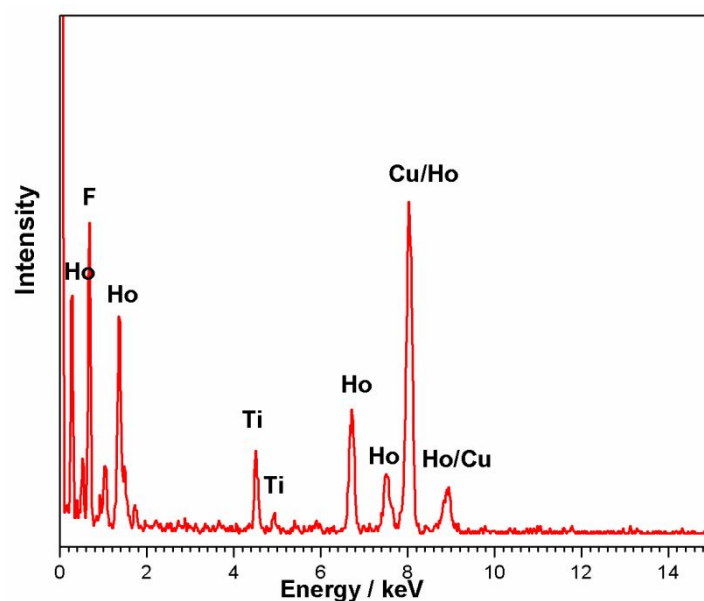
## AUTHOR ADDRESS

<sup>†</sup> School of Geography, Earth and Environmental Science, University of Birmingham,  
Edgbaston, Birmingham, B15 2TT, UK

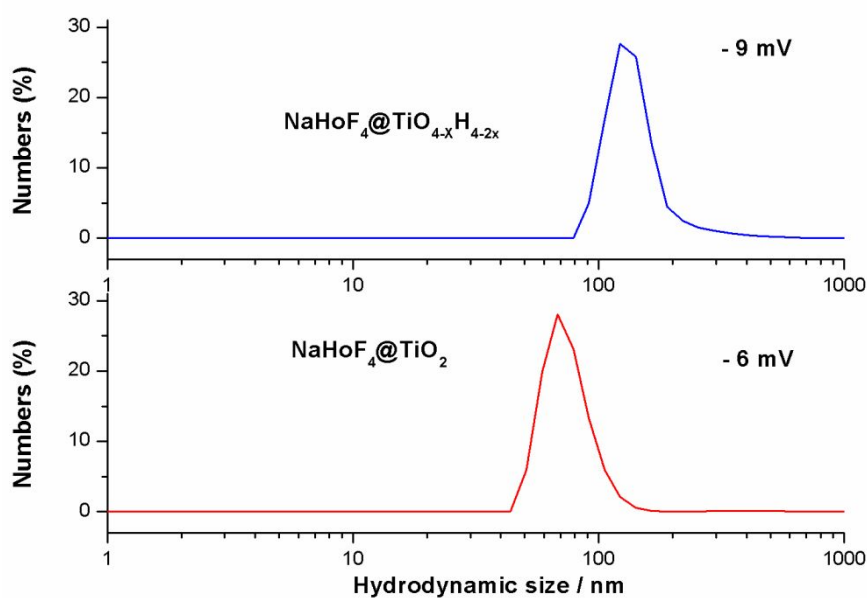
<sup>§</sup> Department of Mathematical Sciences, University of Loughborough, Loughborough, LE11  
3TU, UK

<sup>‡</sup> Nanoscale and Microscale Research Centre, Cripps South Building, University of  
Nottingham, Nottingham, NG7 2RD, UK

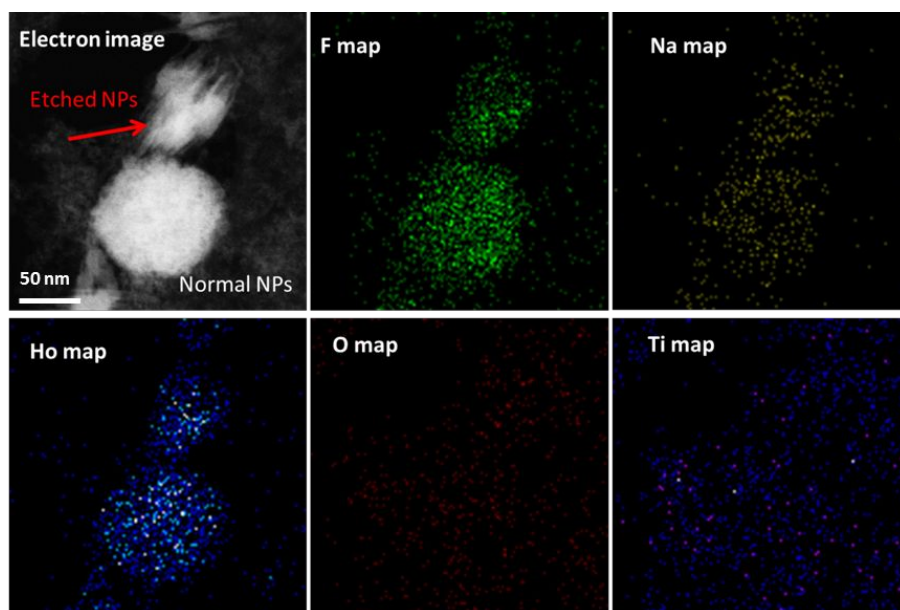
KEYWORDS: spICP-MS, core-shell nanoparticles, large scale synthesis, exposure and risk  
assessment, quantification



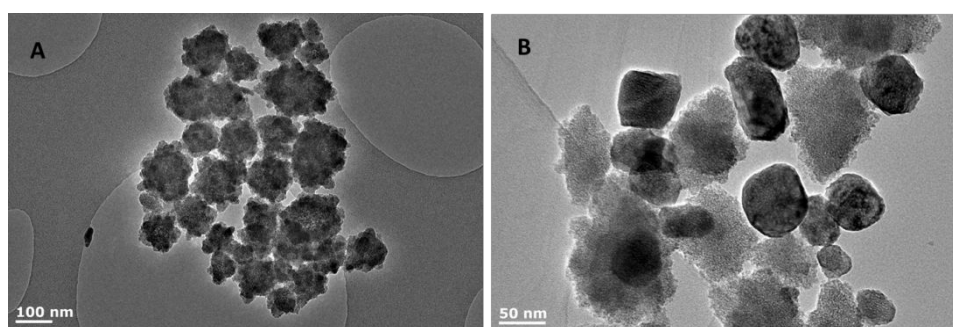
**Figure S1.** Energy dispersive X-ray spectrum of NaHoF<sub>4</sub>@TiO<sub>2</sub> NP sample. The NaHoF<sub>4</sub>@TiO<sub>2</sub> sample was obtained in a mixture of ethanol and water, in the presence of PVP.



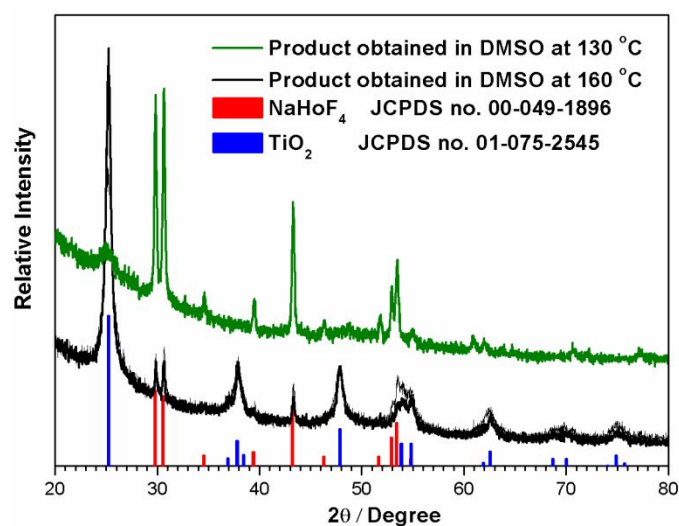
**Figure S2.** Hydrodynamic size distribution and zeta potential of NaHoF<sub>4</sub>@TiO<sub>4-x</sub>H<sub>4-2x</sub> and NaHoF<sub>4</sub>@TiO<sub>2</sub> NPs obtained in ultrapure water (pH = 7).



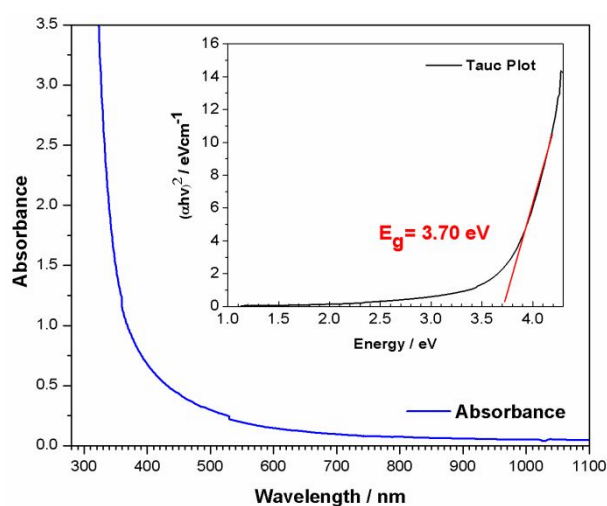
**Figure S3.** STEM-EDX spectroscopy mapping showing  $\text{NaHoF}_4@\text{TiO}_2$  NPs with different morphologies (normal and etched). The etched morphology was attributed to the breakdown of Ho-F by formation of H-F or Al-F.



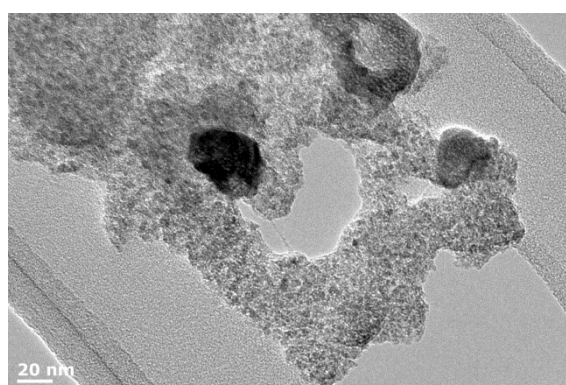
**Figure S4.** TEM images of products obtained in a more polar environment, *i.e.* in a mixture solvent of DMSO, instead of ethanol, and  $\text{H}_2\text{O}$  at 130 °C (A) and 160 °C (B).



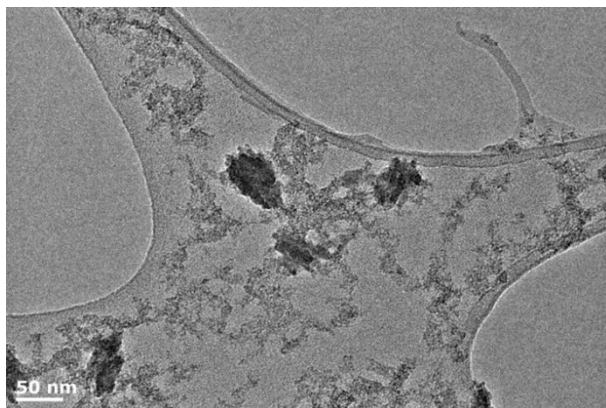
**Figure S5.** XRD of products obtained in the more polar environment, a mixture solvent of DMSO, instead of ethanol, and H<sub>2</sub>O at 130 °C and 160 °C, showing a lower amount of NaHoF<sub>4</sub> at the higher temperature.



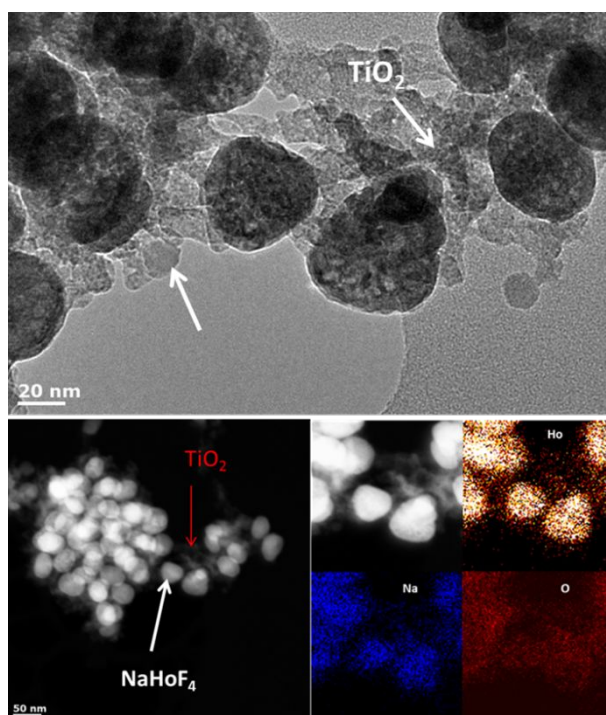
**Figure S6.** UV-Vis spectrum of NaHoF<sub>4</sub>@TiO<sub>2</sub> NPs



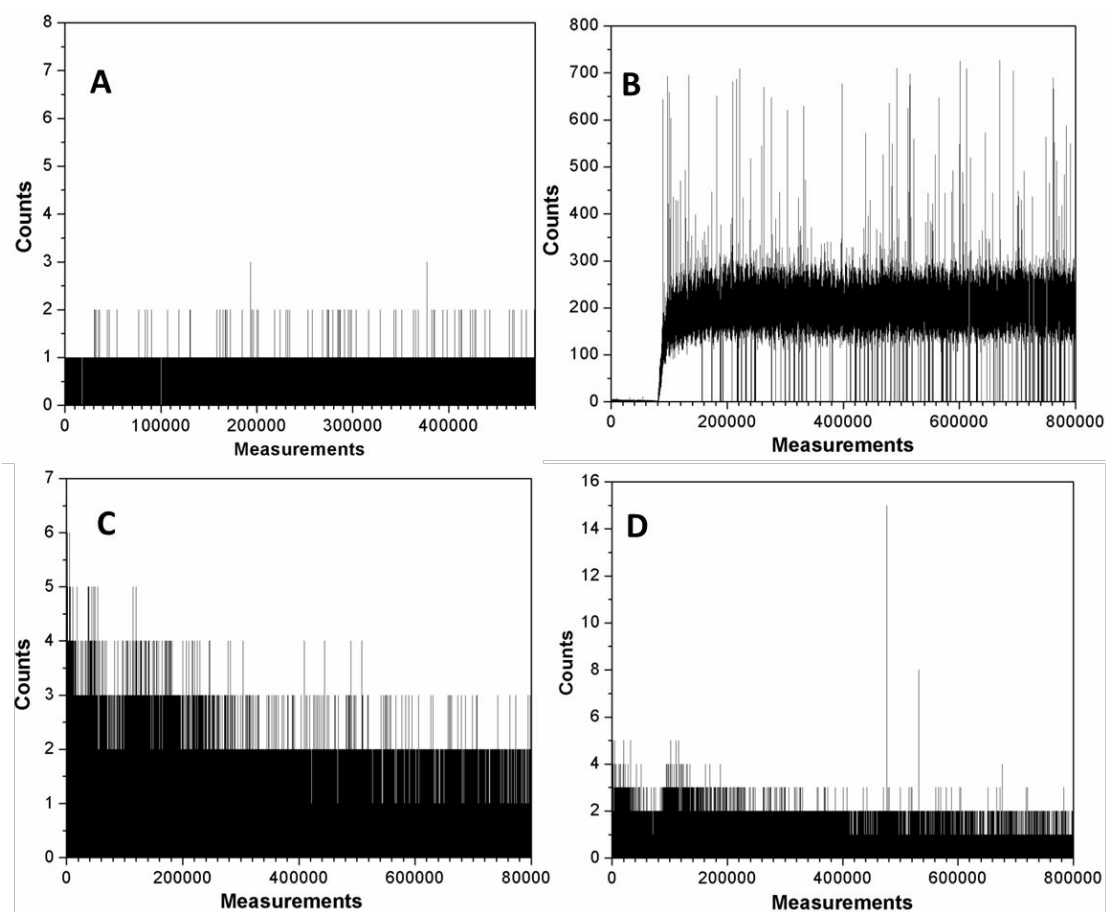
**Figure S7.** TEM image of products obtained in the presence of excess ammonia water at step 3, showing a mixture of two particles TiO<sub>2</sub> and NaHoF<sub>4</sub>.



**Figure S8.** TEM image of products obtained after stirring at 60 °C for 24 hours at step 3, without the following reflux at 100 °C, showing no  $\text{TiO}_2$  particles were formed.



**Figure S9.** TEM image (upper) and HADDF image (bottom-left) of products obtained *via* the sol-gel method using bisphosphonate PEG stabilized  $\text{NaHoF}_4$  NPs as seeds.



**Figure S10.** Real-time signal of Ti and Ho in MilliQ water and river (canal) water. a) Ti in MilliQ water, b) Ti in river water, c) Ho in MilliQ water, and d) Ho in river water.

**Table S1: Instrumental parameters used during single particle analysis**

Nebulizer Gas Flow [NEB]	1.12
Auxiliary Gas Flow	1.2
Plasma Gas Flow	18
ICP RF Power	1600
Flow Rate	0.34 g min <sup>-1</sup>
Transport Efficiency	13.62 %
Dwell Time	50 us

**Table S2: Canal water information**

Parameter	Value	Note
Turbidity	43 cm	This was also the depth of the canal at point of measurement
Temperature	12.3 °C	
Dissolved O <sub>2</sub>	94.4 % and 9.96 mg/ L	
pH	8.4	
Conductivity	710 µS	
Canal flow rate	0.0050854 m/s	Below the limit of detection for the flow rate instrument

**Notes about site and date:** The measurement was carried out on 30/04/2019 while the particle analysis was performed in June 2018. The site was frequented by cyclists and walkers. It is situated about 10 meters away from an electrified train line and the University train station. The water was slightly murky and brown in colour but not prohibiting in ability to see the bottom of the canal. Fish and insects were present within the water. Some leaves and organic detritus were found on top of the canal water. Some plastic bags and other assorted rubbish floated on top of the canal water. The weather was clear and there was a slight wind that blew parallel to the canal, this gave the water the appearance of some flow.

#### Size calculation of core-shell NPs from spICP-MS results

- 1) The real time peaks from single elements (Ti and Ho) were obtained sequentially *via* spICP-MS. The frequency of the peak represents the number of particles, while the intensity of a peak corresponds to the amount of element contained in each particle.
- 2) The mass of NaHoF<sub>4</sub> (or TiO<sub>2</sub>) is calculated from the mass of Ho (or Ti) as follows:

$$Mass (NaHoF_4) = Mass(Ho) \times \frac{Molecular\ weight\ (NaHoF_4)}{Atomic\ weight\ (Ho)}$$

$$Mass (TiO_2) = Mass(Ti) \times \frac{Molecular\ weight\ (TiO_2)}{Atomic\ weight\ (Ti)}$$

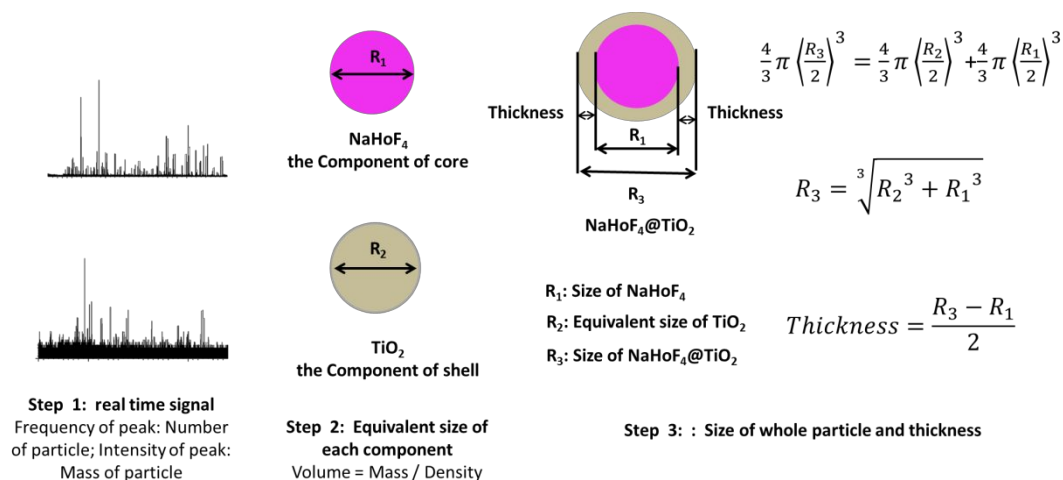
- 3) The volume of NaHoF<sub>4</sub> (or TiO<sub>2</sub>) is calculated from the mass, using the density of the bulk material (anatase TiO<sub>2</sub>, 3.9 g/cm<sup>3</sup> and hexagonal NaHoF<sub>4</sub>, 3.99 g/cm<sup>3</sup>)

$$volume = \frac{Mass}{density}$$

$$\text{Density (NaHoF}_4\text{)} = \frac{\text{molecular weight (NaHoF}_4\text{)} \times \text{molecular number (Z)}}{\text{Avogadro's constant} \times \text{cell volume (V)}} = \frac{263.91 \times 1 \text{ g}}{6.022 \times 10^{23} \times 109.94 \text{ \AA}^3} = \frac{3.99 \text{ g}}{\text{cm}^3}$$

The crystallographic data for NaHoF<sub>4</sub> was adapted from JCPDS 00-049-1896.

- 4) In the case of the core-shell NPs, as confirmed by TEM, the frequency of Ti and Ho should be similar. The volume of the whole core-shell NPs equals the sum of the volumes of the Ti and Ho components. The diameter of the core-shell NPs can thus be calculated as shown in **Figure S9**.



**Figure S11.** Schematic illustration of the size measurement of a core-shell NP by spICP-MS.