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Electronic Supplementary Information

Biological and Environmental Media Control Oxide Nanoparticle Surface Composition: The Roles of Biological Components (Proteins and Amino Acids), Inorganic Oxyanions and Humic Acid

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Experimental Methods

Nanoparticle Characterization. TiO_2 and α-Fe_2O_3 nanoparticles discussed here were characterized extensively for their particle size, morphology, surface area, crystallinity and surface functionality. The particle size and morphology was obtained using transmission electron microscopy (TEM – JEOL 1230, Japan). Particles surface area was measured using a multipoint BET analyzer (Quantachrome). The samples were degassed for 24 hrs at 110^{o}C prior to analysis and measurements were made in triplicates. X-ray diffraction (D8, Bruker XRD) was used to obtain the crystallinity. These characterization data are provided in the Figure S1. Additionally, attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) was used to probe the surface functionality of the nanoparticle surface before adsorption (*vide infra*).

Surface Analysis of Nanoparticles in Biological and Environmental Media. The surface of the nanoparticles in different biological and environmental media was probed using attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy. This technique has been described in greater detail in our previous publication on the use of ATR-FTIR spectroscopy as a tool to probe the interfacial surface region of nanomaterials.[1] Briefly, a thin film of the nanoparticle of interest was made on the ATR-FTIR crystal by placing a suspension of nanoparticles (1 mL of ~1.5 mg/mL) and letting dry overnight. The samples still contained adsorbed water on the surface. Subsequently, pure water and the media were introduced respectively through a flow system over the nanoparticle thin film and the corresponding single beam IR transmittance spectra were collected as a function of time. These single beam IR spectra of the media were then referenced to the background spectrum of pure water in order to convert into absorbance units.

Source of Media, Chemicals, and Nanoparticles. All the solutions used in this study were prepared in HPLC grade Optima water. TiO_2 nanoparticles were purchased from Nanostructured and Amorphous Materials, Inc. α-Fe_2O_3 nanoparticles were synthesized in the lab according to the following protocol.[2] Solid $FeCl_3.6H_2O$ (2.35 g) was dissolved in methanol (40 mL) and refluxed for several minutes and to add water (3 mL). Methanol (30 mL) containing NaOH (1.04 g) was then added drop wise to this solution and refluxed for 48hrs. The resulting brown-red precipitate was collected by centrifugation and washed three times in water and oven dried for 24 hrs. Commercially purchased media, chemicals and nanoparticles are summarized in Table S1.

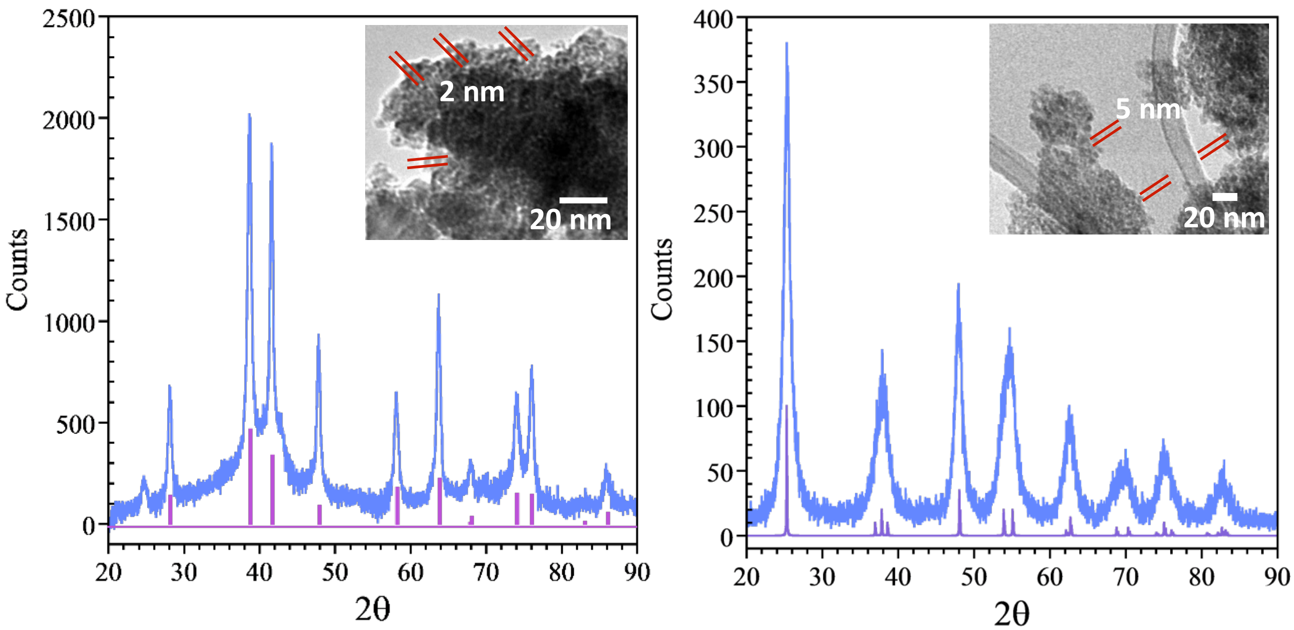

Figure S1: Transmission electron microscopy (TEM) images in the inset and X-ray diffraction (XRD) data are shown above for (a) iron oxide (synthesized in the lab) and (b) titanium dioxide (purchased from Nanostructured and Amorphous Materials, Inc.). The XRD patterns for hematite (right) and anatase are shown in (a) and (b) respectively. The particle size for these are 2 and 5 nm, respectively, see text for further details.

Table S1: Sources of commercial materials including media, chemicals and nanoparticles.

Materials	Source
Bovine serum albumin (BSA, ≥98.0% lyophilized powder)	Sigma - Aldrich
L-aspartic acid (≥98.0%),	Sigma – Aldrich
lysozyme (≥90.0%, lyophilized powder),	Sigma – Aldrich
Citric acid (≥99.5%)	Sigma - Aldrich
Difco minimal (M9) media	BD&Company
Roswell Park Memorial Institute (RPMI) media	Thermo Fisher Scientific
Suwanee river humic acid	International Humic Substances Society (IHSS)
Optima water (HPLC grade)	Fisher Scientific

Reference:

1. I. A. Mudunkotuwa, A. A. Minshid and V. H. Grassian, *Analyst*, 2014, **139**, 870-881.
2. J. Borcherding, J. Baltrusaitis, H. Chen, L. Stebounova, C.-M. Wu, G. Rubasinghege, I. A. Mudunkotuwa, J. C. Caraballo, J. Zabner, V. H. Grassian and A. P. Comellas, *Environmental Science: Nano*, 2014, **1**, 123-132.