A Novel Method of Investigating Wet Materials in EM

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Electron microscopy (EM) is an excellent instrument for high resolution investigation of nano-particles. However, the inability to sustain hydrated conditions in the high vacuum environment of the EM poses an unavoidable drawback in hydrated materials research. Removal of water may result in undesirable morphological and structure change. Research and development on examining hydrated materials in EM, wet environmental cell TEM (WETEM) in particular has gained much momentum in the last decade despite having first been investigated more than half a century ago [1]. Although wet-cell environmental TEM (WETEM) provides the unique capability of imaging wet materials and resolving real-time dynamic environmental processes at micro- and nano-scales [2], high costs of commercial products (special environmental TEM holders) prevents many researchers from investigating wet materials in EM, especially in TEM. This paper presents a novel and cost effective approach for the microstructure investigation of hydrated materials in EM.

A simple, low cost method of sample preparation is to trap hydrated wet materials in between two carbon thin films [3]. However, this technique requires fabrication of carbon film and a special device to check for leaks before inserting the "embedded" wet sample into the TEM column. Ionic liquid (IL; also known as liquid electrolyte) is a salt in liquid state. IL has properties of high conductivity, high affinity to biological organisms solid in ambient temperature, high osmotic pressure and zero vapor pressure. These properties facilitate investigation of wet samples in a regular high vacuum SEM and TEM. A few different samples, a bi-layer polymer jelly capsule, carbon nanotubes and expandable clay nanoparticles (smectitie), were selected for this experiment. For SEM examination, samples were mounted on slightly modified Al stubs that have a small dish-like (concave) surface for holding wet materials. Samples of suspended nanoparticles were pipetted onto regular holey carbon films for TEM study. While both SEM and TEM samples were still wet, a very small drop (3 μl) of IL (Hitachi IL1000) was quickly applied on the sample to form a very thin IL film on the sample surface. Samples were examined in the EM after IL treatment.

Superficially, no significant morphology differences were detected between smectite samples prepared by coating with IL and conventional air-dry techniques (Figs. 1 and 2). Upon closer examination, suspended clay nanoparticles coated or "wrapped" by a very thin layer of IL showed better dispersion of clay particles with less contrast. On the other hand, conventional air-dried samples showed strong contrast with larger aggregates. The less defined particle edge and low contrast of IL treated sample are due mainly to the electron scattering caused by water molecules in the wet sample. Nevertheless, a high resolution lattice image can still be seen. The large d-spacing as shown in electron diffraction indicated the presence of water in the sample, i.e., intercalation of water molecules in lattice layers despite immersion in the high vacuum EM column. TEM tomography of IL treated sample revealed smectite nanoparticles "floating" in the water (Fig. 3). Application of a minute amount of IL on a bi-layer polymer jelly capsule resulted in distinguished layers and elimination of artifacts (Fig. 4) [4]. Similarly, samples coated with a thin layer of IL revealed well-dispersed carbon nanotubes without reliance on the cryo-TEM method, thus highlighting the time- and cost-efficient qualities of this new technique (Fig. 5).

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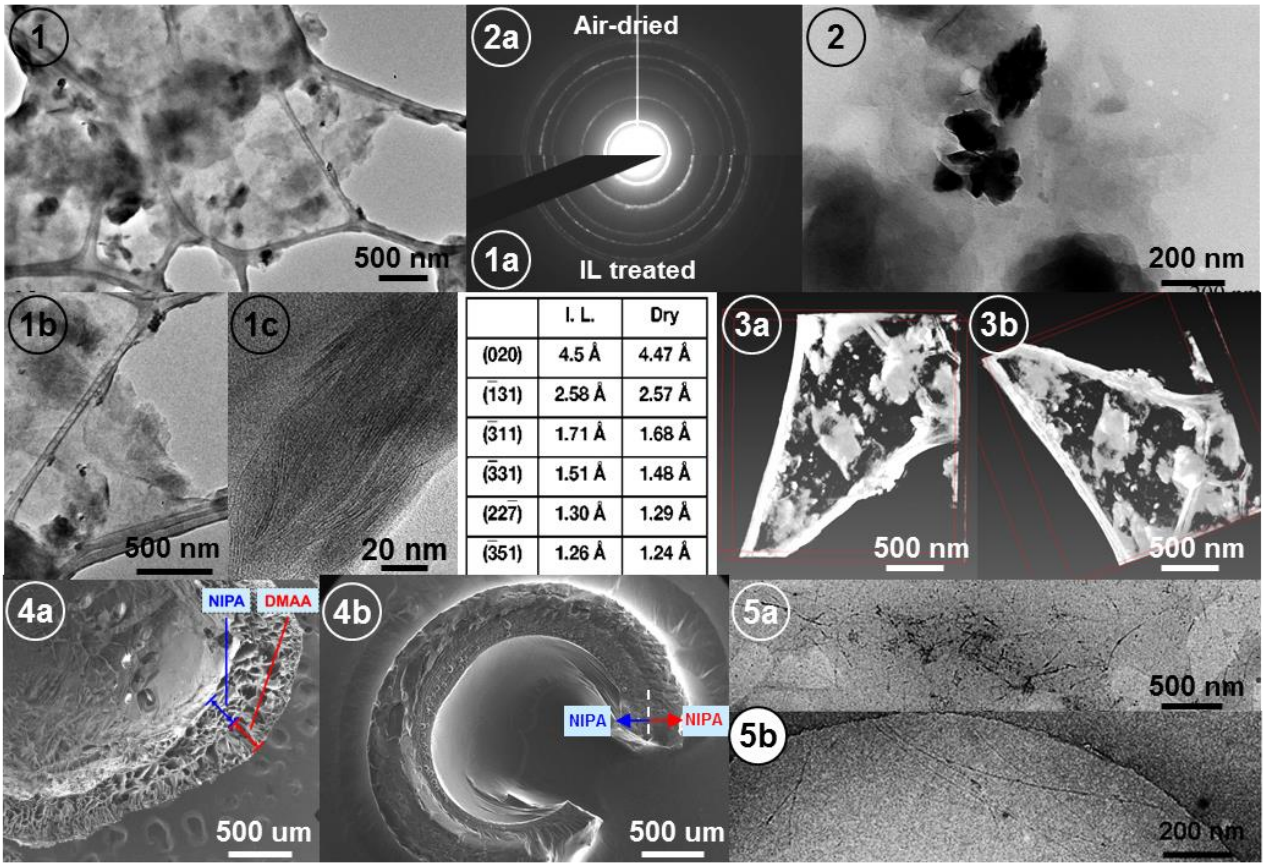

Fig. 1. Low magnification TEM micrograph shows wet smectite clay nanoparticles of various morphologies "filling" the hole in a Lacey carbon grid with ionic liquid. SAD pattern depicts larger d-spacing as compare with air-dried sample (a); higher magnification image reveals smectite clay composed of thin platy flakes, laths, needle-like fibers without well-defined boundaries and edges (b); and lattice fringes in HRTEM image (c).

Fig. 2. TEM micrograph of smectite prepared by conventional air-dry method depicts typical thick aggregated that formed after drying sample in air. SAD pattern reveals a little smaller d-spacing than that of IL treated sample (also see the table below SAD pattern).

Fig. 3. TEM tomography of IL treated smectite reveals clay nanoparticles and aggregates "floating" in the holes of a Lacey carbon grid. Images (c) and (d) are viewing from different orientation.

Fig. 4. SEM micrographs of a bi-layer polymer hydrogel capsule demonstrate that artifacts resulted from conventional air-dried technique (a), but could be eliminated by a thin coating of IL on the specimen (b).

Fig. 5. A TEM image illustrates that well-dispersed CNT can be observed using IL technique (a) instead of using cryo-TEM method which requires special equipment and can be time consuming (b).