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Supporting Information

Hollow nanostructures of metal oxides as emerging electrode materials for high performance supercapacitors

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1. Synthesis of materials:

1.1 *Synthesis of SnO_2 and Mn_3O_4 solid nanoparticles by co-precipitation method*

In this typical synthesis process, CTAB was mixed with DI water under stirring to obtain a homogeneous solution (0.08 M). The diluted solution of $NH_3·H_2O$ (25 wt% solution, 10 ml) was then added to the already prepared CTAB solution under continuous stirring. As soon as the solution became homogeneous, a separately prepared solution of $SnCl_4$ (0.34 M) was added, under vigorous stirring. After stirring for 4 h, the products were aged at ambient temperature for 96 h. The resulting product was filtered and washed with distilled water to remove surfactant, and then annealed at 600 ºC for 5 h to obtain the final product.

For synthesis to Mn_3O_4, in a solution of 0.22 M $MnCl_2.4H_2O$, 1.37 mM hexadecyl trimethyl-ammonium Bromide was added under constant stirring. After complete mixing of the precursor solution, 0.44 M NaOH solution was prepared separately and added dropwise to the first solution and was kept under constant stirring for another 24 h. The final precipitate was filtered and washed with de-ionized (DI) water and ethanol for 3 and 2 times, respectively. The obtained precipitate was dried in the oven for overnight at 80 °C to obtain the desired product.

In co-precipitation method, two or more salt solutions are mixed in appropriate stoichiometric ratio. The mixed salt solutions result in the formation of mixed hydroxide states which tend to agglomerate with time and form bigger particles. To control the crystallite size, different surfactants like CTAB, SDS, etc. are added to the mixed salt solution. The mixed hydroxide complex when calcined at an appropriate temperature, leads to removal of the surfactant and the OH group which yields the desired oxide material. The rate of heating controls the average size of particles obtained with a moderate heating rate being the most common.

1.2 *Synthesis of hollow nanostructure of Mn_3O_4 by mini-emulsion method*

Hollow particles of Mn_3O_4 were also synthesized using the mini-emulsion synthesis technique. 0.5 M manganese acetate solution was made with manganese acetate tetrahydrate. To this, 1 wt% of PIBSP was mixed in the ratio of 1:4, respectively. The mixture was stirred for half an hour and then sonicated for 5 min. A white emulsion was obtained at the end of sonication. In a round bottom flask, the sample along with 2 mL of TEA was added and kept under reflux for 4 h. The sample solution was then centrifuged and washed with DI water and ethanol for 3 and 2 times, respectively. The collected precipitate was kept for drying in the oven at 80 °C for 8h.

Cu_2O Hollow and Solid Particles

Analytical grade reagents, without further purification, were used as raw materials. For the synthesis of Cu_2O hollow particles (Cu-HN), 2 g of $Cu(NO_3)_2$. $6H_2O$ was initially taken in 80 mL of deionized (DI) water and stirred until a clear blue colored solution was obtained. The solution was then heated upto 70 °C and NaOH together with the reducing agent viz., dextrose, were added. The overall concentration of NaOH and dextrose in the solution were kept at 0.86 M and 0.16 M, respectively. On addition of NaOH and dextrose, solution's color changed to dark blue that, after few minutes, turned to brick red. The solution was kept stirring for 60 min to ensure complete reaction. The obtained precipitate was subsequently centrifuged and washed three times using de-ionized (DI) water and ethanol. The final precipitate was dried at 80 °C for 12 h in vacuum.

To obtain solid Cu_2O particles (Cu-OCT), experimental procedure similar to above was followed but with reagents concentrations reduced to half. 1 g of $Cu(NO_3)_2.6H_2O$ was mixed with 0.43 M of NaOH and 0.08 M of dextrose. Rest of the processes for initiating reaction, purification and annealing were similar.

1.3 $NaFePO_4$ Solid Particles

In the typical synthesis of $NaFePO_4$, two-step semi-solid-state synthesis route was used. Stoichiometric ratios of $Fe(NO)_3$ and $NH_4H_2PO_4$ were mixed in de-ionized water with a certain amount of citric acid (CA). The solution was then kept under heating to raise the temperature to 60 °C with the addition of ethylene glycol (EG) to prevent premature gelling. Then $NaNO_3$ was added to solution maintaining the stoichiometric ratio. The molar ratio of M: CA: EG used was 1:0.5:0.5, where M is the sum of all metal ions, i.e., Na and Fe. Afterward, the solution was further heated to 120 °C for 24 h to make the solution-solid mixture. Then the solid mixture was crushed to make a fine powder and kept heated at 300 °C for 2 h to complete the gas release. Then the sample was gridded well and finally; the product was heated at 600 °C for 6 hrs. to have the pure phase material.

1.5 $NaFePO_4$ Hollow Particles

Porous and hollow $NaFePO_4$ microstructures were synthesized using one-pot facile hydrothermal route followed by calcination in air. In a typical experimental procedure, 25 ml of 0.1 M ferric nitrate solution was mixed with 25 ml of 0.1 M stearic acid solution. Subsequently, 245.1 mg trisodium citrate ($Na_3C_6H_5O_7, 2H_2O$) was added, and the solution was stirred for 2 h. An appropriate amount of ammonium dihydrogen phosphate ($(NH_4)H_2PO_4$) was added to the precursor solution to ensure Na: Fe: PO_4 concentration ratio was 1:1:1. 50 ml of this yellow-colored solution was then transferred to Teflon-lined stainless steel (capacity 250 ml) autoclave. The autoclave was kept at 180 ºC for 24 h, before allowing it to cool up to the room temperature slowly. By centrifuging the sample at 3200 rpm, the precipitate was collected. The precipitate was subsequentially washed three times using de-ionized water and dried overnight in a vacuum oven at 70 ºC. The dried sample was crushed and annealed at 600 ºC for 4 h in the air to obtain hollow $NaFePO_4$ powder. Growth mechanism is already published in Chandra et al.

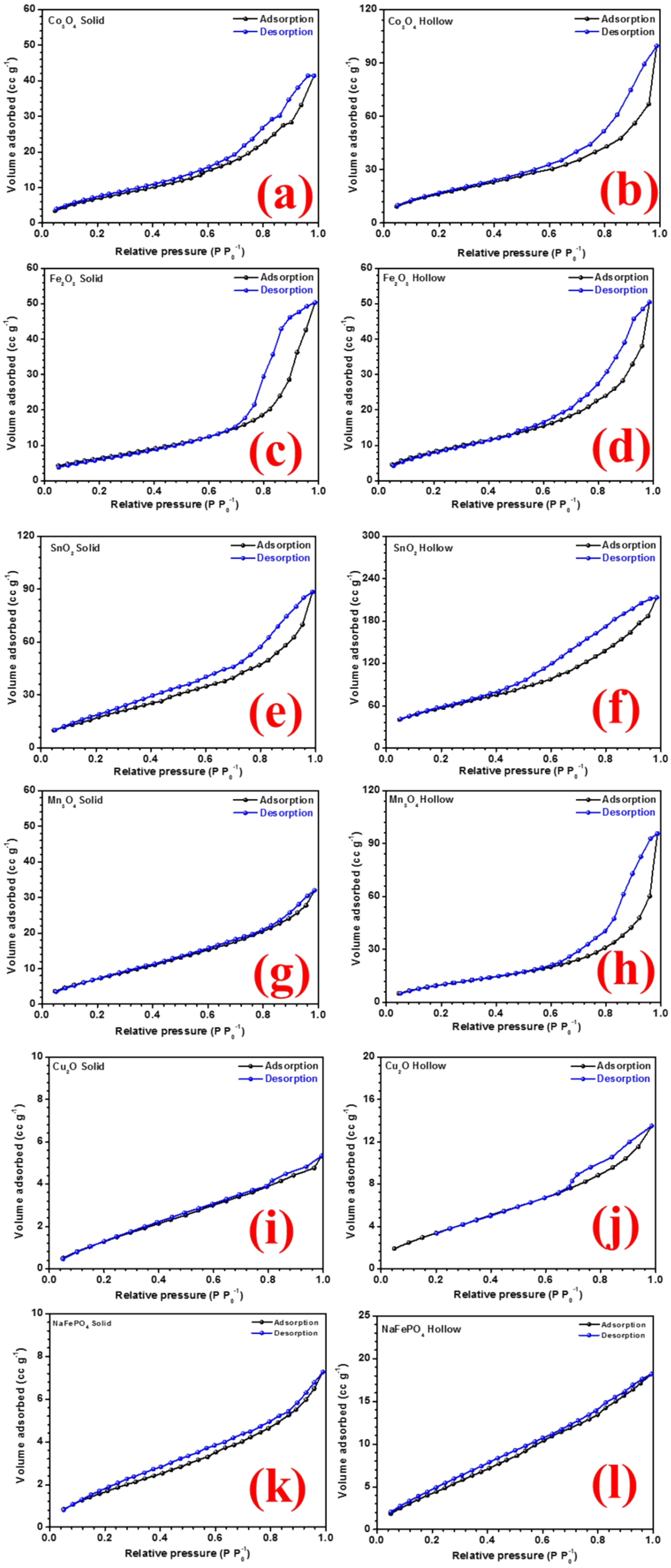
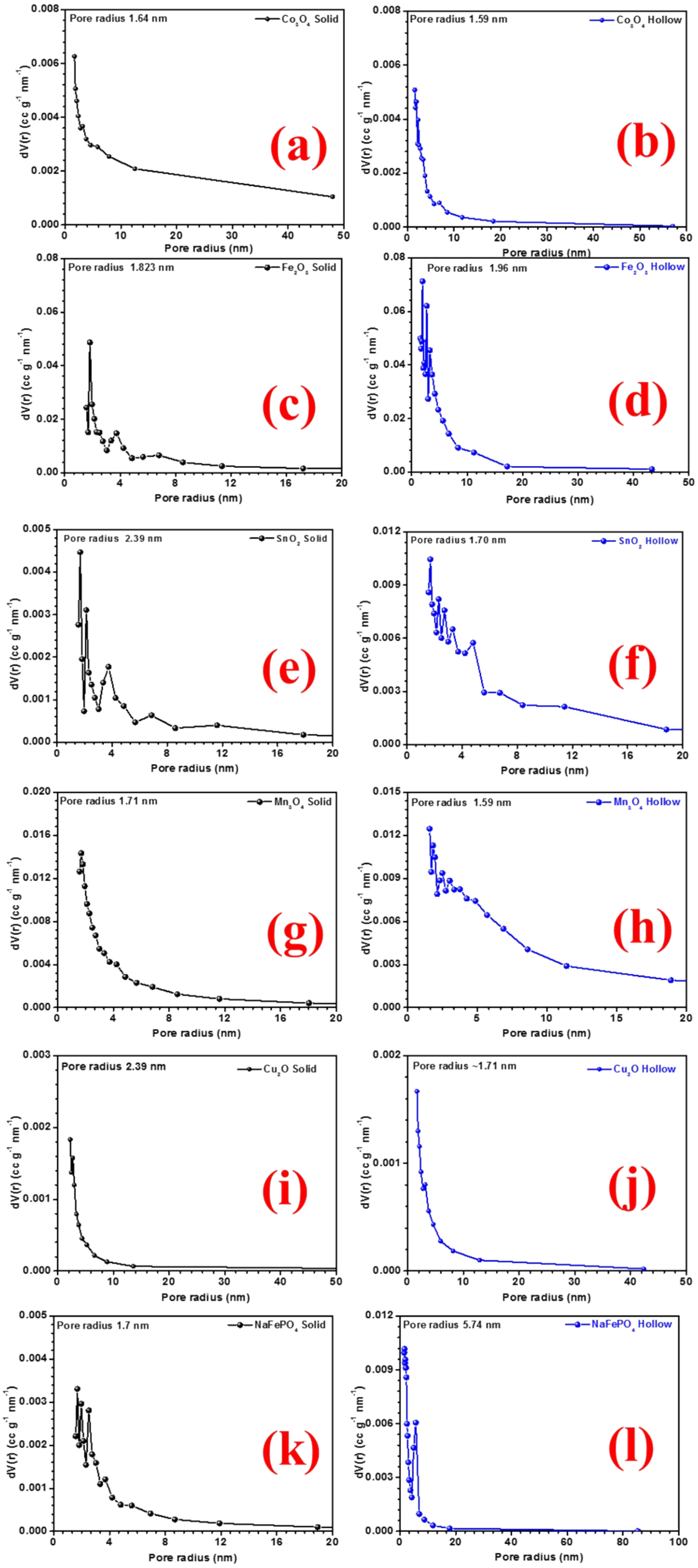


Fig. S1 BET N_2 adsorption desorption isotherms of (a,b) Co_3O_4, (c,d) Fe_2O_3, (e,f) SnO_2, (g,h) Mn_3O_4, (i,j) Cu_2O and (k,l) $NaFePO_4$ for solid and hollow structures, respectively.


(a)
Pore radius 1.64 nm
Co3O4 Solid
(b)
Pore radius 1.59 nm
Co3O4 Hollow
(c)
Pore radius 1.823 nm
Fe2O3 Solid
(d)
Pore radius 1.96 nm
Fe2O3 Hollow
(e)
Pore radius 2.39 nm
SnO2 Solid
(f)
Pore radius 1.70 nm
SnO2 Hollow
(g)
Pore radius 1.71 nm
Mn3O4 Solid
(h)
Pore radius 1.59 nm
Mn3O4 Hollow
(i)
Pore radius 2.39 nm
Cu2O Solid
(j)
Pore radius ~1.71 nm
Cu2O Hollow
(k)
Pore radius 1.7 nm
NaFePO4 Solid
(l)
Pore radius 5.74 nm
NaFePO4 Hollow
dV(r) (cc g-1 nm-1)
Pore radius (nm)

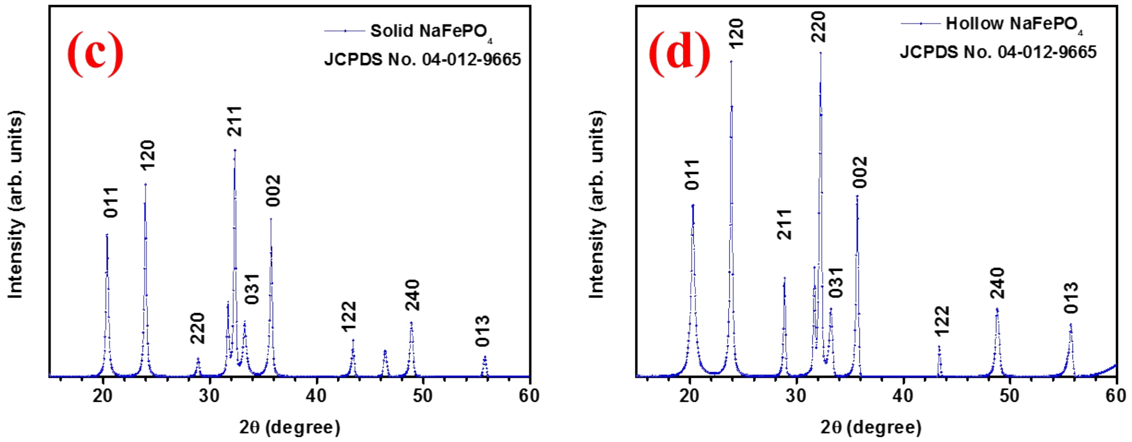
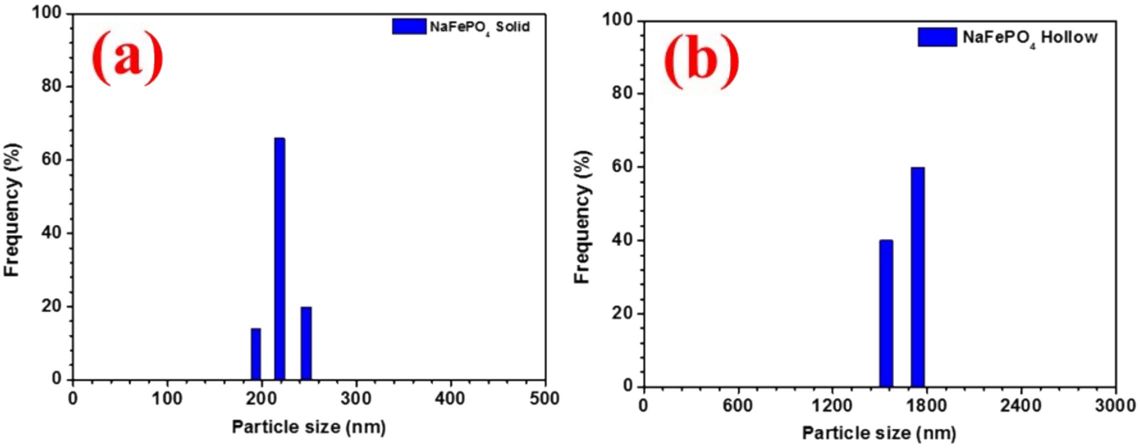


Fig. S3 XRD profiles of $NaFePO_4$ (a) solid and (b) hollow structures respectively.

Fig. S2 Pore size distributions of (a,b) Co_3O_4, (c,d) Fe_2O_3, (e,f) SnO_2, (g,h) Mn_3O_4, (i,j) Cu_2O and (k,l) $NaFePO_4$ for solid and hollow structures, respectively.

Fig. S4 Particle size distribution of $NaFePO_4$ for (a) solid and (b) hollow structures, respectively.



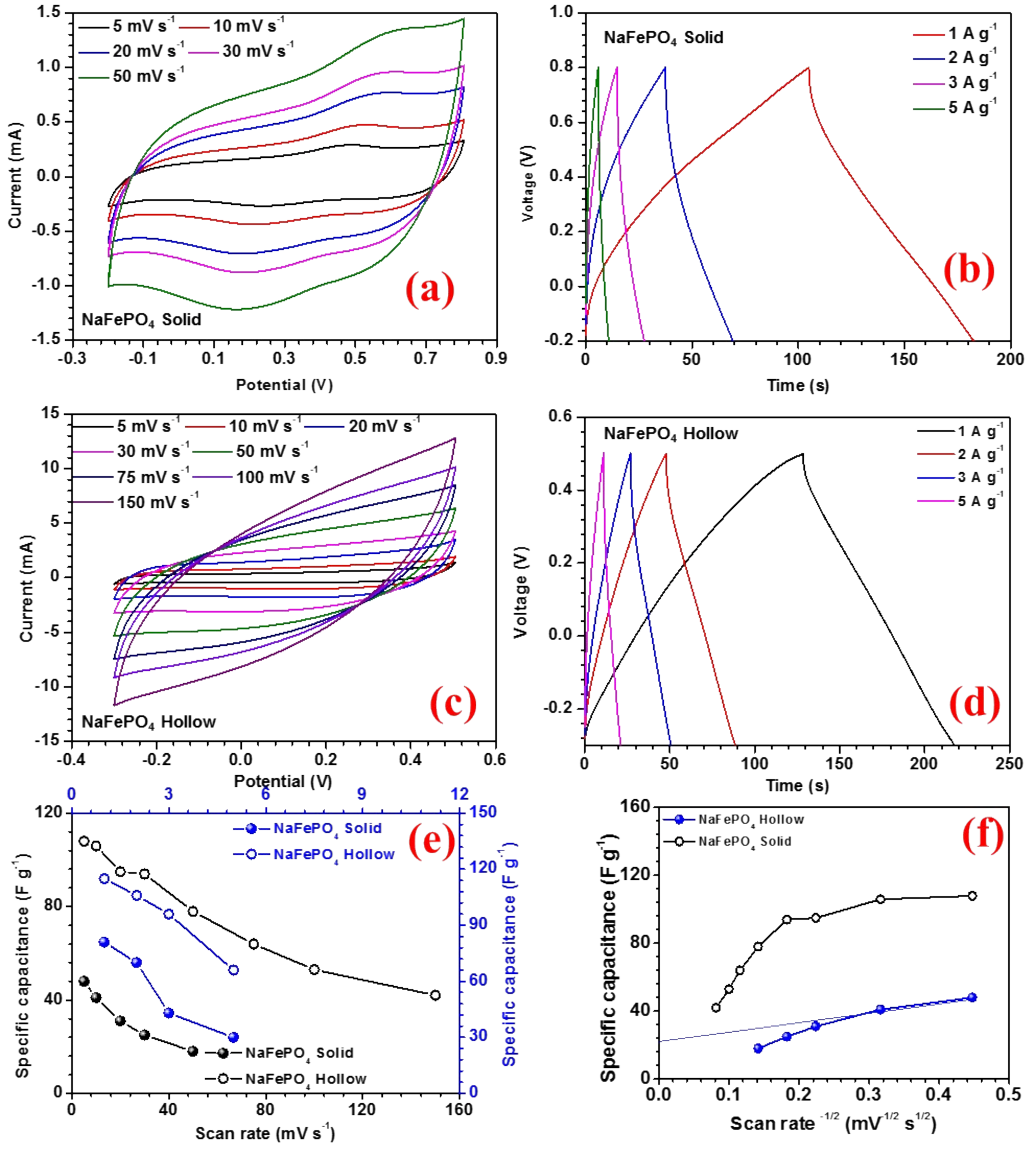


Fig. S5 CV and CD profiles of $NaFePO_4$ (a,b) solid and (c,d) hollow structures, respectively; (e,f) variation of specific capacitance with scan rate and current density, respectively.

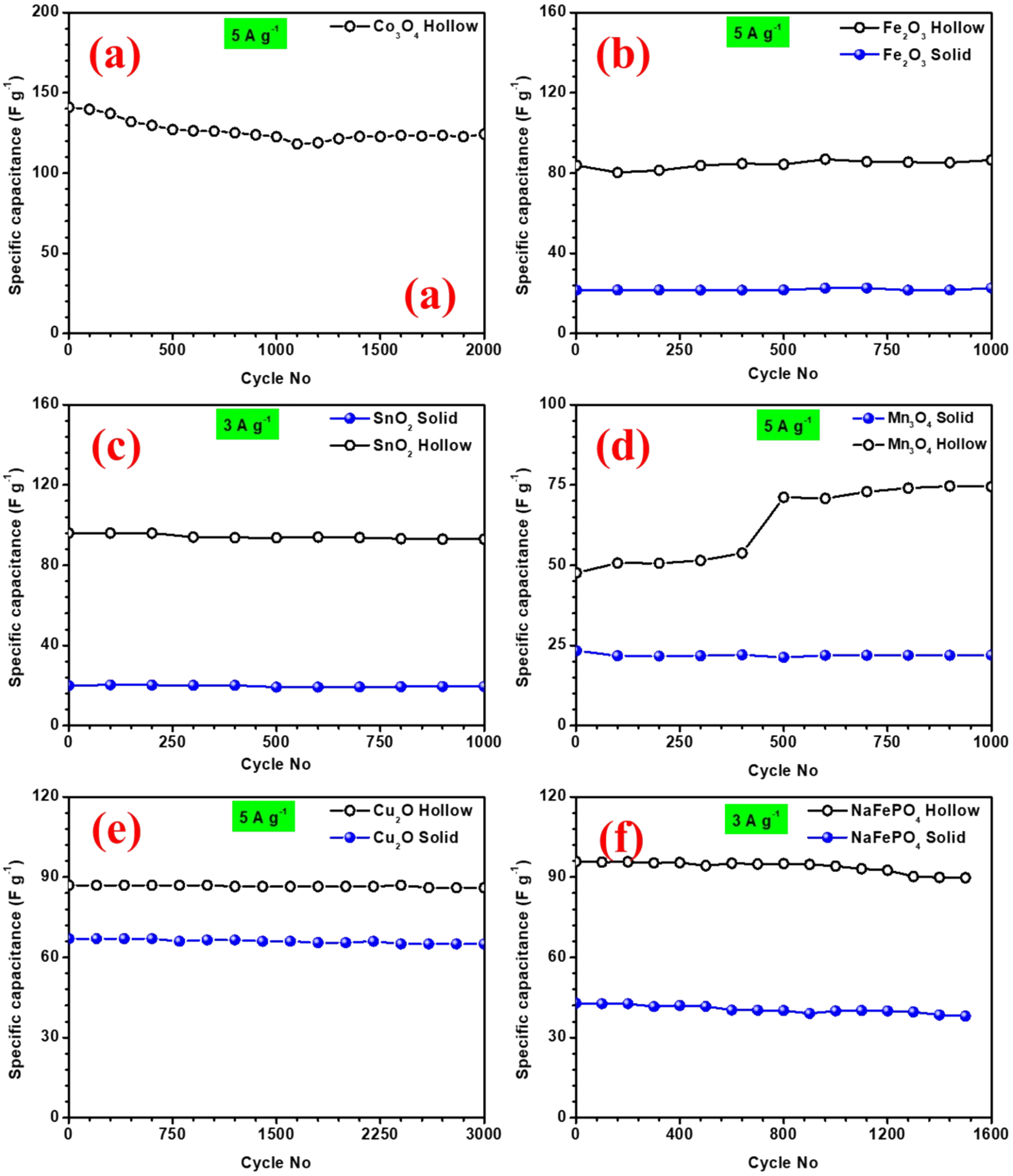


Fig. S6 Cyling performance of (a) Co_3O_4, (b) Fe_2O_3, (c) SnO_2, (d) Mn_3O_4, (e) Cu_2O and (f) $NaFePO_4$.