## **Electronic Supplementary Information**

# Iron Triad (Fe, Co, Ni) Nanomaterials: Structural Design, Functionalization and Their Applications

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## Abbreviations

NPs, nanoparticles; NCs, nanocrystals; LIBs, lithium-ion batteries; ECs, electrochemical capacitors; SSA, specific surface area; 1D, one-dimensional; 2D, two-dimensional; 3D, three-dimensional; PVP, polyvinylpyrrolidone; PS, polystyrene; MOFs, metal-organic frameworks; LDHs, layered double hydroxides; rGO, reduced graphene oxide; GO, graphene oxide; FTO, fluorine doped tin oxide; NWs, nanowires; CNTs, carbon nanotubes; TEOS, tetraethoxysilane; PANI, polyaniline; PDA, polydopamine; PPy, polypyrrole; azICG, azide-modified indocyanine green derivative; CuAAC, copper(I)-catalyzed azide alkyne cycloaddition; APS, ammonium persulphate; *p*-TSA, *p*-toluenesulfonic acid; SEI film, solid electrolyte interfacial film; LHs, layered hydroxides; DSSCs, dye-sensitized solar cells; CEs, counter electrodes; TOPO, trioctylphosphine oxide; ORR, oxygen reduction reaction.

## **Galvanic replacement reaction**

At the first beginning, the galvanic replacement reaction represents a simple way of preparing multimetal hollow structures. The electrochemical potential difference between two metals drives the reaction. For example, Xia's group used the synthesized Ag nanocubes as sacrificial templates and HAuCl<sub>4</sub> as the etching agent. [S1, S2] As the reduction potential of Au<sup>3+</sup>/Au (1.50 V vs SHE) is more positive than that of Ag<sup>+</sup>/Ag (0.80 V vs SHE), the chemical reaction below will take places.

 $3Ag_{(s)} + Au^{3+}_{(aq)} > Au_{(s)} + 3Ag^{+}_{(aq)}$ 

The produced Au is confined to the nanocube surface, growing on it and adopting its morphology, as interior Ag is oxidized to produce a hollow structure. The shape evolution is shown in Figure S1.



**Fig. S1** SEM and TEM (inset) of (A) Ag nanocubes with rounded corners and (B-D) product after reaction with 0.6, 1.6, and 3.0 mL of 0.1 mM HAuCl4 solution, respectively. (E) Illustration for shape evolution, from a Ag nanocube through a Au/Ag nanocage then into a predominately Au nanocage (ref.S1, copyright 2008 American Chemical Society).

Obviously, Ag dissolution occurs at all cube corners (Figure S1-B). The stabilizing polymer poly(vinyl pyrrolidone) (PVP) during reaction is attached strongly on {100} facets of Ag. Then the unprotected corners of {111} facets become primary sites for Ag dissolution, and Au deposition occurs at the {100} faces. Thus, cubic nanocages with pores at all corners (Figures S1-C, S1-D) are produced. This process is illustrated in Figure S1-E.

By this kind of method, the different hollow structure of the Au NPs can be obtained by changing the morphology of the Ag NPs. Moreover, this Ag template-engaged replacement reaction can be applied to any metal ( $Pd^{2+}/Pd$ ,  $Pt^{2+}/Pt$ ) whose redox potential is more positive than the Ag<sup>+</sup>/Ag pair.

## Nanoscale Kirkendall effect

The nanoscale Kirkendall effect was first proposed by Alivisatos' group in 2004. [S3] Starting with cobalt nanocrystals, the reaction in solution with oxygen and either sulfur or selenium leads to the formation of hollow nanocrystals of the resulting oxide and chalcogenides. The process can be illustrated in Figure S2.



**Fig. S2** Schematic illustration for formation of a hollow CoSe particle from a solid cobalt particle by nanoscale Kirkendall effect (based on the experimental result from ref. S3).

When selenium reacts with cobalt nanocrystal, the voids occur as the reaction and merge at the boundary, forming the gap between the CoSe layer and the Co core (Figure S2-ii). As the reaction proceeds in time, more cobalt atoms diffuse out to the shell, and the accompanying transport of vacancies leads to growth of the initial gap (Figure S2-iii, iv, v). This results in the formation of bridges of material (Figure S2-iv, v) between the core and the shell that persist until the core is completely consumed (Figure S2-vi). These bridges provide a fast transport path for outward diffusion of cobalt atoms that can then spread on the inner shell surface. Finally, a hollow CoSe with thicker shell is obtained. The nanoscale Kirkendall effect provides a general route to the synthesis of hollow nanostructures of a large number of compounds, including oxides, chalcogenides, and phosphides [S4].

## Summary of specific surface area (SSA) values for three typical nanostructures

Туре	Components & Morphology	SSA (m <sup>2</sup> g <sup>-1</sup> )	Reference
hollow	bowl-like SnO <sub>2</sub> @C	~103.8	[85]
Porous	porous ZnO/ZnFe <sub>2</sub> O <sub>4</sub> /C hollow octahedra	~140	[S6]
+hollow			
ultrathin 2D	imidazolium-IL functionalized Co(OH) <sub>2</sub> sheets	~400.4	[S7]
+functionalization			
ultrathin 2D+GO	carbonized PANI/GO hybrid material with Fe <sup>3+</sup> doping	~218	[S8]
+ functionalization			
Mesoporous	mesoporous iron oxide nanopyramid arrays on Ti foil	~175	[S9]
+3D			
Mesoporous	flower-like mesoporous FeOOH	~225	[S10]
+3D	flower-like mesoporous Fe <sub>2</sub> O <sub>3</sub>	~116	
commercial purchase	Fe <sub>2</sub> O <sub>3</sub> solid NPs (~30 nm in size)	~47	[S10]
	(for comparison)		

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