

Atomic and Electronic Structure of $\gamma\text{Fe}_2\text{O}_3/\text{Cu}_2\text{O}$ Heterostructured Nanocrystals

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Solar fuels have been invoked as alternatives to non-renewable fossil fuels in an increasing number of studies aimed at utilizing the inexhaustible energy available from solar radiation. During natural photosynthesis, CO_2 is reduced while light is converted into chemical energy with the help of water. Artificial photosynthesis, on the other hand, simulates this process by introducing semiconducting photocatalysts into heterogeneous systems in order to facilitate water oxidation and CO_2 photoreduction.¹ In this scenario, the discovery of the Photosystem-II structure has enabled parallel paths towards new materials design strategies in artificial photosynthesis by stabilizing photosynthetic reactions in lower band gap semiconductors using visible light.² “Bandgap engineering” of heterostructured nanocrystals has provided an effective way to manipulate photogenerated charge dynamics, ex. using a Type-II band alignment.³ In this study, we analyze the atomic and electronic structures of photoactive $\gamma\text{Fe}_2\text{O}_3/\text{Cu}_2\text{O}$ heterostructured nanocrystals (HNCs). $\gamma\text{Fe}_2\text{O}_3$ is a metastable, ferrimagnetic n-type semiconductor and Cu_2O is an intrinsic p-type semiconductor. They have attracted much interest due to their natural abundance, low cost and significant visible light absorption.⁴ However, both $\gamma\text{Fe}_2\text{O}_3$ and Cu_2O suffer from short minority carrier diffusion lengths (<10 nm) and lifetimes (~10 ps) so the HNC size must be kept in the few nm range. In this study, we have used aberration corrected scanning transmission electron microscopy (STEM) and electron energy-loss spectroscopy (EELS), in combination with first principles density-functional theory calculations to delve deeply into the atomic and electronic structure of $\gamma\text{Fe}_2\text{O}_3/\text{Cu}_2\text{O}$ HNCs.

Synthesis of $\gamma\text{Fe}_2\text{O}_3/\text{Cu}_2\text{O}$ HNCs was carried out by a solution-phase seeded growth approach. Preliminary investigations using X-ray/UV photoelectron spectroscopy have been performed to confirm a Type-II band alignment with longer excited state lifetimes and larger charge carrier densities. The samples were studied in aberration corrected Nion UltraSTEM200 and UltraSTEM100 dedicated STEMs, equipped with Gatan Enfium and Enfina EEL spectrometers, respectively. Figures 1(a) and (b) show atomic resolution high angle annular dark field (HAADF) images of isolated $\gamma\text{Fe}_2\text{O}_3$ particles. The images show very high quality nanoparticles, single crystal and mono-domain, with sizes in the desired 5-10 nm range. Crystalline Cu_2O bulk-like precipitates can also be detected (Figure 1(c)). By increasing the growth temperature from 100°C to 150°C, this colloiddally unstable byproduct can be removed, rendering a higher density of $\gamma\text{Fe}_2\text{O}_3/\text{Cu}_2\text{O}$ dimers and hence, an increased HNC yield and improved photocatalytic properties. Under optimal reaction conditions, the HNCs are enriched in dimers with some amount of remaining isolated $\gamma\text{Fe}_2\text{O}_3$ particles. Trimers and higher oligomers are removed upon size-selective precipitation with ethanol. Figure 2(a) shows an atomic resolution Z-contrast image of a typical $\gamma\text{Fe}_2\text{O}_3/\text{Cu}_2\text{O}$ HNC. The $\gamma\text{Fe}_2\text{O}_3$ component has a diameter of 8 nm while the Cu_2O particle has a diameter of 5 nm. The system is crystalline, but as a result of the seeded growth method, the interface between both components is not well defined. Figure 2(b) shows a compositional color map

derived from EELS elemental mappings of the HNC. Maps obtained from the O K edge (green), Fe $L_{2,3}$ (blue) and the Cu $L_{2,3}$ edges (red) are overlaid. Averaged EEL spectra taken from the $\gamma\text{Fe}_2\text{O}_3$, Cu_2O components and also from the HNC interface are shown in Figure 2(c). A 2 eV shift of the O K -edge pre-peak at the onset is noticeable between the two components. Since the HNC interface plays an important role in enhancing the charge carrier density as well as the excited state lifetime, this chemical shift could be a result of band bending at the interface p-n junction. First principles density functional theory calculations will be presented to understand the charge transfer at the HNC interface.

References:

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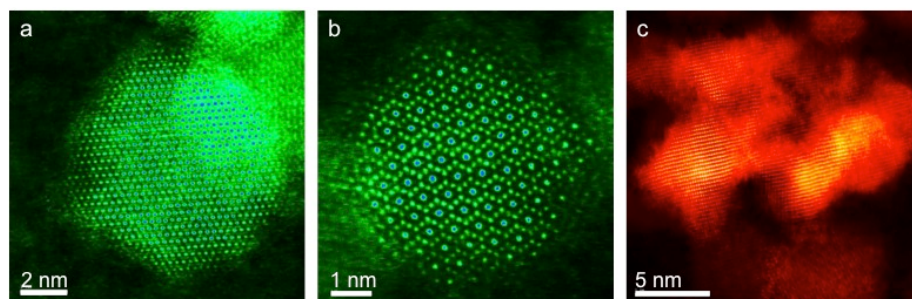


Figure 1. (a) and (b) STEM HAADF images of isolated $\gamma\text{-Fe}_2\text{O}_3$ particle; (c) STEM HAADF image of bulk Cu_2O precipitate. Data obtained in the Nion UltraSTEM200, operated at 200 kV.

Figure 2. (a) STEM HAADF image of $\gamma\text{-Fe}_2\text{O}_3/\text{Cu}_2\text{O}$ HNC; (b) EELS elemental mapping of $\gamma\text{-Fe}_2\text{O}_3/\text{Cu}_2\text{O}$ HNC obtained by integrating the absorption edge intensities after background removal using a power law fit. Principal component analysis was used to remove random noise; (c) EEL spectra from the $\gamma\text{-Fe}_2\text{O}_3$ (blue) particle, the Cu_2O (red) and from the HNC interface (black). Data acquired in the UltraSTEM100 operated at 100 kV.

