Electronic Supplementary Information

Iron Oxide and Various Metal Oxide Nanotubes Engineered by One-Pot Double Galvanic Replacement Based on Reductiob Potential Hierarchy of Metal Templates and Ion Precursors

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Experiments

Materials:
Silver nanowires, diam. × L 20 nm (± 2 nm) × 12 μm (± 2 μm) 5 mg/mL (in water), Polyvinylpyrrolidone (PVP, Mw ~ 55,000) and Tin(II) chloride were purchased from Sigma-Aldrich. Iron(II) perchlorate hydrate was purchased from Alfa Aesar. Potassium permanganate, Copper(I) chloride and Nickel(II) chloride were purchased from Fisher Scientific.

Mn_3O_4 Nanotube Synthesis: Manganese oxide nanotubes were synthesized by a modified version of a previously published method.[1] 3 mL of silver nanowires, 2.75 mL of 0.3 mM PVP (aq) and 18.95 mL of 1 mM $KMnO_4$ were added to a three-necked 50 mL flask with a reflux condenser. The flask was heated to 100 ^oC in air under magnetic stirring and left to react for 40 minutes, producing Mn_3O_4 nanotubes. To perform a second galvanic replacement, no additional steps are needed. To reserve Mn_3O_4 nanotubes, the solution was removed from heating and left to cool to room temperature. After cooling, the solution was centrifuged at 3000 G for 10 minutes and the supernatant was discarded. The pellet was then resuspended in deionized water.

Fe_2O_3 Nanotube Synthesis: The temperature of the Mn_3O_4 nanotube reaction mixture was lowered to 80 ^oC. Then, 12 mL of 1 mg/mL aqueous iron(II) perchlorate solution was added to the flask. Heating continued at 80 ^oC in air under magnetic stirring for 120 minutes, producing Fe_2O_3 nanotubes. After cooling, the solution was centrifuged at 3000 G for 10 minutes and the supernatant was discarded. The pellet was then resuspended in deionized water.

SnO2 Nanotube Synthesis: First, 4 mg of tin(II) chloride was dissolved in 15.8 ml of 5M HCl and 2.0 μl of deionized water. Then, 3 mL of the Mn_3O_4 nanotube reaction mixture was transferred to a different 50 mL three-neck flask equipped with a reflux condenser. The flask was heated to 90 ^oC in air under magnetic stirring, and 5.0 ml of the tin(II) chloride solution was added. Heating continued at 90 ^oC for 90 minutes, producing SnO_2 nanotubes.

CuO Nanotube Synthesis: First, 3 mg of copper(I) chloride was dissolved in 50 mL of deionized water. Then, 3 mL of the Mn_3O_4 nanotube reaction mixture was transferred to a different 50 mL three-neck flask equipped with a reflux condenser. The flask was heated to 90 ^oC in air under magnetic stirring, and 20.0 ml of the copper(I) chloride solution was added. Heating continued at 90 ^oC for 90 minutes, producing CuO nanotubes.

NiO_2 Nanotube Synthesis: First, 20 mg of nickel(II) chloride was dissolved in 1 mL of deionized water. Then, 3 mL of the Mn_3O_4 nanotube reaction mixture was transferred to a different 50 mL three-neck flask equipped with a reflux condenser. The flask was heated to 90

^{o}C in air under magnetic stirring, and 20.0 ml of the nickel(II) chloride solution was added. Heating continued at 90 ^{o}C for 90 minutes, producing NiO_2 nanotubes.

Microscopy and Elemental Analysis

Transmission electron micrographs were taken using a JEOL JEM-2100 TEM at 200 kV with a LaB6 gun. Images were captured using 4GB Gatan ultrascan camera model 994 US 1000XP and Digital Micrograph V. 2.1. For the elemental mapping, scanning transmission electron microscope (STEM,) and energy-dispersive X-ray spectroscopy (EDXS) were carried out in a FEI-Titan Themis 200 TEM operating at 200 kV equipped with a 4k x 4k Ceta 16M CMOS camera. A high angle angular dark field (HAADF) detector was used for STEM and Windowless Super-X EDS detector system with ESPRIT software was applied for EDXS.

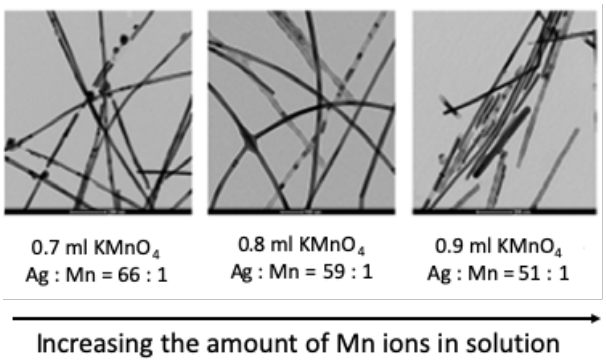

Figure S-1. TEM images of Mn_3O_4 nanotubes synthesized in Ag nanowire solution (5 mg/ml) containing various amounts of Mn ions. 0.7 ml, 0.8 ml, and 0.9 ml (from left to right) of $KMnO_4$ (1 mM) was added to 1 ml of Ag nanowire solution.

Half Reaction	Electric Reduction Potential (V)
$Ag^{+}_{(aq)} \rightarrow Ag_{(s)}$	0.8 [1]
$MnO_4^{-}{}_{(aq)} \rightarrow Mn_3O_{4(s)}$	1.47 [2]
$Mn_3O_{4(s)} \rightarrow Mn^{2+}_{(aq)}$	1.82 [3]
$Fe^{3+}_{(s)} \rightarrow Fe^{2+}_{(aq)}$	0.77 [3]
$NiO_{2(s)} \rightarrow Ni^{2+}_{(aq)}$	1.68 [4]
$Cu^{2+}_{(s)} \rightarrow Cu^{+}_{(aq)}$	0.0161 [5]
$Sn^{4+}_{(s)} \rightarrow Sn^{2+}_{(aq)}$	-0.094 [5]

Table S1. A breakdown of the half-reactions in the reduction potential landscape in Figure 1-(c).

References

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