I. Experimental Details:

**Synthesis.** Typically, the first step was the synthesis of Fe$_3$O$_4$ nanorod film. 0.946 g FeCl$_3$·H$_2$O and 0.497 g Na$_2$SO$_4$ was mixed with 70 mL distilled water for 10 minutes at room temperature. Then, the resulting solution was transferred into a Teflon-lined stainless steel autoclave with a rectangular titanium (Ti) foil lying at the bottom and kept at 160 °C for 6 h. After cooling down to room temperature, the obtained film was taken out and immersed into a 100 mL aqueous solution containing 0.25 g glucose for 24 h. Finally, the film was dried at 60 °C and further annealed at 550 °C in the flow of Ar for 3 h. SnO$_2$ porous shell was coated on the surface of Fe$_3$O$_4$ nanorod core by a simple hydrothermal method. In detail, a 70 mL solution containing 0.0333 g K$_2$SnO$_3$·3H$_2$O and 0.3 g urea was heated in autoclave at 90 °C with the Fe$_3$O$_4$ film immersed in. After 2 h, the core-shell nanorod film was taken out and annealed at 500 °C in Ar gas for 2 h to improve the crystallinity and adhesion to the substrate.

**Characterizations.** The microstructure and morphology of the film was characterized by powder X-ray diffraction(XRD, Bruker D-8 Avance) measurement, transmission electron...
microscopy (TEM) (JEM-2010FEF, 200 kV) and scanning electron microscopy (SEM, JSM-6700F). The BET specific surface area was measured on a Bel Sorp-mini (S/N-00230) Analyzer (accelerated surface area and porosimetry system). CHI 760D electrochemical workstation with a three-electrode mode was used to perform cyclic voltammetry and constant current charge-discharge behavior. Nanorod films were directly used as the working electrode. The reference electrode and counter electrode were Ag/AgCl and a platinum plate, respectively. Electrochemical impedance spectroscopy (EIS) was recorded on PARSTAT2273 by applying an AC voltage with 5 mV amplitude in a frequency range from 0.01 Hz to 100 kHz at open circuit potential. All the electrochemical experiments were carried out in 1 M Na$_2$SO$_3$ solution at room temperature.

**II. Figures:**

![Fig.S1](image.png)

*Fig.S1.* (a) Low-magnification and (b) enlarged SEM images of Fe$_3$O$_4$@SnO$_2$ hybrid film electrode after 2000 cycles.
**Fig. S2.** EIS results of Fe$_3$O$_4$@SnO$_2$ and pristine Fe$_3$O$_4$ films after long-term cycling. Although the $R_{ct}$ value of both the electrodes increases to $\sim$12 $\Omega$, it is still relatively small.