Studies of the Hierarchical Structure in UCT Manganese Oxides

Bahareh Deljoo[1,2], Tahereh Jafari[2], Steven L. Suib[1,2,3], Mark Aindow[1,2]

[1.] Dept. of Materials Science and Engineering, University of Connecticut, Storrs, CT, USA
[2.] Institute of Materials Science, University of Connecticut, Storrs, CT, USA
[3.] Dept. of Chemistry, University of Connecticut, Storrs, CT, USA

In a recent report from our group, inverse micelles were used as the soft template in the synthesis of well-ordered mesoporous manganese oxide using a sol-gel-based method. The materials synthesized using this method are known as University of Connecticut (UCT) mesoporous materials. UCT materials are formed in an acidic mixture that consists of a defined ratio of hydrotropic ion precursor, metal precursor, interface modifier, and surfactant. The surfactant molecules form inverse micelles, which encapsulate the reagents during the synthesis process. These features serve as uniformly sized nano-reactors within which hydrolysis and condensation of oxo-clusters occurs. Upon calcination, highly monodisperse nanoparticles will form within the inverse micelles, and the subsequent packing of these nanoparticles during aggregation leads to monodisperse meso-pores defined by intra-particle voids. The surfactant and hydrotropic nitrate ions in this process play key roles in controlling aggregation and condensation of oxo-clusters. Moreover, by modifying the ratio of the components in the mixture, and the process conditions with respect to the chosen metal precursor, this method can be used to synthesize mesoporous oxide materials from across the periodic table, including transition metals and non-metals [1-4].

The focus of the present work is on the synthesis of mesoporous manganese oxide, which is a promising candidate for catalytic and adsorption applications due to the variety of oxidation states and polymorphic structures that can be adopted. In this study, we have synthesized a series of mesoporous UCT manganese oxides by adding different surfactants to the primarily gel. This gel consists of $Mn(NO_3)_2$ as the metal precursor, 1-butanol as the interface modifier, and HNO_3 as the hydrotropic ion precursor. The ratios of the constituents in the gel and the amount of surfactant required to produce optimized UCT mesoporous manganese oxides were identified in preliminary synthesis trials. These values were then used to synthesize six different UCT manganese oxides with the only variable being the choice of surfactant. The hierarchical structures exhibited by these mesoporous materials were then studied using a combination of N_2 adsorption, XRD, SEM and TEM techniques. Here we present a selection of data from the sample that gave the highest specific surface area (166 m^2/g) from N_2 adsorption experiments; this sample was produced using P123 as the surfactant.

The wide-angle XRD data from this sample confirmed that the synthesized powder was a fully crystalline mixture of MnO_2, Mn_3O_4, and Mn_5O_8 phases. This is consistent with the Mn adopting a mixed oxidation state in this material. The broadening of the XRD peaks was used to evaluate the crystallite sizes for the phases, and in each case these were uniform and <10 nm. The mesopore sizes were investigated using small-angle XRD and N_2 adsorption, and both measures gave mean pore sizes of 4.0 nm. The microstructure the sample studied using an FEI Teneo LoVac FEG-SEM and an FEI Talos F200X FEG-TEM. Examples of the secondary electron SEM images are shown in Figure 1. These images reveal that the nanoparticles are assembled into spherical aggregates of around 0.1-2.0 µm in diameter. These spheres are themselves aggregated into coarser features 10-100 µm in diameter. The internal microstructures of the spherical aggregates are revealed more clearly in TEM images such as those shown in figure 2. The intra-particle mesopores are visible as variations in contrast in images obtained from the smallest

aggregates (Fig 2a). The characters of the nanoparticles themselves are revealed in higher resolution phase contrast lattice images (Fig 2b) and selected area diffraction patterns (Fig 2c); for the region shown the nanoparticles are a mixture of MnO_2 and Mn_3O_4 single crystals [5].

References:

[1] AS Poyraz *et al*, Nat. Commun. **4** (2013), p. 2952.
[2] AS Poyraz *et al*, Appl. Mater. Interfaces **6** (2014), p.10986.
[3] Z Luo *et al*, Chem. Mater. **27** (2015), p. 6.
[4] T Jafari *et al*, Langmuir **32** (2016), p. 2369.
[5] These SEM/TEM studies were performed using the facilities in the UConn/FEI center for Advanced Microscopy and Materials Analysis (CAMMA)
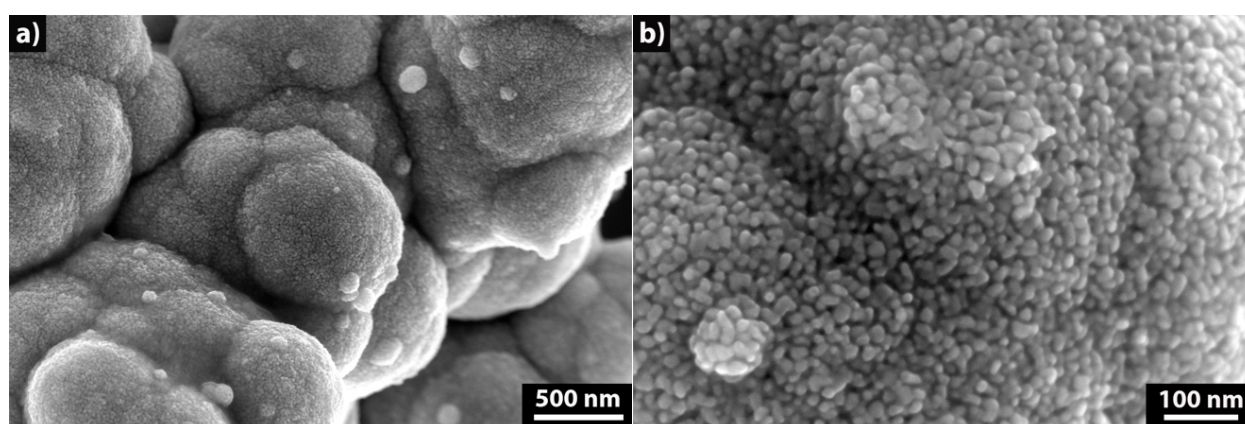
Figure 1. (a) and (b) SEM images of UCT manganese oxide produced using P123.
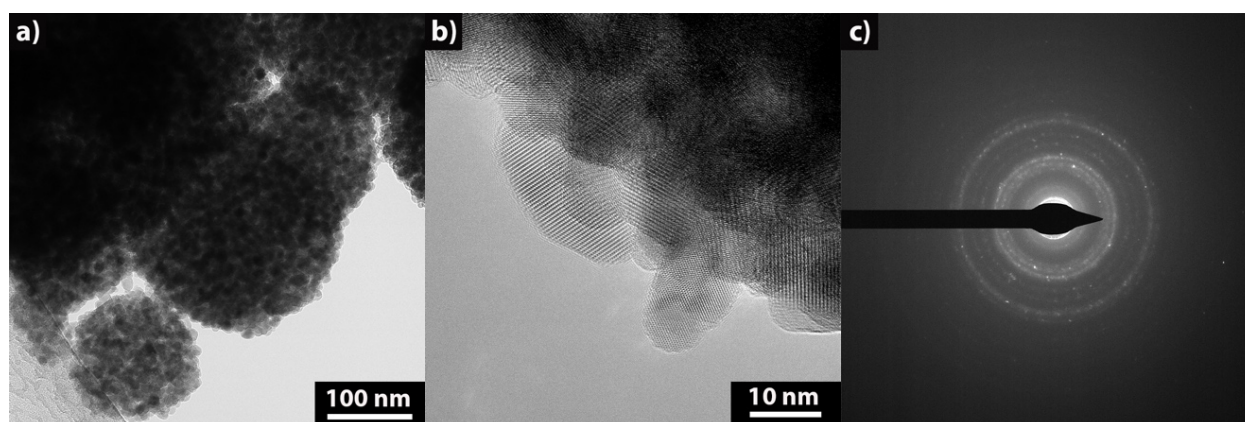
Figure 2. (a) and (b) TEM images, and (c) SADP from the sample shown in Fig. 1.