Electronic Supplementary Information (ESI) for

Molecular level insight on the adsorption of carboxylic acids to oxide nanoparticles in aqueous solution by X-ray photoelectron spectroscopy

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1. Chemicals

The experiments presented in the main article text are performed with Ludox CL (W.R. Grace and Company, Sigma-Aldrich). Ludox CL is a core-shell type colloid produced commercially by coating amorphous silica (core) nanoparticles in a monolayer of Al_xO_y (shell), and is sold as a 30 wt.% suspension in aqueous solution that is free of any ligand (surface coating). We refer to this colloid as $Al_xO_y@SiO_2$ throughout the main article text. Technical details of the suspension provided by the manufacturer include: amorphous structure, positive particle charge, 12 nm average particle diameter, and a specific surface area of 230 m^2/g. Dilutions to the desired wt.% are done using Milli-Q water after filtering the stock suspension through 7 μm retention paper (Whatman no. 52) that serves to remove any agglomerates that might have developed during shelf-life. Formic acid (99%, Acros Organics) was used as-received. pH is adjusted using concentrated HCl (37%, ACS Reagent, Sigma-Aldrich) and measured using a four-point calibrated Mettler Toledo Expert electrode.

2. Transmission Electron Microscopy (TEM)

The mean diameter and particle size distribution of the $Al_xO_y@SiO_2$ suspension is measured by transmission electron microscopy on a FEI Tecnai F30 FEG microscope operating at 300 kV. A small drop from a 3 wt.% suspension is placed directly on a copper TEM grid with carbon film support and allowed to dry in ambient air. A representative TEM micrograph and the particle size distributions calculated from 100 particles (ImageJ software

package) are shown in **Fig. 1b** and **1c**, respectively, of the main article text. The particles are roughly spherical in shape and exhibit a narrow size distribution centered at 12 nm, in perfect agreement with the size estimate provided by the manufacturer.

3. Electrophoretic Mobility

Electrophoretic mobility experiments of 1 wt.% $Al_xO_y@SiO_2$ and 1 wt.% $Al_xO_y@SiO_2$ in 0.2 M HCOOH are performed with a Malvern Zetasizer (Nano-ZS, ZEN 3600) instrument at room temperature. Disposable capillary cells (DTS 1060) are used as cuvettes. Each sample is averaged for 30 mins. Zeta potentials are calculated from the electrophoretic mobility results using Smoluchowski theory.[1]

4. X-ray Photoelectron Spectroscopy (XPS)

In situ XPS experiments are performed at the SIM beamline[2] of the Swiss Light Source (SLS) using a liquid microjet. A general introduction to XPS at the water-nanoparticle interface is given elsewhere.[3] The SLS near ambient pressure photoemission (NAPP) endstation is used.[4] All experiments are performed in vacuum (1×10^{-4} mbar) using a 26 µm quartz nozzle and the flow rate 0.40 mL/min. 5 wt.% suspensions Al_xO_y are used for XPS. The Scienta R4000 *HiPP*-2 spectrometer is operated in constant energy mode. The primary photon energy of the beamline is set at 450 eV and ionizes the Si 2p, Al 2p and C 1s orbitals. The broad survey spectrum of **Fig. 1a** in the main article text is recorded using the simultaneous combination of 450 eV and 900

eV (second order radiation). The latter ionizes the O 1s orbital. The binding energy scale is calculated as BE = hv – KE. **Fig. 1a** uses a kinetic energy scale because the use of two photon energies prohibits the conversion to binding energy. The entrance cone of NAPP has an aperture of 0.5 mm and a working distance to the surface of the liquid microjet of 0.5 mm. The analyzer is operated at 50 eV pass energy, in steps of 100 meV and dwell time 0.1 s. The entrance slit was 0.3 mm (width) × 25 mm (length) and curved. All condensed phase liquid peaks are fit using Gaussian functions. Gas phase peaks are fit using Voigt functions.

References

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