Real Time Imaging of Materials Transformations in Liquid Environment

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An understanding of how materials grow and transform in their working environment is essential to the development of functional materials and efficient devices for energy applications. We study a wide range of physical and chemical processes of materials in liquids using transmission electron microscopy (TEM). With the development of liquid cells, real time imaging of the colloidal nanoparticle growth with subnanometer resolution has been achieved. Unique growth mechanisms concerning size and shape evolution of nanocrystals, surfactant effects, the role of platinum in formation of metal or oxide nanocrystals, etc. have been achieved (Figure 1&2). Nanocrystal growth in a liquid cell remarkably resembles those in flask synthesis. We also use our home-made electrochemical cells to study the dynamic electrochemical processes at electrode-electrolyte interfaces. Using commercial electrolyte LiPF₆ in EC and DEC for lithium ion batteries, lithium dendritic growth and SEI formation are captured with great details (Figure 3). Inhomogeneous nucleation of lithium dendrites, dynamic dendritic growth and dissolution, electrolyte decomposition, and SEI formation have been observed. The composition and structure of SEI are characterized using advanced TEM techniques including EDS and nano-beam diffraction series, which show that the SEI layer is composed of C and F species with LiF nanocrystals (~5 nm) distributed in the entire SEI layer. Using the same electrochemical cell set up, we make a Li-S nanobattery to study polysulfide transformations. The experimental results show that when an electric current of -3.5 x10⁻⁶ A is applied, precipitation of Li₂S₂ and Li₂S can be observed and they dissolve when the current is switched to 2 x10⁻⁶ A.

References

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FIG. 1. Surfactant effects on the growth of Pt-Fe nanoparticles. (A) Formation of stable platinum iron nanowires when 30% oleylamine was used; (B) Formation of unstable platinum iron nanowires when 20% oleylamine was used; (C) Individual platinum iron nanoparticles are stabilized when more than 50% oleylamine was used; (D) A schematic shows shape of platinum iron nanoparticles is influenced by oleylamine concentration as well as the configuration of neighboring nanoparticles.

FIG. 2. The growth of Fe$_3$Pt-Fe$_2$O$_3$ core-shell nanostructure in a liquid cell. (A) Sequential HRTEM images show the Fe$_3$Pt-Fe$_2$O$_3$ core-shell nanostructure formation. Blue highlights the Fe$_3$Pt and orange represents Fe$_2$O$_3$ from fast Fourier transform (FFT); (B) EDS mapping of a core-shell nanoparticle; (C) Schematic illustration of the formation pathway of Fe$_3$Pt-Fe$_2$O$_3$ core-shell heterostructure from a precursor solution of Pt(acac)$_2$ and Fe(acac)$_3$ (with Fe:Pt ratio of 4:1) dissolved in benzyl ether in the presence of oleylamine and oleic acid.

FIG. 3. In situ study of electrode-electrolyte interfaces in Li ion batteries using an electrochemical liquid cell. (A) Scheme of in situ TEM observation of the electrochemical reaction using an electrochemical liquid cell; (B-E) Time series of TEM images showing inhomogeneous Au lithiation, electrolyte decomposition, lithium metal dendritic growth, and SEI formation; (F) HAADF image of the Ti electrode with SEI film passivated on it. (G-H) The corresponding EDS maps of F K-series, C K-series; (I) EDS line scan starting from Si$_3$N$_4$ membrane across the SEI layer and ending on the Ti electrode, marked in panel F; (J) A schematic showing nano-beam diffraction characterization of SEI layer after the reaction, the pictures in the bottom showing the reconstructed bright-field image or dark-field image from a nano-beam diffraction series with each pixel corresponding to a reconstructed virtual diffraction pattern.