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One-pot Synthesis of Manganese Oxide Nanoparticles from Microemulsion Systems

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Manganese oxide nanoparticles can be obtained simply by mixing surfactant/water/oil ternary systems containing dialkyldimethylammonium chloride, manganese(II) nitrate hexahydrate, and *n*-hexane. This finding is valuable in the design of a one-pot synthesis of nanoparticles from microemulsion systems.

Microemulsions are thermodynamically stable isotropic solutions in which water or oil phases are embedded in micelles of surfactant molecules. Several methods for preparing nanoparticles from microemulsion systems have been reported since Boutonnet et al. prepared monodispersed particles by reducing metal salts dissolved in the water pools of microemulsions.[1–5] Most of the previous methods incorporate the use of sol–gel or hydrothermal methods that involve heating or calcination. In general, these methods waste heat energy, and the optimization of the preparation conditions is difficult.[6] Here, we present a new one-pot method for synthesizing trimanganese tetraoxide, which is used in lithium-ion batteries.[7] In this method, the nanoparticles can be prepared simply by mixing an aqueous phase containing the cationic surfactant, dialkyldimethylammonium chloride (DDAC), and manganese(II) nitrate hexahydrate and an oil phase of *n*-hexane under exposed conditions to the air.[8]

Figure 1 shows a phase diagram of the ternary systems DDAC/*n*-hexane/water containing 7 wt % manganese(II) nitrate hexahydrate. The phases were classified into four regions and were determined by the composition ratio of DDAC. When the surfactant composition $\phi_S = 40$–60 wt %, the systems were in a homogeneous transparent liquid phase just after preparation (Figure 1, $W_m + S$). These systems were found to be in the solubilized state in which *n*-hexane was solubilized in the micelles. This was because optical anisotropy, X-ray scattering, and X-ray diffraction were not observed in polarizing microscopic images, small-angle X-ray scattering (SAXS) profiles, and wide-angle X-ray diffraction (WAXD) profiles. Interestingly, these transparent liquids became brown one day after preparation. One week after preparation, the liquids changed to brown dispersions with dark brown precipitates (Figure 2a).

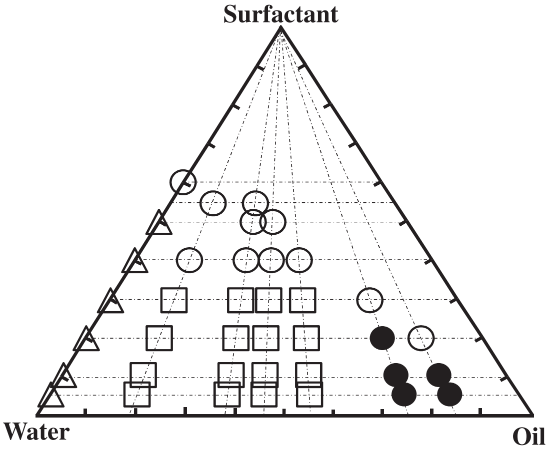

Figure 1. Phase diagram of the ternary system surfactant/water/oil containing Mn(NO$_2$)$_3$•6H$_2$O; white circle: $W_m + S$, black circle: $O + S + W_m$, triangle: LC, square: $O + O/W$. Here, W_m, S, O, and LC denote the micellar, solid, oil, and liquid crystalline states, respectively.

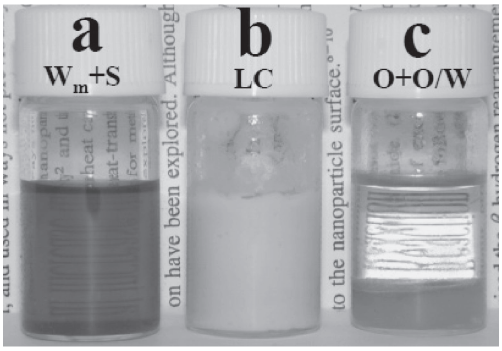

Figure 2. Photograph of surfactant/water/oil ternary systems: (a) 50:30:20, (b) 20:80:0, and (c) 20:48:32 (wt/wt/wt).

In the binary systems DDAC/water with $\phi_S = 5$–50 wt %, the systems were in a viscous turbid liquid state with optical anisotropy (Figure 1, LC; Figure 2b; Supporting Information Figure S1[15]). These turbid liquids are expected to be in a liquid-crystalline state LC because of their SAXS and WAXD profiles shown in Figures S2 and S3.[15] When $\phi_S = 20$ wt %, a scattering peak was observed at 1.90 nm^{-1} in the SAXS profile, while a broad peak was observed at $2\theta = 15$–$40°$ in the WAXD profile. The turbid liquids also became brown 1 week after preparation. When $\phi_S = 5$–30 wt % and the water composition ϕ_W exceeded 35 wt %, the systems were in the macroemulsion state in which oil droplets of about 10 µm diameter were dispersed in the water phase (Figure 1, $O + O/W$; Figure 2c). A transparent oil phase was separated just after preparation. These two phases also changed to brown liquids 1 week after preparation. When $\phi_W < 35$ wt %, the oil and water phases were separated from each other (Figure 1, $O + S + W_m$). In these systems, dark-brown precipitates were separated at the oil–water interfaces 1 week after preparation.

Figure 3 shows a scanning electron microscopy image of the dark-brown powder precipitated from the ternary system DDAC/*n*-hexane/water (50:20:30, wt/wt/wt). The powder consisted of octahedral particles with diameter 10–50 nm and needle-shaped particles of length 100–1000 nm. The crystal structure of these nanoparticles was characterized by WAXD

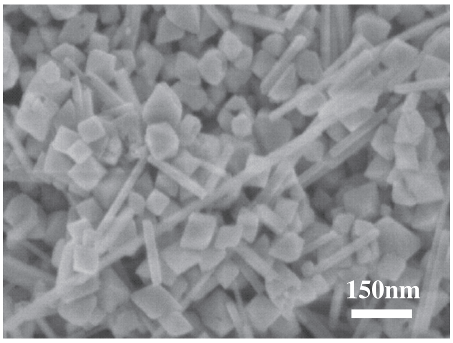

Figure 3. SEM image of Mn_3O_4 particles from the ternary system: surfactant/water/oil 50:30:20 (wt/wt/wt).

measurements. Figure S4[15] shows a WAXD profile of the powder. The X-ray was diffracted when $2\theta = 26.2$, 28.5, 32.5, 36.2, and 37.0°. The profile corresponds to trimanganese tetraoxide Mn_3O_4 (JCPDS-ICDD 24-0734). Some small peaks were observed at $2\theta = 31.6$ and 38.2° corresponding to pentamanganese octaoxide Mn_5O_8 (JCPDS-ICDD 39-1218). Here, we propose that the Mn_3O_4 nanoparticles and small amount of Mn_5O_8 nanoparticles were formed by the two-step oxidation of divalent manganese ions through manganese hydroxide. The chemical equations are as follows:

$$Mn^{2+} + 2(OH^-) \rightarrow Mn(OH)_2 \qquad (1)$$

$$3Mn(OH)_2 + (1/2)O_2 \rightarrow Mn_3O_4 + 3H_2O \qquad (2)$$

When 3 wt % ascorbic acid was added to the ternary systems as an antioxidant agent, white powder was precipitated one and half months after preparation. When the surfactant composition $\phi_S =$ 50–60 wt %, the systems were in the solubilized state in which *n*-hexane was solubilized in the micelles (Figure S5,[15] W_m). One month after preparation, the transparent liquids changed to yellow dispersions with white precipitates. Figure S6[15] shows a WAXD profile of the white precipitates. The X-ray was diffracted when $2\theta = 18.6$, 22.5, 24.4, 29.7, 33.5, and 39.3°. This profile corresponds to that of $Mn(OH)_2$ and these results indicate that $Mn(OH)_2$ is an intermediate product of the oxidation processes. A similar formation mechanism for Mn_3O_4 with two-step oxidation processes was reported previously.[9–11]

Some results indicate that the interfaces adsorbing DDAC molecules contribute to nanoparticle formation. Initially, nanoparticles did not form in the *n*-hexane/water binary systems one month after preparation. Second, the amount of precipitated nanoparticles from the ternary systems DDAC/*n*-hexane/water is drastically greater than that from the binary systems DDAC/water. Third, when we used nonionic surfactant, poly(ethylene glycol) monolaurate, and isostearyl glyceryl ether instead of DDAC, no precipitates were obtained. These findings showed that the two-step oxidation reaction can be promoted on the surface of the DDAC micelles containing *n*-hexane. Some researchers have reported accelerations of the reactions on micellar surfaces.[12–14] Solubilization causes the reactants within the micelles to become more concentrated than those in surrounding phases and leads to an acceleration in reaction.

In summary, we have successfully obtained manganese oxide nanoparticles from microemulsion systems. This one-pot synthesis method can be applied to the preparation of other metal oxide nanoparticles. The present findings are useful for the development of energy-efficient manufacturing processes for metal oxide nanoparticles.

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8 *Materials*: Dialkyldimethylammonium chloride (Quartamin D2345P) was obtained from Kao Co. *n*-Hexane and manganese(II) nitrate hexahydrate were purchased from Kanto Chemical Co. and Wako Chemical Co., respectively. Water was purified by a deionized water unit, DX-15, purchased from Kurita Water Industries Ltd.
Preparation: The ternary systems dialkyldimethylammonium chloride/*n*-hexane/water containing 0.21 g of manganese(II) nitrate hexahydrate (a total of 3 g) were prepared as follows: Dialkyldimethylammonium chloride, manganese(II) nitrate hexahydrate, and water were mixed in a glass container (cylindrical shape, diameter: 30 mm, height: 65 mm) with a vortex mixer (Vortex-genie 2, Scientific Industries Co.) for 2 min. After adding *n*-hexane, the mixture was mixed again under similar conditions, heated at 313 K in a constant-temperature tank for 20 min, and stirred using a magnetic stirrer for a month. The mixtures were diluted with water and ethanol and centrifuged at 12000 rpm for 15 min with Table Top Micro Refrigerated Centrifuge 3500 (Kubota Co.). The obtained precipitation was dried under reduced pressure.
Characterization: The phase of the ternary mixture was identified by microscopic observation at 1 week after preparation using a polarizing microscope Nikon Optiphot-pol XTP-11. The liquid crystalline morphology of the ternary mixture was characterized with a small-angle X-ray scattering (SAXS) instrument (M18XHF, MAC Science Co.), consisting of an 18-kW rotating-anode X-ray generator with a Cu target (wavelength $\lambda = 0.154$ nm) operated at 50 kV and 300 mA. This instrument comprises a pyrographite monochromator, pinhole collimation system ($\phi = 0.3$, 0.3, and 1.1 mm), vacuum chamber for the scattered beam path, and two-dimensional imaging plate detector (DIP-220). In order to obtain the WAXD data of the ternary mixture [the crystal structure of the obtained powder], an R-axis Rapid diffractometer [a Mini-frex II diffractometer] (Rigaku Co.) was operated at 45 kV [30 kV] and 200 mA [30 mA] to generate Cu $K\alpha$ radiation ($\lambda = 0.1542$ nm). WAXD photographs of the samples were taken at room temperature by using a graphite monochromator and a 0.3-mm pinhole collimator. The particle shape of the obtained powder was characterized with a scanning electron microscope (JSM-6330F, JEOL Ltd.).

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