

Novel Anodic Nanocrystals: Synthesis and Applications

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The science of energy storage and transport has gained increasing importance in recent years due to increased energy demand worldwide coupled to the diminishing supply of fossil fuels, the byproducts of which have negative environmental impact. Because of these problems, novel fuel sources and storage devices have become research topics of greater interest.²

Batteries are a relatively clean and convenient energy storage device, and Li⁺ ion batteries already have widespread use, frequently as the rechargeable energy source for mobile devices like cell phones, laptops, and electric cars. Unfortunately, Li⁺ batteries exhibit insufficient energy density for the growing energy demand, particularly for large scale applications such as electric vehicles.¹² The anode in a Li⁺ ion battery is typically carbon-based,¹³ and the effect of various structural designs is under study.¹ These anodes function similarly to cages which hold the Li⁺ ions, releasing them gradually over the discharge cycle of the battery. The energy density of the battery is partially limited by the quantity of Li⁺ ions which the anode can hold.^{2,13}

Transition metal oxides exhibit a greater specific capacity for Li⁺ ions than graphite.¹³ However, they exhibit poor robustness, as successive charge/discharge cycles show significant decrease in charge capacity.^{2,3} It is thought that repeated insertion and removal of Li⁺ ions during the charge and discharge cycles cause a large volume change in the metal oxide, which damages the crystal structure of the anode and reduces subsequent storage capacity.^{4,5}

Nanostructured transition metal oxides are more robust than bulk oxides, due to the reduced damage the volume change causes to the crystal structure at the nanoscale. Even simple nanoparticles show a slower decay and higher stable capacity than bulk solid.^{2,6} Current research is focused on the properties of various structures on capacity retention, from nanotubes^{9,10} to metal oxide-carbon composite “nanohorns”.^{2,7} This presentation shall focus on the generation and properties of hollow metal oxide nanocrystals.

In principle, hollow metal oxide nanocrystals should exhibit better capacity retention due to greater resilience toward the volume changes induced by the insertion and removal of the Li⁺ ions during charge and discharge cycles.^{4,5} Hollow metallic nanostructures have frequently been generated using the Kirkendall effect.^{8,11}

The Kirkendall effect occurs when two metals with differing diffusion rates are welded together. The metal with the higher diffusion rate diffuses into the second metal faster than the second metal can replace the material lost to the first. This difference in diffusion rate results in a net migration of the interface, as well as condensation of voids in the first metal. This outcome is ordinarily undesirable due to the degradation of mechanical properties caused by the voids. On the nanoscale, however, this process can be used to generate hollow structures. This is typically done by first generating a seed nanocrystal of one of the desired elements in the shell. This seed is then treated with

another substance in the gas or liquid phase. As the seed surface reacts to form the composite material, the layer of composite hinders further reaction. If the seed material exhibits a greater diffusion rate than the composite, the reaction continues as the seed material diffuses through the composite. This outward diffusion creates a void in the shell center.⁸

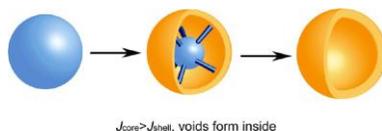


Fig. 1. Schematic of Kirkendall effect in formation of hollow nanocrystals⁸

Because the Kirkendall effect relies upon differing diffusion rates between two components, it can be very useful in synthesizing hollow multimetallic nanocrystals, or hollow monometallic oxides, but the synthesis of hollow multimetallic oxide nanocrystals remains a challenge.⁵

In a recent publication, M. H. Oh et al have demonstrated the use of the galvanic replacement reaction to synthesize hollow multimetallic oxide nanocrystals from monometallic oxide nanocrystals.⁵ Galvanic replacement is an atomic exchange between two metals driven by the reduction potential difference between them. The higher oxidation state metal ions in the nanocrystal are replaced by lower oxidation state metal ions from the solution.^{4,5}

To form the hollow multimetallic oxide nanocrystals, they first prepared Mn_3O_4 nanocrystals, (Figure 2A). The Mn_3O_4 nanocrystals were then treated with iron(II) perchlorate ($Fe(ClO_4)_2$) and heated. They found that the Mn_3O_4 nanocrystals transformed into $\gamma-Fe_2O_3$ hollow nanocages. Replacement completion was shown using inductively coupled plasma-atomic emission spectrometry, which shows Fe:Mn ratio of 91:9. Powder XRD shows the degree of transformation from the tetragonally distorted Mn_3O_4 spinel to the cubic $\gamma-Fe_2O_3$ spinel as a function of the amount of iron added (Figure 2F).⁵

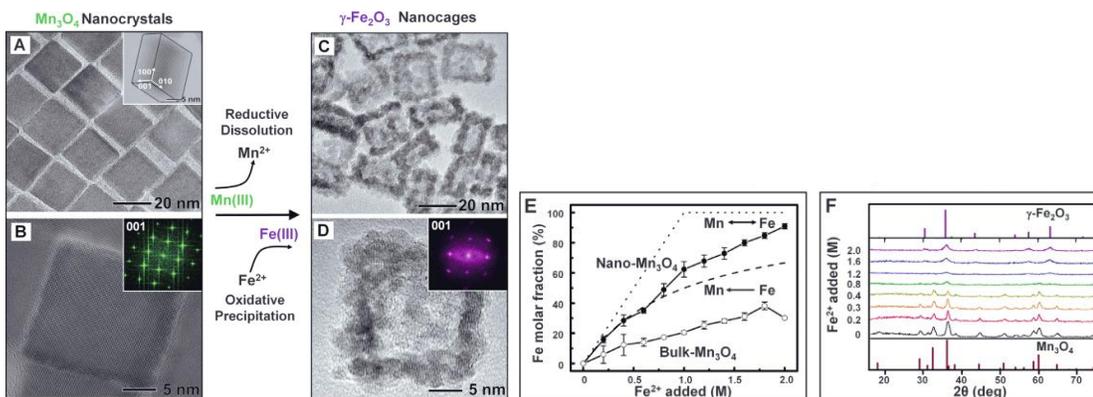


Fig. 2(A and B) TEM image of Mn_3O_4 nanocrystals w/FT inset
(C and D) TEM image of $\gamma-Fe_2O_3$ nanocrystals w/FT inset
(E) ICP-AES data of molar fraction of Fe in product as a function of the amount of Fe added (solid circles) and bulk counterpart (open circles).
(F) Powder XRD of product as function of Fe added.⁵

The formation of a hollow core was studied by treating the Mn₃O₄ nanocrystals with varying amounts of iron(II) perchlorate and imaging the resulting γ -Fe₂O₃ nanocrystals. When less iron was added, the resulting nanocrystals had thick walls with only partially dissolved cores. Pinholes developed on the surface of the nanocrystals, suggesting that the pores develop inside the nanocrystals by a mechanism similar to pinhole corrosion, in which the pinholes serve as conduits during the dissolution process. As greater quantities of iron were added, the pinholes widened into clear openings.⁵

The potential of hollow metal oxide nanocrystals to serve as Li⁺ ion anode materials was tested by coating the various samples of γ -Fe₂O₃ nanocrystals with polypyrrole and carbonizing them. This treatment afforded solid solution samples of Mn_{3-x}Fe_xO₄ in which hollow structure was retained. These samples were subjected to multiple charge/discharge cycles and the charge capacities were measured. The hollow nanocrystals give a reversible capacity of ~1000 mAhg⁻¹ with minimal capacity loss over 50 cycles.⁵

Hollow metal oxide nanocrystals offer a promising solution to increasing Li⁺ ion battery capacity, due to the low cost of the synthetic process and simple scalability.^{4,5}

References

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