Characterization of pH-responsive vinyl polymer/silica colloidal nanocomposite particles in the wet state by soft x-ray spectromicroscopy

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Polymer-silica colloidal nanocomposites were prepared by free-radical copolymerization of 4-vinylpyridine (4VP) monomer and ethylene glycol dimethacrylate (EGDMA) in the presence of 20 nm silica sols in aqueous media. These nanocomposite particles swell and acquire microgel character at low pH due to protonation of the 4VP residues, as confirmed by dynamic light scattering (DLS). For example, the intensity-average particle diameter was 230 nm at pH 8.8 but increased to 550 nm at pH 2.5. This pH-responsive behavior is critical for the use of these nanocomposite particles as 'Pickering' emulsifiers [1].

In this work scanning transmission X-ray microscopy (STXM) studies at energies near the C-1s, N-1s, and O-1s absorption edges using the beamline 5.3.2 at Advanced Light Source provide direct experimental evidence that the nanocomposite particles swell at low pH. We conducted the STXM measurement in a wet cell between two silicon nitride membranes (the cell thickness is less than 1 micron). Nanocomposite particles were dispersed in water at between pH 2 and pH 10 adjusted by adding HCl and NaOH. The observed particle sizes at both low pH and high pH correspond well to the values determined by DLS. The acid-base interaction between the silica sol and the pyridine was studied using nitrogen 1s NEXAFS spectroscopy [2].

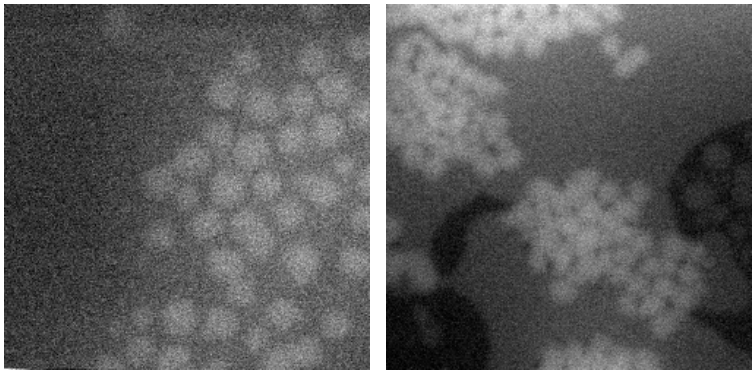

Figure 1: Left and right images show the STXM optical density images at N1s absorption edge energy, at pH 2.3 and pH 8.2, respectively. Image size: $(5\ \mu m)^2$

References

[1] – Fujii, S., Read, E. S., Binks, B. P., Armes, S. P., *Adv. Mater.*, in the press 2005 (and refs therein).
[2] - Gyan K. Agarwal et al., J. Phys. CHem. B, **107**, 12497 (2003)