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Direct Imaging and Spectroscopic Characterization of Stimulus-Responsive Microgels

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Microgel particles with diameters ranging from 100 nm to 1 μm have attracted significant attention recently.[1] Such particles offer a number of potential applications in various fields including drug delivery,[2] chemical separations,[3] sensors,[4] catalysis,[5] dynamically tunable microlenses,[6] templates for synthesis of inorganic nanoparticles,[7] water purification,[8] viscosity modifiers[9] and as "smart" particulate emulsifiers.[10] Stimulus-responsive microgel particles can swell or de-swell on application of certain external "triggers" such as pH, temperature, addition of electrolyte, etc. Microgel particles are usually employed in their wet solvated state, and in situ characterization of these particles under such conditions is essential for understanding their colloidal behavior. Appropriate techniques for characterizing solvated microgels include dynamic light scattering (DLS), ^{1}H NMR, small-angle neutron scattering and fluorescence spectroscopy.[1]

Optical microscopy (OM) is a useful technique for sizing large particles in solution. However, due to the wavelength of visible light and other optical constraints, the effective resolution limit for OM is approximately 1 μm. Furthermore, it is very difficult to observe even micrometer-sized microgels directly due to the very small difference in refractive index between the swollen particles and the continuous phase. DLS is a very convenient technique for assessing the (de-)swelling of microgels.[1] However, no morphological and spectroscopic information can be obtained with this sizing technique.

Herein we describe the first direct, real space characterization of *swollen* pH-responsive microgel particles in aqueous solution using scanning transmission X-ray microscopy (STXM). STXM combines excellent compositional sensitivity via near-edge X-ray absorption fine structure spectroscopy (NEXAFS)[11] with high spatial resolution and has been recently used to study a number of polymer systems.[12] The so-called "water window" between the carbon and oxygen 1s absorption edges enables STXM to characterize fully hydrated organic samples such as biofilms[13] and synthetic polymers.[14] The Polymer STXM[15] at beam line 5.3.2 of the Advanced Light Source (ALS) used in this work provides images with better than 50 nm spatial resolution and a NEXAFS spectral resolution $E/\Delta E$ > 2000. The present STXM study is the first to provide images of submicrometer-sized swollen microgel particles and to simultaneously determine their chemical state in situ.

The lightly cross-linked poly(4-vinylpyridine)-silica (P4VP−SiO_2) nanocomposite microgel particles investigated were synthesized by free radical copolymerization of 4-vinylpyridine with ethylene glycol dimethacrylate in the presence of an ultrafine 20 nm silica sol in aqueous solution as described by Fujii et al.[10a] Scanning electron microscopy (SEM) studies of the dried microgel (Figure 1a) indicated a mean particle diameter of around 200 nm. The pK_a value of the microgel was determined by acid titration to be approximately 3.7. Aqueous electrophoresis studies on a dilute aqueous dispersion of these P4VP−SiO_2 microgel particles indicated an isoelectric point at approximately pH 6.5, which is in excellent agreement with that reported earlier.[10a] The milky-white aqueous latex observed at pH 10 became less turbid at pH 3.0 (see Figure 2), because the refractive index difference between the microgel particles and the aqueous solution becomes much smaller after swelling at low pH, which leads to much less scattered light (in contrast, DLS studies confirmed that non-crosslinked P4VP−SiO_2 particles completely *dissolved* at pH 2 to give relatively viscous aqueous polymer solutions). A more systematic DLS study of a lightly cross-linked P4VP−SiO_2 microgel in dilute aqueous solution is summarized in Figure 2. At pH 8.8 the intensity-average diameter was approximately 230 nm, which is slightly larger than the number-average diameter estimated from the SEM image shown in Figure 1. Below a critical pH of around 4, protonation of the

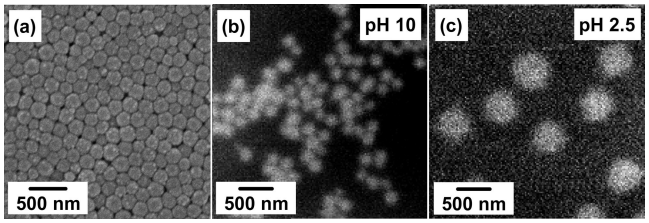

Figure 1. (a) SEM image of dried nanocomposite microgel particles. (b, c) STXM optical density images of aqueous dispersions of nanocomposite microgel particles in their non-swollen (pH 10) and swollen (pH 2.5) states, respectively.

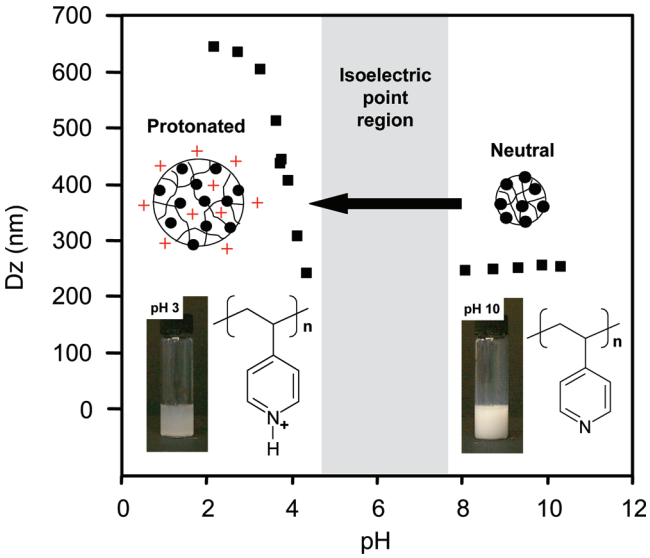

Figure 2. Variation of hydrodynamic diameter with solution pH for lightly cross-linked P4VP−SiO_2 nanocomposite microgel particles. The shaded region indicates the pH range in which flocculation was observed. The midpoint of this region corresponds approximately to the isoelectric point. The digital photographs indicate the visual appearance of this nanocomposite microgel dispersion at pH 3 and pH 10.

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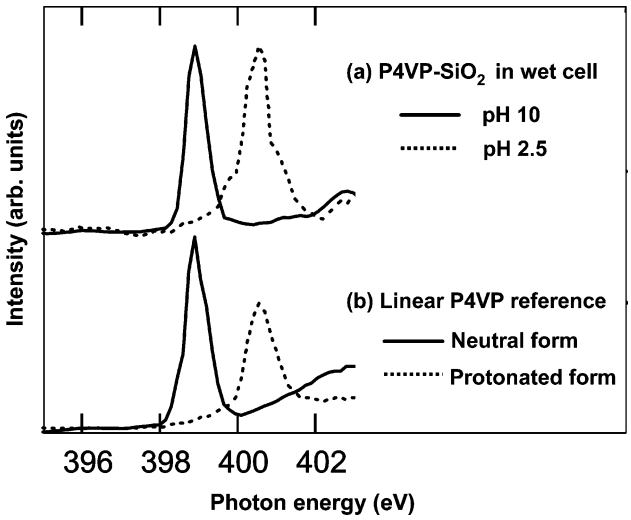

Figure 3. N 1s NEXAFS spectra of (a) P4VP−SiO_2 nanocomposite microgel particles in the wet cell at pHs 10 and 2.5, and (b) linear P4VP homopolymer dried in either its neutral or fully protonated form on Si_3N_4.

4-vinylpyridine residues leads to significant swelling. At lower pH, the lightly cross-linked nanocomposite microgel particles become fully protonated and highly swollen. Their intensity-average particle diameter is around 620 nm at pH 3, which indicates a volumetric swelling factor of more than an order of magnitude.

We focused on nitrogen (N 1s) NEXAFS for both STXM imaging and spectroscopic studies. This was due to the ease of handling multicomponent complex samples in wet cells at this particular energy but also because the pH-sensitive chemical environment of the nitrogen atoms is of particular interest in this system. Figure 3b shows the N 1s NEXAFS spectra obtained for neutral and protonated linear P4VP homopolymer, which was used as a reference. For neutral P4VP placed on a Si_3N_4 membrane, the lowest photon energy peak is at 398.9 eV. This is due to the N 1s to π^* transition and is in good agreement with NEXAFS spectra of a pyridine multilayer on a metal surface.[16] In the spectrum recorded for the protonated, cationic P4VP film (cast onto Si_3N_4 from an aqueous H_2SO_4 solution at pH 1) the π^* peak shifts to a significantly higher energy of 400.4 eV. This is primarily due to a 1s core level shift due to reduced screening in the cationic state.[17] Similar changes in the N 1s NEXAFS spectra were reported for another cationic polyelectrolyte, polyaniline.[17] Thus, these well-resolved peaks are excellent markers for the protonated and neutral states of the pyridine rings, and the corresponding two photon energies provide sufficient chemical contrast between the microgel particles at high and low pH.

The STXM optical density image shown in Figure 1b was recorded at 398.9 eV and indicates a number-average particle diameter of approximately 190 nm for the non-swollen P4VP−SiO_2 particles at pH 10. Taking into account the effect of polydispersity, this is in good agreement with the SEM and DLS data reported above. The swollen cationic microgel at pH 2.5 in Figure 1c was imaged at 400.4 eV. Its number-average diameter was determined to be 510 nm, which is somewhat smaller than the intensity-average diameter of 620 nm reported by DLS, as expected. The STXM images suggest that the swollen microgel particles are well dispersed, rather than aggregated.

After obtaining the images in Figure 1, b and c, N 1s NEXAFS spectra were acquired from the individual microgel particles to estimate their degree of protonation (Figure 3a). The resulting N 1s NEXAFS spectra at both low and high pH have sharp peaks at photon energies that are the same as those for the corresponding reference spectra (Figure 3b). Although there are subtle differences between the spectra obtained for the swollen microgel particles and the dried protonated P4VP homopolymer reference, there is little or no evidence for *neutral* nitrogen species being present in either case.

In summary, STXM has been used to observe and characterize acid-swellable microgel particles directly in aqueous acidic solution. Moreover, NEXAFS studies confirm that the nitrogen atoms of these P4VP-based cationic microgel particles are completely protonated at low pH.

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Supporting Information Available: Synthesis and characterization details for the P4VP-SiO_2 microgel particles; STXM sample preparation and measurement conditions. This material is available free of charge via the Internet at http://pubs.acs.org.

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