Supporting Information

S-1: Experimental details

S-1-1: Synthesis

i) Preparation of N-doped hollow carbon sphere (N-HCS).

Firstly, 3 ml ammonia aqueous solution (25 wt.%) and 45 mL ethanol were mixed with 30 mL DI water to form a mixed solution. Then 3.55 g tetraethylorthosilicate (TEOS) were added to above solution and stirred for one hour at ambient temperature. Secondly, 0.45 g resorcinol, 0.68 g formaldehyde and 1.8 mL ethylenediamine (EDA) were added to above solution, and the mixture was strongly stirred for 24 hours at ambient temperature. Thirdly, it was sealed in an autoclave and heated at 100 ^{o}C for 24 hours. The obtained gel was washed by DI water and ethanol, followed by drying at 80 ^{o}C overnight to obtain the intermediate product. The intermediate products were heated at 900 ^{o}C for 2 hours with the heating rate of 5 ^{o}C/min under Ar atmosphere. Finally, the obtained product was etched firstly by diluted HF solution for one day, and then washed by DI water until pH value of filtrate reaches 7.

ii) Encapsulating iodine into N-HCS substrate.

The encapsulation of iodine into N-HCS was realized with a thermal treatment method. Firstly, as-prepared N-doped hollow carbon sphere (N-HCS) were mixed with iodine particles. Then the mixture was sealed in a glass bottle, which was evacuated to vacuum and then heated at 180 ^{o}C for 24 hours. After washing the obtained products with water-ethanol mixed solution, the feeble iodine was removed and the NHCS-iodine composite (with iodine content of 32 wt.%) was achieved.

iii) Fabricating fish-spawn-like Polymer@N-HCS-iodine array.

Firstly, the PVP-I_2 polymer is prepared by mixed 0.43 g iodine particles and 0.57 g PVP with 10 mL methanol. The mixture was strongly stirred and reflux at 60 ^{o}C to form a homogenous solution.

Next, impregnation process was carried out. The PVP-I_2 solution was slowly added to the NHCS-iodine substrate that was placed in a sealed glass vessel (Figure S-2). The vacuum was used to ensure effective impregnation. After impregnation, continuous vacuum was employed until the solvent was all removed and the final product was achieved, which has the composition of 71 wt.% of NHCS-I substrate and 29 wt% of the PVP-I polymer based on the following analysis.

iv) Preparation of PVP-I_2 reference sample.

For comparison, the PVP-I_2 reference sample was prepared by directly drying the mixture of 0.43 g iodine particles, 0.57 g PVP and 10 mL methanol. After dried under vacuum, the pure polymer (PVP-I_2) reference sample was achieved.

S-1-2: Materials characterization

Powder X-ray diffraction (XRD, Bruker D8/Germany) using Cu Kα radiation was employed to identify the crystalline phase. The morphology was observed with a scanning electron microscope (SEM, HITACHIS-4700) and a transmission electron microscope (TEM, JEOS-2010 PHILIPS). The element distribution of the sample was confirmed by energy dispersive X-ray detector (EDX). The Raman spectra were collected on a Jobin-Yvon Labor Raman system by exciting a 514.5 nm Ar ion laser (Raman, HR-800 HORIBA). Thermogravimetric analysis (TGA, NETZSCH STA 449C) in flowing nitrogen was used to measure the iodine content in the samples. The electronic conductivities of all the samples are measured using the four-point probe method (LORESTA GP, MCP-T610).

S-1-3: Electrochemical measurements

The electrode was made from a mixture of the active material, conductive carbon black and polytetrafluoroethylene (PTFE) in a weight ratio of 8:1:1. The mixture was rolled into a film and the electrode was punched from it. The coin cells were assembled to carry out electrochemical measurements. To fabricate lithium (metal)-iodine battery, lithium metal foil was employed as counter electrode, and the electrolyte was 1M LiTFSI in a mixed solvent of DOL/DME (v/v=1:1) with $LiNO_3$ (1 wt.%). To fabricate sodium (metal)-iodine battery, sodium metal foil was employed as counter electrode, and 1 mol·L^{-1} $NaClO_4$ dissolved in propylene carbonate (PC) was used as electrolyte. To fabricate iodine-carbon lithium-ion or sodium-ion full batteries, the 3D array was used as cathode, the N-doped hollow carbon spheres (NHCS) was used as anode, the lithium-ion (LiTFSI based) and sodium-ion ($NaClO_4$ based) electrolytes were used as electrolytes. Piror to full battery fabrication, both electrodes were electrochemical activated to elude the irreversible reactions during initial few cycles. Galvanostatic charge-discharge tests were performed on a Land battery testing system (Wuhan, China). EIS and CV measurements were conducted using a Zivelab electrochemical workstation.

S-2: Description of the electrochemical performance

The performance of the iodine electrode and the iodine based batteries are described by the follow equations,

i) The capacity of the iodine electrode with carbon contribution

The capacity of the iodine electrode is calculated based on the capacity of the electrode and the mass of iodine, which can be expressed as following,

$$C_{all} = \frac{Q_{all}}{m_{iodine}} \qquad \text{(S-1)}$$

Where C_{all} is the specific capacity of iodine electrode with carbon contribution; Q_{all} is the total capacity of the iodine based electrode, which includes the capacitance capacity induced by carbon based host; m_{iodine} is the mass of iodine.

ii) The capacity of the iodine electrode without carbon contribution

After removing the capacitance contribution of carbon host, the capacity of pure iodine is achieved, which is calculated based on the following equation,

$$C_{iodine} = \frac{Q_{all} - Q_{Carbon}}{m_{iodine}} \qquad \text{(S-2)}$$

Where C_{iodine} is specific capacity of pure iodine in the iodine electrode; Q_{all} is the total capacity of the iodine based electrode; Q_{Carbon} is the capacitance capacity of carbon host; m_{iodine} is the mass of iodine.

iii) Relative capacity (*RC_r*)

The relative capacity is calculated based on the following equation,

$$RC_r = \frac{C(i)}{C(0.2)} \qquad \text{(S-3)}$$

Where *RC* is the relative capacity, *C(i)* is the specific capacity at a certain rate, *C(0.2)* is the specific capacity at 0.2 *C*.

iv) Cycling retention

The cycling retention is calculated based on the following equation,

$$C_r = \frac{Q(after)}{Q(before)} \qquad \text{(S-4)}$$

Where C_r is the capacity retentions after cycling, *Q*(after) is the specific capacitance of the electrode after cycling, *Q*(before) is the specific capacitance of the electrode before cycling.

v) Calculation of the energy density for the battery

The energy density of the battery is calculated based on the following equation,

$$E = \frac{Q \times U}{m} \qquad \text{(S-5)}$$

Where E is the energy density of the battery; *Q* is the total capacity of the battery; U is the operation voltage of the battery; m is the mass of both cathode and anode.

vi) Calculation of the power density for the battery

The energy density of the battery is calculated based on the following equation,

$$P = \frac{I \times U}{m} \qquad \text{(S-6)}$$

Where P is the power density; I is the current density; U is the operation voltage; m is the mass of the cathode and anode.

vii) Relative discharge capacity (RDC_r) during self-discharge testing

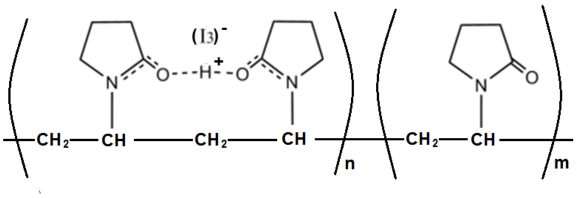
The relative discharge capacity is calculated based on the following equation,

$$RDC_r = \frac{C(resting)}{C(fresh)} \qquad \text{(S-7)}$$

Where RDC_r is the relative discharge capacity in the self-discharge testing, *C(fresh)* is the discharge capacity obtained for the sample in fresh lithium-iodine battery, *C(resting)* is the discharge capacity obtained after 120-hour resting at 50% DOD.

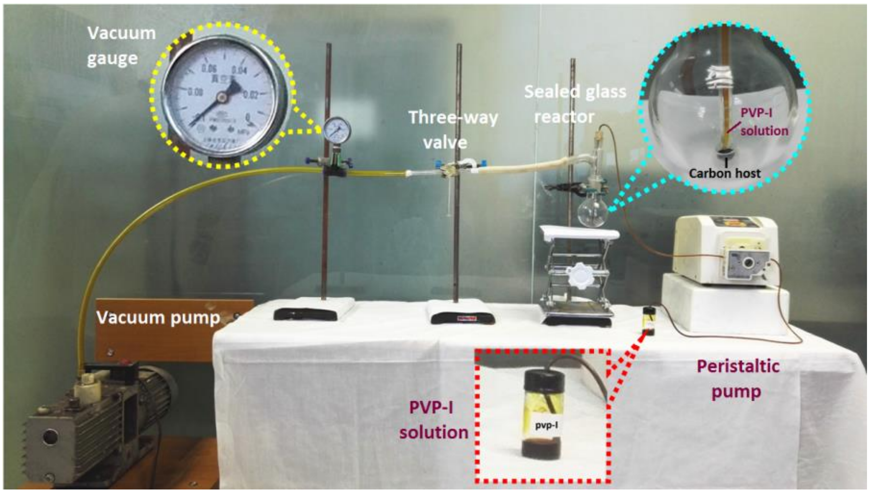
S-3: Supporting figures

Figure S-1



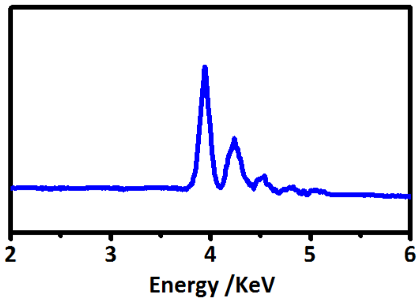
The chemical formula of poly(vinylpyrrolidone)-iodine complex.

Figure S-2



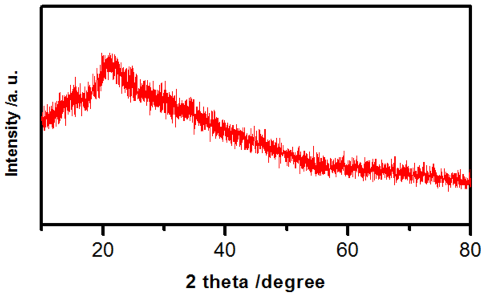
Lab-assembled system for preparation of hierarchical fish-spawn-like arrays.

Figure S-3



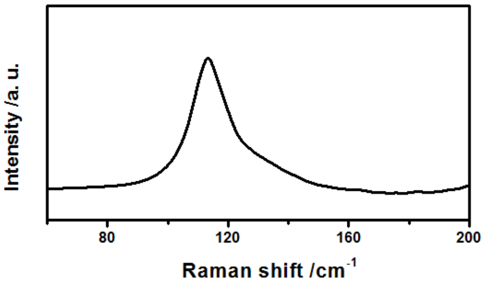
EDX results of the iodine element in the NHCS substrate.

Figure S-4



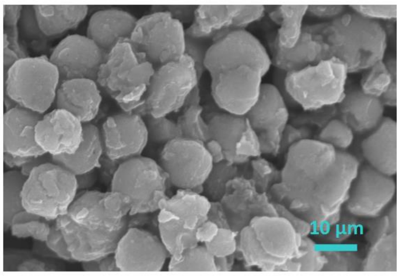
XRD pattern of the PVP-I polymer.

Figure S-5



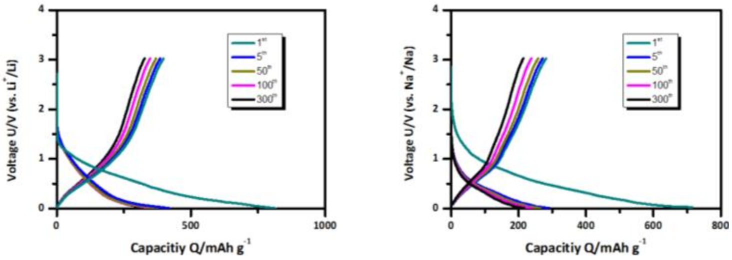
Raman spectroscopy of the PVP-I polymer.

Figure S-6



Morphology of the PVP-I composite.

Figure S-7



Charge/discharge curves of the hollow carbon spheres in the lithium (left) and sodium (right) systems.

S-4: Investigation of polyiodide shuttle in cycled batteries

The cycled batteries were dissembled and both the separator and the cells were washed with ethanol. The obtained solution was analyzed to examine the content of iodine.

S-5: Calculation of the ion conductivity

The ion diffusion coefficient (*D*) can be calculated on the basis of the Randles-Sevcik equation,

$$i_p = 0.4463\left(\frac{F}{RT}\right)^{1/2} n^{3/2} A D^{1/2} C^{*} \upsilon^{1/2} \qquad \text{(S-7)}$$

Where i_p, n, A, C^* and v are the peak current, number of exchanged electrons, surface area, ion concentration and sweep rate, respectively.