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University College Cork, Ireland Coláiste na hOllscoile Corcaigh Size and space controlled hexagonal arrays of superparamagnetic iron oxide nanodots: magnetic studies and application

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## **Supporting Information:**

## Determination of phases of iron oxide nanodots before and after annealing.

XPS was used to confirm the crystalline phase of the iron oxide nanodots on Si substrate after UV/Ozone treatment and further calcination. High resolution Fe2p spectra were recorded to distinguish different phases of iron oxides. Fe 2p core level spectrum recorded on iron oxide nanodots prepared after UV/Ozone treatment (Figure 1a) consists of two peaks associated with Fe  $2p_{3/2}$  at 711 eV and Fe  $2p_{1/2}$  at 724.4 eV and broadened due to the existence of Fe<sup>+2</sup> and Fe<sup>+3</sup> ions. The Fe  $2p_{3/2}$  and Fe  $2p_{1/2}$  binding energies (BEs) for Fe<sup>+2</sup> and Fe<sup>+3</sup> were determined by curve-fitting using Gaussian-Lorentzian line shapes. The measured Fe  $2p_{3/2}$  and Fe  $2p_{1/2}$  BEs are 709.7 and 723 eV (assigned to Fe<sup>+2</sup>) and 711.6 and 725 eV (Fe<sup>+3</sup>) matches literature values.<sup>1</sup> The concentration ratio of Fe<sup>+3</sup>/ Fe<sup>+2</sup> was calculated from the curve-fitted peak areas as about 2:1 as expected for Fe<sub>3</sub>O<sub>4</sub>. Fe 2p core level spectrum of iron oxide nanodots after calcination (Figure 1b) consists of two sharp peaks associated with Fe

 $2p_{3/2}$  and Fe  $2p_{1/2}$  at 711.3 and 725.1 eV accompanied by high binding energy satellite structures (+8 eV shift). These data are consistent with the existence of Fe<sup>+3</sup> (Fe<sub>2</sub>O<sub>3</sub>) ions only.<sup>2-3</sup>



Figure 1 High resolution spectrum for Fe 2p core level revealed (a)  $Fe_3O_4$  and (b)  $Fe_2O_3$  phase.

## Determination of crystalline structure of iron oxide nanodots before and after annealing by TEM.

The crystalline information of these systems is exemplified further by TEM (Figure 2). The nanodots on Si substrate were scratched by a sharp edge blade and disperse into ethanol for the preparation of TEM grid. Clear lattice fringes can be seen from Figure 2a revealed the single crystalline nature of the UV/Ozone treated sample. The lattice fringes were regularly separated with a spacing of 0.2967 nm, which agrees well with the (220) lattice index of cubic Fe<sub>3</sub>O<sub>4</sub> (Figure 2a).<sup>4</sup> Similarly, the single crystalline nature of the high temperature calcined sample was revealed by the HRTEM image (Figure 2b). Lattice fringes were regularly separated at 0.252 nm agreeing with the (110) lattice spacing of rhombohedral hematite.<sup>5</sup>



Figure 2 HRTEM image of (a)  $Fe_3O_4$  and (b)  $Fe_2O_3$  nanodots. Inset of (b) shows corresponding fringe spacings from nanodots.

## M-H measurements.

The magnetization Vs. field (M-H) measurements were carried out on  $Fe_2O_3$  nanodots. The diamagnetic contribution from the quartz substrates was estimated, subtracted from the directly measured results shown in Figure 3.



Figure 3 M-H curve of different diameter Fe<sub>2</sub>O<sub>3</sub> nanodots.

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