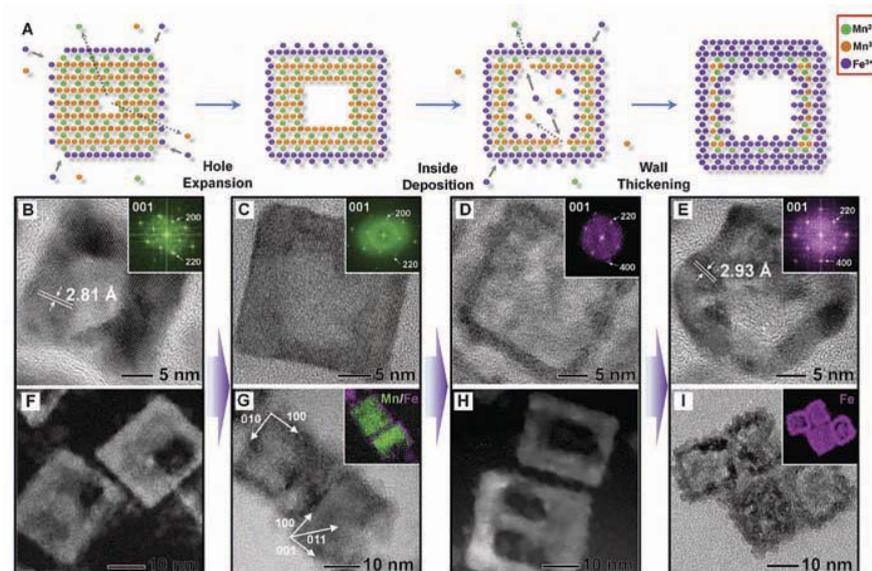


# Galvanic Replacement Reactions in Metal Oxide Nanocrystals

Hollow oxide nanocrystals have been considered as one of the most effective materials for next generation applications in energy storage, catalysis, and medicine. Considerable advances have been made in the synthesis of hollow oxide and semiconductor nanocrystals. However, synthesizing hollow nanocrystals of multimetallic oxides still remains a substantial challenge. The galvanic replacement reactions provide a simple and versatile route for producing hollow nanostructures with controllable pore structures and compositions. However, these reactions have been limited to the chemical transformation of metallic nanostructures.

A team of researchers from Korea (SNU, Kyung Hee Univ., and POSTECH), Germany (MPI-Fritz Haber and Humboldt Univ.), and Portugal (Univ. of Aveiro) has demonstrated a galvanic replacement reaction in metal oxide nanocrystals, producing hollow oxide nanostructures. When manganese oxide ( $\text{Mn}_3\text{O}_4$ ) nanocrystals are reacted with aqueous iron(II) perchlorate solution, hollow box-shaped nanocrystals of  $\text{Mn}_3\text{O}_4/\gamma\text{-Fe}_2\text{O}_3$  (“nanoboxes”) are produced (Fig. 1). With a low concentration of the solution, the core of  $\text{Mn}_3\text{O}_4$  nanocrystals are dissolved partially, and the nanoboxes are formed with relatively thick walls. As the concentration of the solution increases, the nanoboxes are ultimately transformed into hollow



**Fig. 1:** (A) Schematic illustration of the transformation of  $\text{Mn}_3\text{O}_4$  nanocrystals, showing the evolution of their morphology via the localized dissolution of  $\text{Mn}_3\text{O}_4$  and the surface precipitation of  $\gamma\text{-Fe}_2\text{O}_3$ . (B to E) HRTEM images of the hollow nanostructures synthesized by the reaction of  $\text{Mn}_3\text{O}_4$  nanocrystals with 1 ml of aqueous solutions of iron(II) perchlorate having different concentrations: (B) 0.4 M, (C) 0.6 M, (D) 1.0 M, and (E) 1.6 M. Insets show the corresponding FT patterns. (F) High-angle annular dark-field scanning TEM (HAADF-STEM) image of the nanoboxes shown in (B). (G) TEM image and a corresponding EFTEM image of the nanoboxes shown in (C). (H) HAADF-STEM image of the nanocages shown in (D). (I) TEM image and a corresponding EFTEM image of the nanocages shown in (E).

cage-like nanocrystals of  $\gamma\text{-Fe}_2\text{O}_3$  (“nanocages”). Transition metal oxides like  $\text{Mn}_3\text{O}_4$  and  $\gamma\text{-Fe}_2\text{O}_3$  are attractive materials for Li ion batteries due to the higher specific capacities as compared to typical graphitic anodes. The galvanic replacement reactions in the oxide nanocrystals can be a promising technique for engineering the structures and tuning the chemical compositions to improve the electrochemical properties. Indeed, these synthesized oxide nanoboxes and nanocages exhibited good performance as anode mate-

rials for lithium ion batteries. It is likely due to their nonequilibrium compositions and hollow structures. The generality of this approach was also demonstrated with other metal pairs, including  $\text{Co}_3\text{O}_4/\text{SnO}_2$  and  $\text{Mn}_3\text{O}_4/\text{SnO}_2$ .

## Reference

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