

Supplementary Material (ESI) for Chemical Communications

Mesoporous Co₃O₄ monolayer hollow-sphere array as electrochemical pseudocapacitor material

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1. Experimental

1.1 Chemical materials

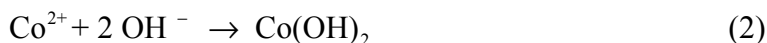
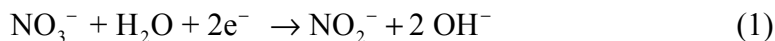
All solvents and chemicals were of reagent quality and were used without further purification. The polystyrene (PS) spheres with a diameter of 600 nm were purchased from Alfa Aesar Corporation. They were well dispersed in deionized water and prepared as a suspension with concentration of 2.5 wt. % before fabricating colloidal monolayers.

2.1 Preparation of mesoporous Co₃O₄ hollow-sphere array

The preparation of monolayer PS sphere template was prepared as follows. Firstly, 5 drops of PS sphere suspension were dropped onto the surface of clean nickel foil substrate with 2×2 cm² in size. After holding the substrate stationary for 1 min to obtain good dispersion of the suspension, the substrate was then slowly immersed into deionized water. Once the suspension contacted the water's surface, a monolayer of PS spheres was observed on the surface of the water as well as the nickel foil substrate. To prevent any further additions to the substrate, it was kept immersed. Then, a few drops of 2 % dodecylsodiumsulfate solution were added to the water to change the surface tension. As a result, the monolayer of PS spheres that suspended on the surface of water was pushed

aside due to the change in the surface tension. Then the substrate was lifted up through the clear area, making sure that no additional PS spheres were deposited on the monolayer during this process and followed by heating at 110 °C in an oven for 5 min to bond the monolayer with the nickel foil substrate.

The electrodeposition was performed in a standard three-electrode glass cell at 20 °C, the above template electrode as working electrode, saturated calomel electrode (SCE) as reference electrode and a Pt foil as counter-electrode. The precursor films were electrodeposited from aqueous solution containing 1.0 M Co(NO₃)₂ and 0.1 M NaNO₃ using a Chenhua CHI660C model Electrochemical Workstation (Shanghai). The electrodeposition experiment was carried out at a constant current of 0.5 mA cm⁻² for 400 s. The electrodeposition process of the Co(OH)₂ precursor film would include an electrochemical reaction and a precipitation reaction expressed as follows:



Afterwards, the samples were immersed in toluene for 24 h to remove the PS sphere template. Finally, the as-prepared samples were dried at 85 °C, and then annealed at 200°C in argon for 1 h. The loading weight of Co₃O₄ is about 0.5 mg cm⁻².

2.3 Characterization and electrochemical measurements

The sample was characterized by X-ray diffraction (XRD, Philips PC-APD with Cu Kα radiation). The morphologies of samples were observed by field emission scanning electron microscopy (FESEM, FEI SIRION) and transmission electron microscopy (TEM, JEM 200 CX 160 kV).

The electrochemical measurements were carried out in a three electrode

electrochemical cell containing 1 M KOH aqueous solution as the electrolyte. Cyclic voltammetry (CV) measurements were performed on a CHI660c electrochemical workstation (Chenhua, Shanghai). CV measurements were carried out at a scanning rate of 10 mV s⁻¹ between 0 V and 0.6 V at 25 °C, Co₃O₄ array as the working electrode, Hg/HgO as reference electrode and a Pt foil as counter-electrode. The galvanostatic charge-discharge tests were conducted on a LAND battery program-control test system. The as-prepared electrodes, together with a nickel mesh counter electrode and an Hg/HgO reference electrode were tested in a three-compartment system. The specific capacitance is calculated according to the following equation:

$$C = \frac{I \Delta t}{M \Delta V} \quad (3)$$

where C (F g⁻¹) is specific capacitance, I (mA) represents discharge current, and M (mg), ΔV (V) and Δt (sec) designate mass of active materials, potential drop during discharge and total discharge time, respectively.

2. Morphological and structural characterizations

2.1 TEM image of mesoporous Co₃O₄ nanoflake

The mesoporous walls are clearly shown in Fig. S1. The mesopores have a diameter ranging from 2 nm to 5 nm.

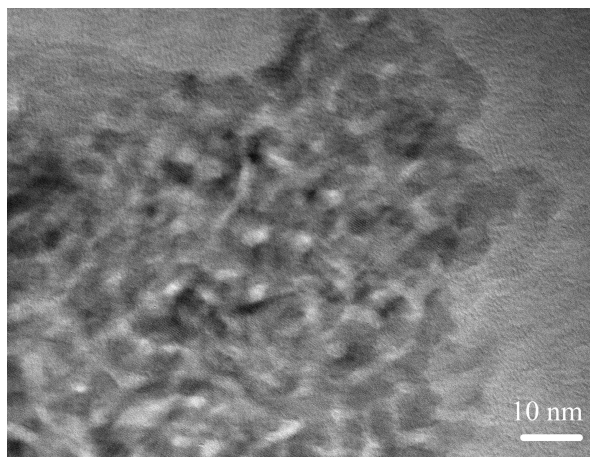


Fig. S1 TEM image of mesoporous Co_3O_4 nanoflake

2.2 XRD of mesoporous Co_3O_4 hollow-sphere array on nickel foil

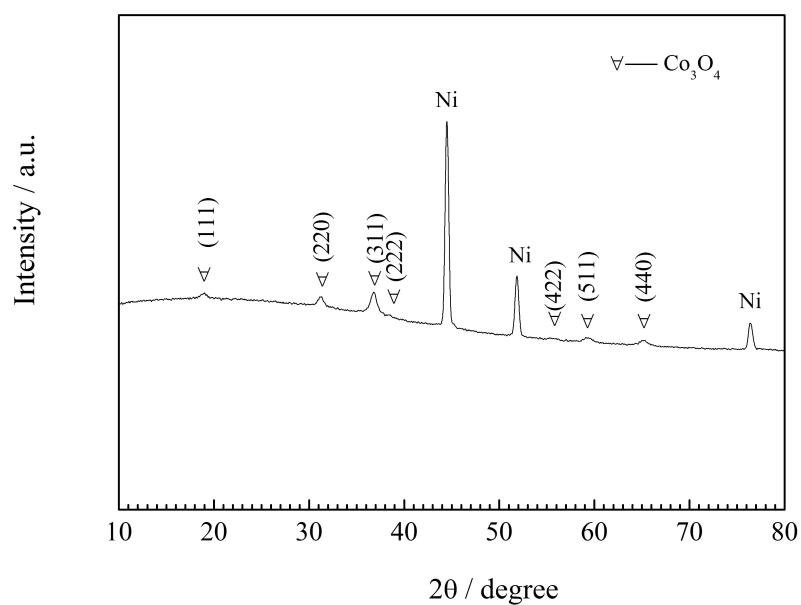


Fig. S2 XRD pattern of mesoporous Co_3O_4 hollow-sphere array on nickel foil

Excluding three strong peaks from the nickel foil substrate, the sample shows typical diffraction peaks at 19.1, 31.2, 36.8, 38.5, 55.7, 59.1 and 65.3 °, which correspond to (111), (220), (311), (222), (422), (511) and (440) crystal planes of spinel Co_3O_4 phase

(JCPDS 47-1049), respectively, indicating that the crystalline Co_3O_4 film has been formed after annealing.

2.3 Specific capacitances of mesoporous Co_3O_4 hollow-sphere array at various discharge current densities.

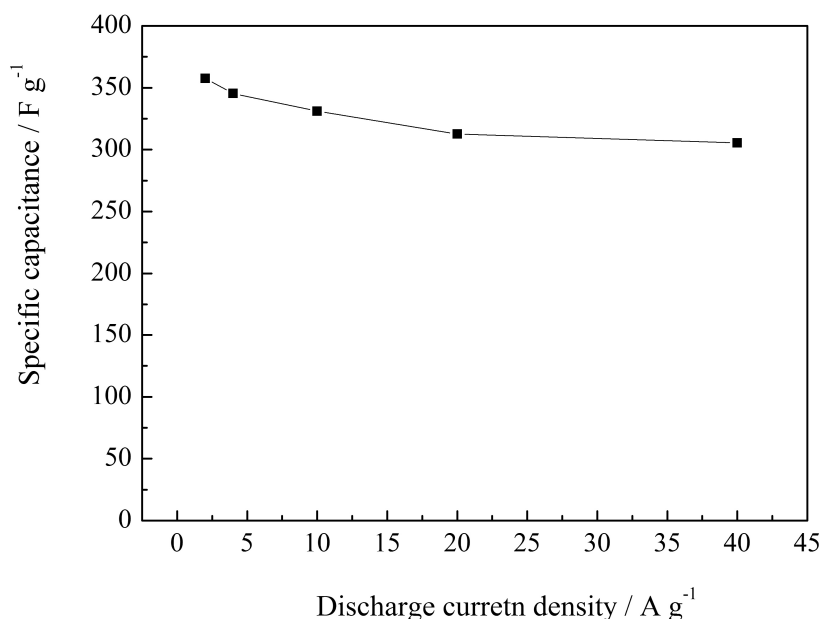


Fig. S3 Specific capacitances of mesoporous Co_3O_4 hollow-sphere array at various discharge current densities.

2.4 SEM image of mesoporous Co_3O_4 hollow-sphere array after 4000 cycles

After 4000 cycles, the mesoporous Co_3O_4 hollow-sphere array maintains its basic morphology, indicating this porous architecture can help to alleviate the structure damage caused by volume expansion during the cycling process, resulting enhanced cycling performance.

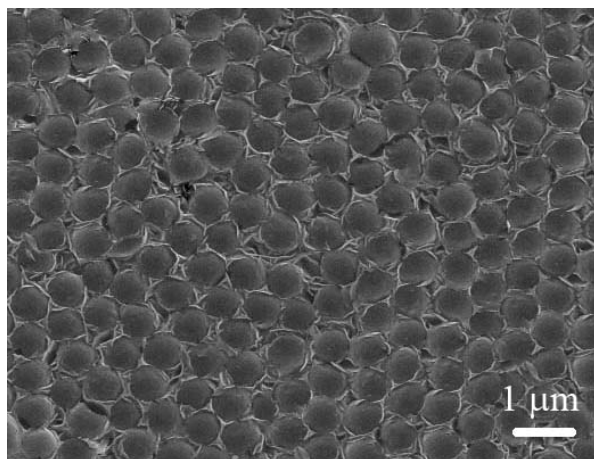


Fig. S4 SEM image of mesoporous Co₃O₄ hollow-sphere array after 4000 cycles