

Electronic Supplementary Information (ESI) for Chemical Communications. This journal is (c) The Royal Society of Chemistry 2021.

Electronic Supplementary Information (ESI)

Engineering a novel microcapsule of Cu₉S₅ core and SnS₂ quantum dot/carbon nanotube shell as Li-ion battery anode

Jinyun Liu^{*a}, Mengfei Zhu^a, Kai Mu^b, Tianli Han^a, Zeng Pan^c, Yuqing Gan^a,
Huigang Zhang^{*d,e}, Ting Si^{*b}

Experimental

All chemicals were analytical reagent grade purchased from Aladdin and used without purification.

Synthesis of ZnO nanorods: In order to form the pores in the microcapsule shell, ZnO nanorods were prepared as sacrificing template. 1.338 g of Zn(NO)₂·6H₂O and 0.6309 g of hexamethylenetetramine were respectively dissolved in 45 mL of deionized water. The two solutions were mixed and put into in a 100 mL Teflon-lined stainless steel autoclave and reacted at 95 °C for 4 h. The sample was collected, cleaned by centrifugation, and dried at 70 °C in an oven.

Preparation of QDs/CNTs: The preparation of SnS₂ QDs is as follows: 0.06 g of CNTs and 0.034 g of SnCl₂·2H₂O were dissolved in a mixed solution of 20 mL of deionized water and 40 mL of N-methylpyrrolidone (NMP), and stirred for 1 h. Then, 0.046 g of L-cysteine were added after stirring for 1 h, the solution was put into in a 100 mL Teflon-lined stainless steel autoclave and reacted at 180 °C for 6 h. The sample was obtained by centrifugation, dried overnight at 70 °C, and calcined at 600 °C for 2 h under Ar gas.

Preparation of CS Nanoflowers: 7.72 g of Cu(NO)₂·3H₂O was dissolved in 100

mL of dimethyl sulfoxide, then 3.2 g of polyvinyl pyrrolidone was added and stirring for 10 min. At last, 4.0 g of thioacetamide was added and stirring for 10 min. The solution was put into in a 100 mL Teflon-lined stainless steel autoclave and kept at 120 °C for 10 h. The sample was obtained by centrifugation, dried overnight at 70 °C, and finally calcined at 550 °C for 3 h in Ar gas.

Preparation of porous CS-QDs/CNTs microcapsules: The microcapsules were prepared through a liquid-driven coaxial flow focusing microfluidic approach. First, 20 g of polyvinyl alcohol (PVA) was added into 1 L of deionized water, and placed in a water bath under 70 °C under stirring to form a 2 wt% PVA solution. The inter phase was obtained by dispersing 1.0 g of the CS nanoflowers in 10 mL of the PVA under ultrasonication for 30 min. 0.4 mL of 2-hydroxy-2-methylpropiophenone, 10 g of ethoxylated trimethylolpropane triacrylate, 0.3 g of QDs/CNTs and 0.3 g of the ZnO nanorods were mixed to form the outer phase.

In addition, the PVA solution was used as the driving phase. The typical flow rates of the inner, outer, and driving phases were 3, 6, and 700 mL h⁻¹, which were controlled by the syringe pumps (Suzhou Xunfei Scientific Instrument Co. LTD, XF-101P). The real-time process was monitored by a charge coupled device (CCD) camera (The Imaging Source, DFK-23G274) equipped with microscopic lens. The illumination was provided by a strobe flashlight (Hangzhou Pintuo Electronic Technology Co. LTD, flashing frequency: 3.0 kHz) from another side of the chamber. In order to prevent the cracking of microcapsules, a small amount of PVA solution was firstly added into the collector. Then, the sample obtained in the collector was cured by UV-light illumination for 7 min. The microcapsules were washed several times with water, and dried overnight in a vacuum freeze dryer (LGJ-10). The microcapsules were annealed in a tube furnace at 400 °C for 3 h in Ar gas under a ramp rate of 2 °C min⁻¹. After that, the samples were immersed in a 3 % hydrochloric acid solution to etch the ZnO nanorods which were embedded in the shell, the porous microcapsules were obtained.

Characterization: The samples were characterized on a SEM (Hitachi S-8100, operated at 5 kV), TEM (Hitachi HT7700), HRTEM (JEOL JEM-2010), EDS, XRD (D8 Advance), Raman spectrometer (Renishaw in Via), and XPS (ESCALAB 250).

The pore-size distribution was measured by the Brunauer–Emmett–Teller through nitrogen adsorption–desorption (Nova 2000E). The core content in the microcapsules was measured on a thermogravimetric analyzer (TGA, Setaram Labsys Evo SDT Q600).

Electrochemical tests: The microcapsules, carbon black, and sodium carboxymethyl cellulose (CMC) (mass ratio=8:1:1) were mixed, and dispersed in styrene butadiene rubber (SBR) to form a slurry, then coated on a copper foil. After drying overnight in a vacuum oven at 80 °C, the foil was cut into small discs with a diameter of 12 mm. The mass loading was about 2.13 mg cm⁻², which is expected improvable by further increasing the content of active materials inside the microcapsules and reducing the microcapsule size. Subsequently, the CR2032-typed coin cells were assembled in a glove box (Mikrouna, Super 1220/750/900) in an Ar gas. The Li foil and microporous polypropylene membrane were used as the counter electrode and separator, respectively. The electrolyte contains 1 M LiPF₆ in a solvent consisting of ethylene carbonate and diethyl carbonate (with a volume ratio of 1:1). The electrochemical performance was tested by using a Neware CT-3008 battery tester. For the tests at different temperatures, the batteries were put in a temperature-controlled chamber with a determined temperature. Prolonged lines were used to connect the tester and the batteries. Before starting each test, the batteries were put in the chamber overnight. The CV curves and EIS spectra were recorded on an electrochemical workstation (CHI-660E).

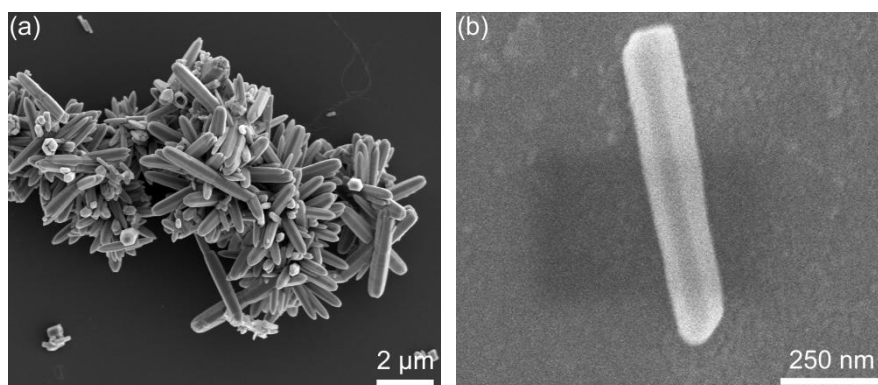


Fig. S1 SEM images of the ZnO nanorods.

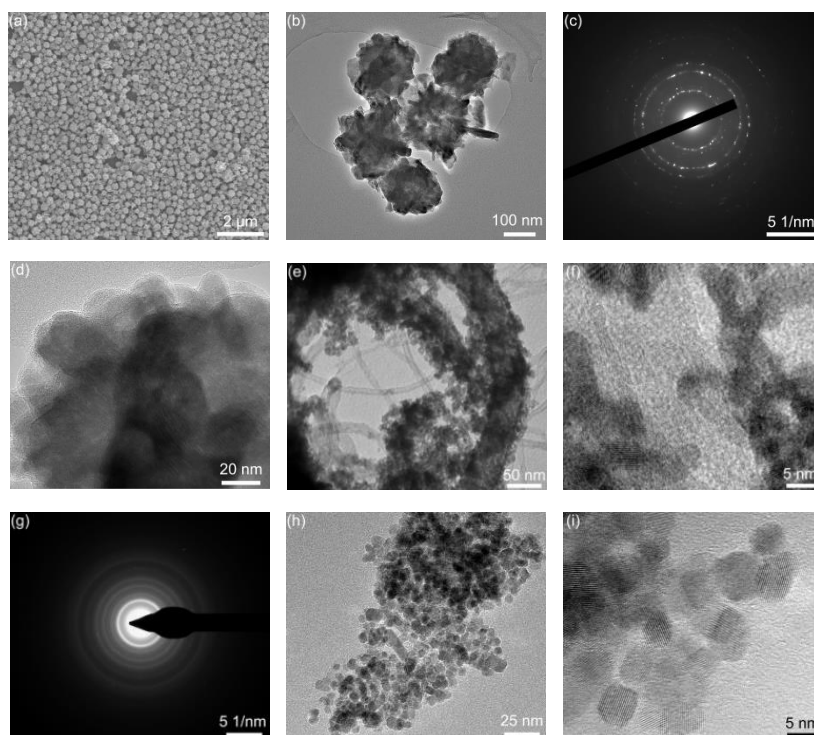


Fig. S2 (a) Low-magnification SEM and (b) TEM images, (c) SAED pattern and (d) HRTEM image of CS nanoflowers. (e) TEM and (f) HRTEM images, and (g) SAED pattern of QDs/CNTs. (h,i) HRTEM images of SnS₂ QDs.

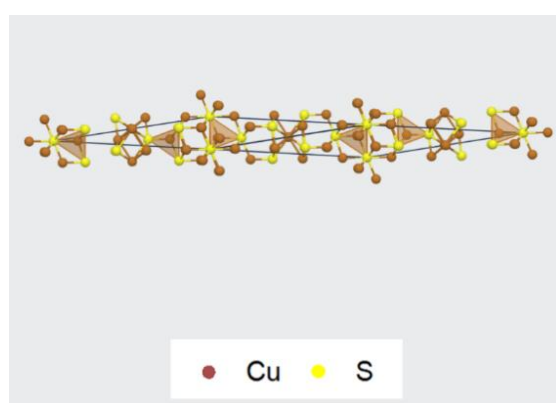


Fig. S3 Crystalline model of the Cu₉S₅.

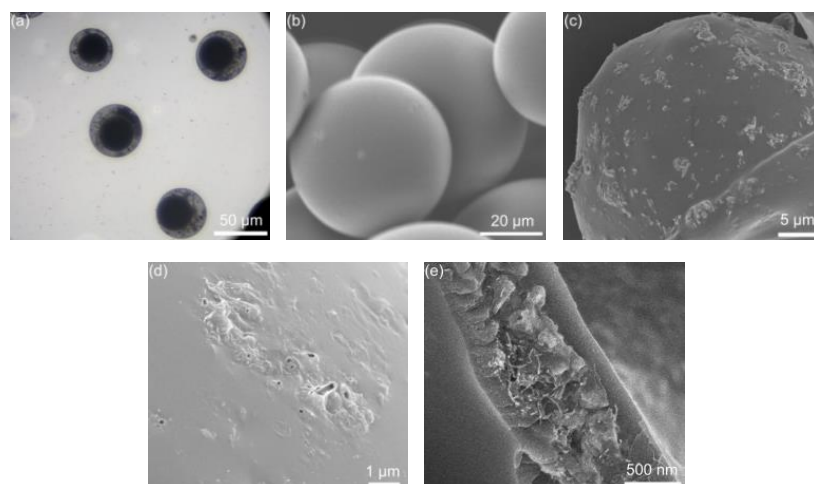


Fig. S4 (a) Optical image of the porous CS-QDs/CNTs microcapsules. SEM images of the microcapsules (b) before and (c) after carbonization. (d) High-magnification SEM images after etching ZnO nanorods. (m) SEM images of a broken microcapsule.

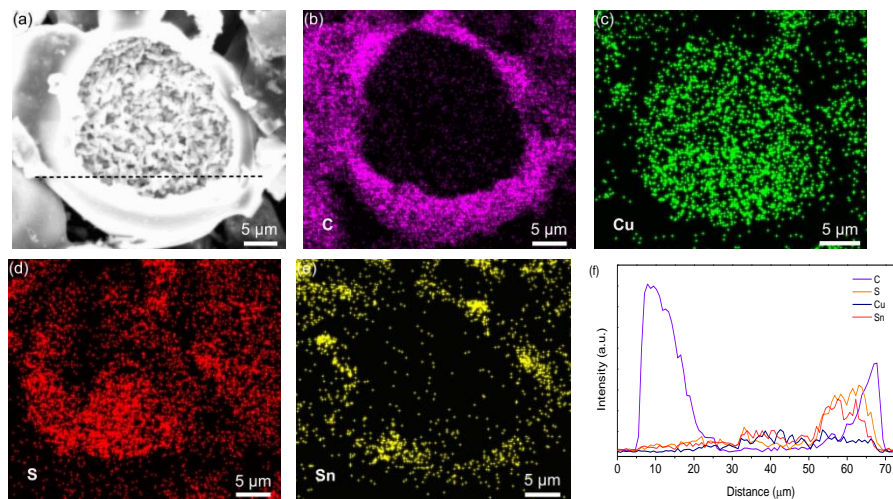


Fig. S5 (a) SEM images of a broken microcapsule. Elemental mapping images of (b) C, (c) Cu, (d) S, and (e) Sn. (f) line-scan curves. Dashed line in (a) indicates the line-scan direction.

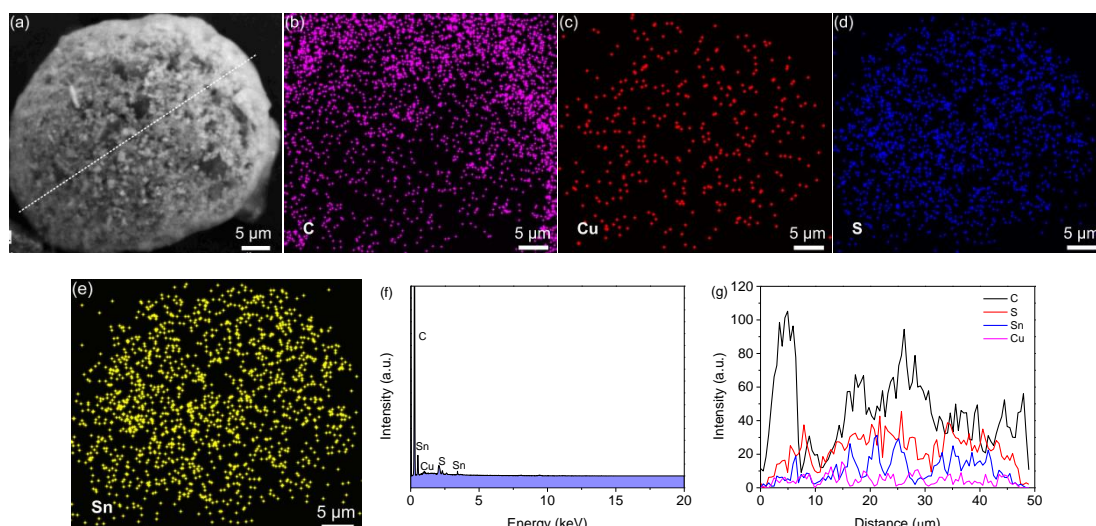


Fig. S6 (a) SEM image of a CS-QDs/CNTs microcapsule. The dashed line indicates the line-scan direction. Elemental mapping images of (b) C, (c) Cu, (d) S, and (e) Sn. (f) EDS spectrum and (g) line-scan curves.

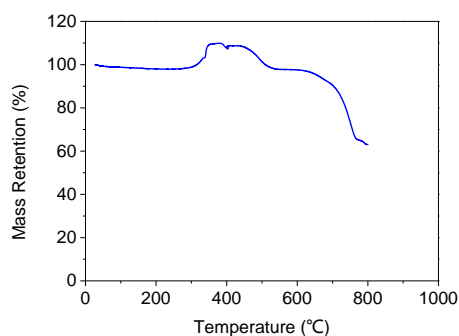


Fig. S7 TGA curve of the CS-QDs/CNTs microcapsule. The change of mass from 270 °C to 370 °C is ascribed to the conversion of Cu_9S_5 to Cu_2S . There is a major loss between 400 °C and 550 °C, which is attributed to the release of SO_2 , and the formation of $\text{CuO}\cdot\text{CuSO}_4$. The mass loss at about 600 °C to 700 °C indicates the decomposition of $\text{CuO}\cdot\text{CuSO}_4$.¹⁻³

Reference:

1. S. Foley, H. Geaney, G. Bree, K. Stokes, S. Connolly, M. J. Zaworotko, K. M. Ryan, *Adv. Funct. Mater.* 2018, **28**, 1800587.
2. M.R. Hosseini, M. Schaffie, M. Pazouki, A. Schippers, M. Ranjbar, *Mater. Sci. Semicond. Process* 2013, **16**, 250.
3. C. Kang, Y. Lee, I. Kim, S. Hyun, T. H. Lee, S. Yun, W.-S. Yoon, Y. Moon, J. Lee, S. Kim, H. J. Lee, *Materials* 2019, **12**, 1324.

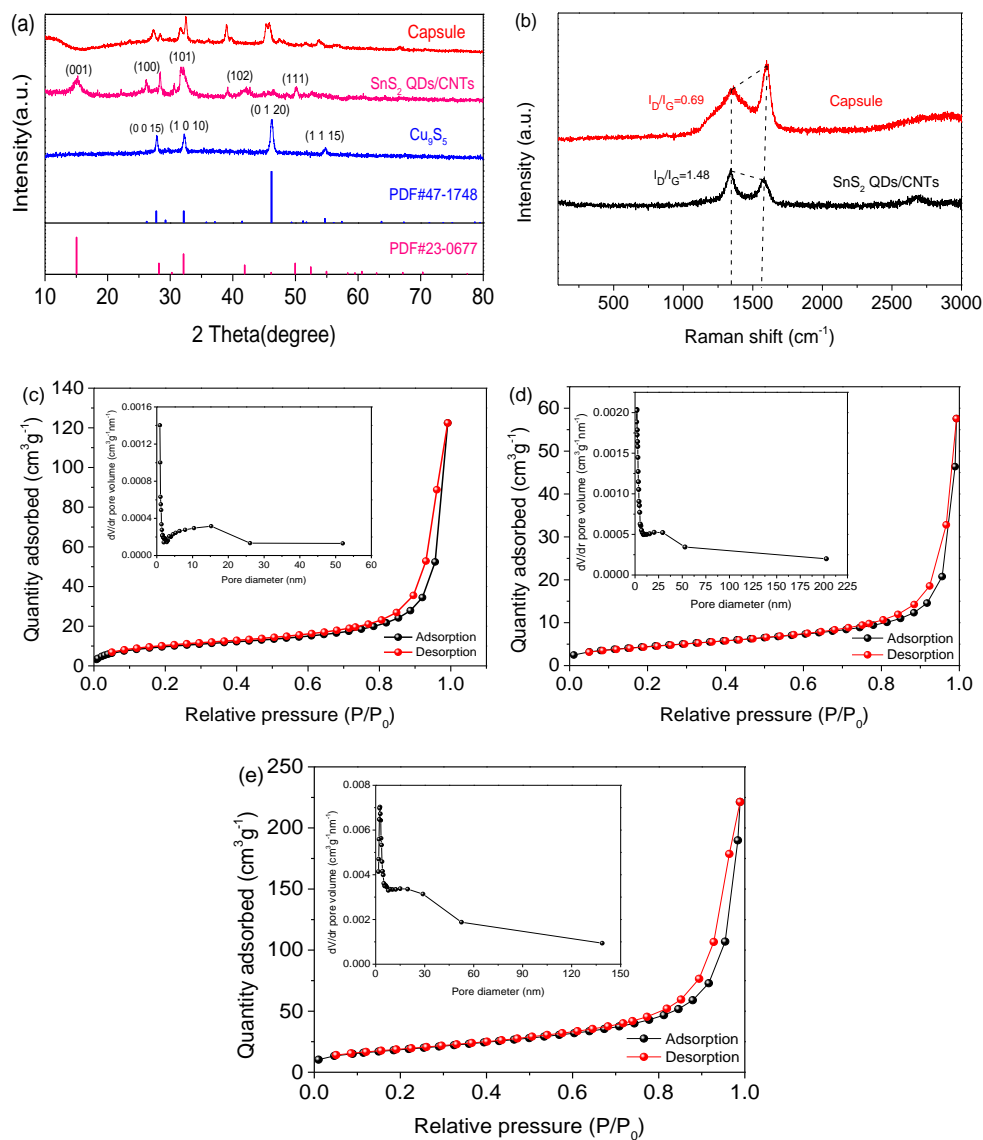


Fig. S8 (a) XRD patterns and (b) Raman spectra of the CS-QDs/CNTs microcapsules. N₂ adsorption-desorption isotherms of the (c) CS-QDs/CNTs microcapsules, (d) pure CS nanoflowers, and (e) QDs/CNTs composite. The insets show the pore-size distribution.

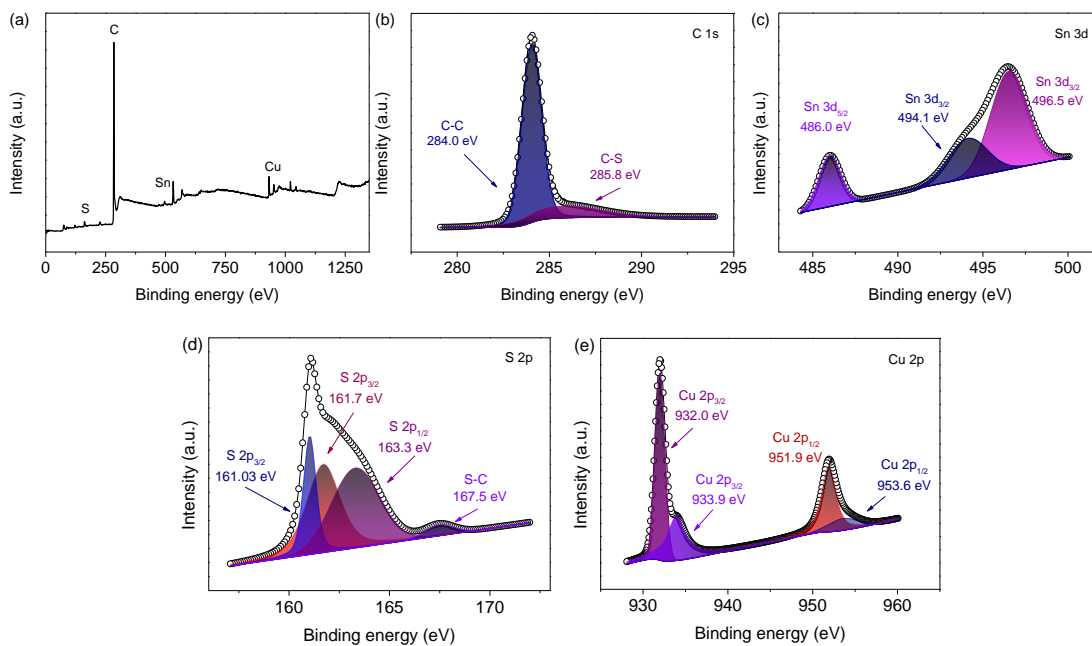


Fig. S9 (a) XPS survey spectrum of the CS-QDs/CNTs microcapsules. High-resolution XPS spectra of (b) C 1s, (c) Sn 3d, (d) S 2p and (e) Cu 2p.

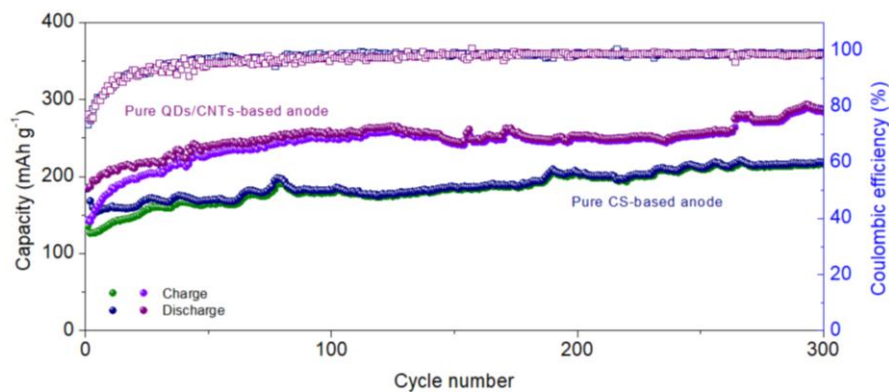


Fig. S10 Cycling performance of pure CS and pure QDs/CNTs-base anodes at 0.2 C.

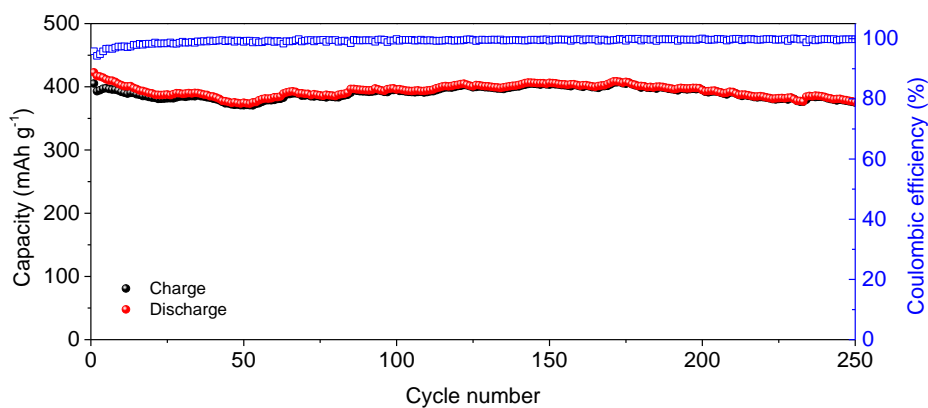


Fig. S11 Cycling performance of the CS-QDs/CNTs microcapsules at 1.5 C.

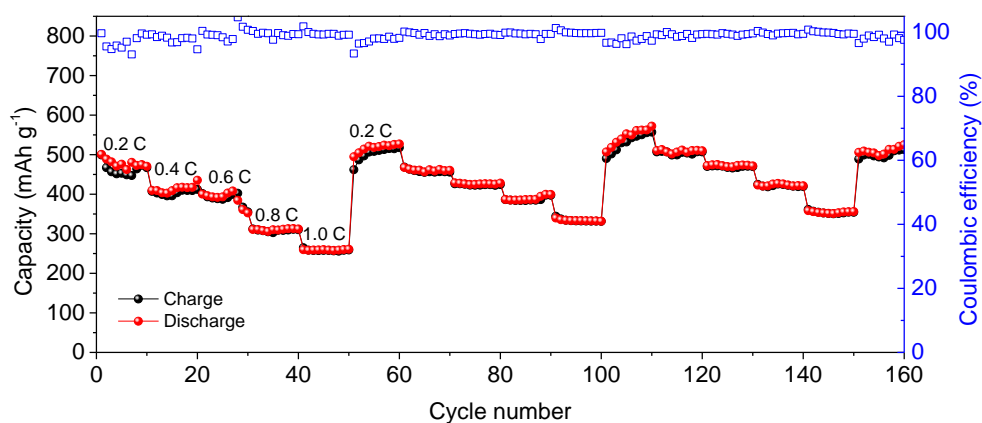


Fig. S12 Rate-performance the CS-QDs/CNTs microcapsules between 0.2 C to 1.0 C.

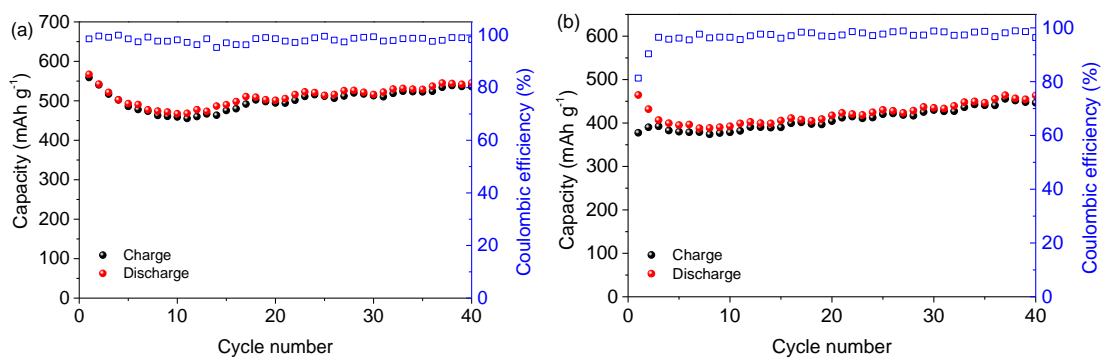


Fig. S13 Cycling performance of the CS-QDs/CNTs microcapsules under conditions of (a) charging at 0.2 C vs discharging at 0.4 C, (b) charging at 0.4 C vs discharging at 0.2 C.

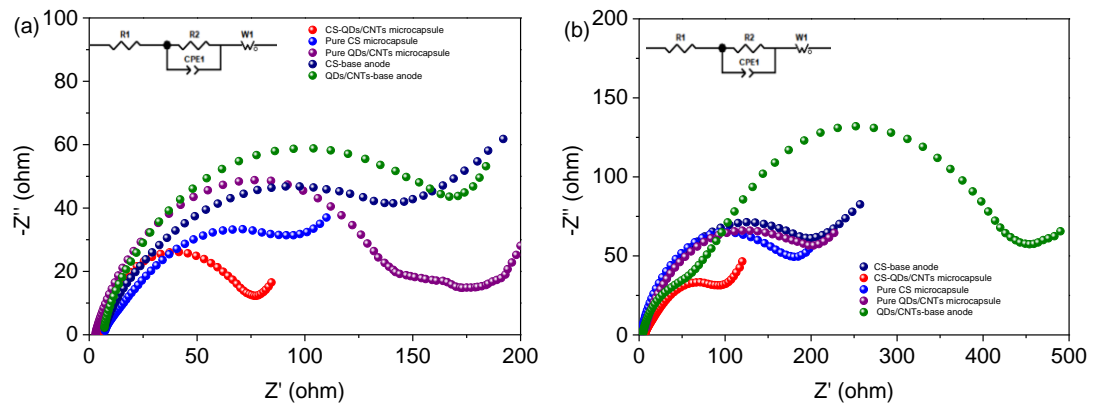


Fig. S14 Nyquist plots of the CS-QDs/CNTs microcapsules, pure CS microcapsules, pure QDs/CNTs microcapsules, CS and QDs/CNTs-based anodes: (a) fresh cell and (b) cell after 100 cycles.

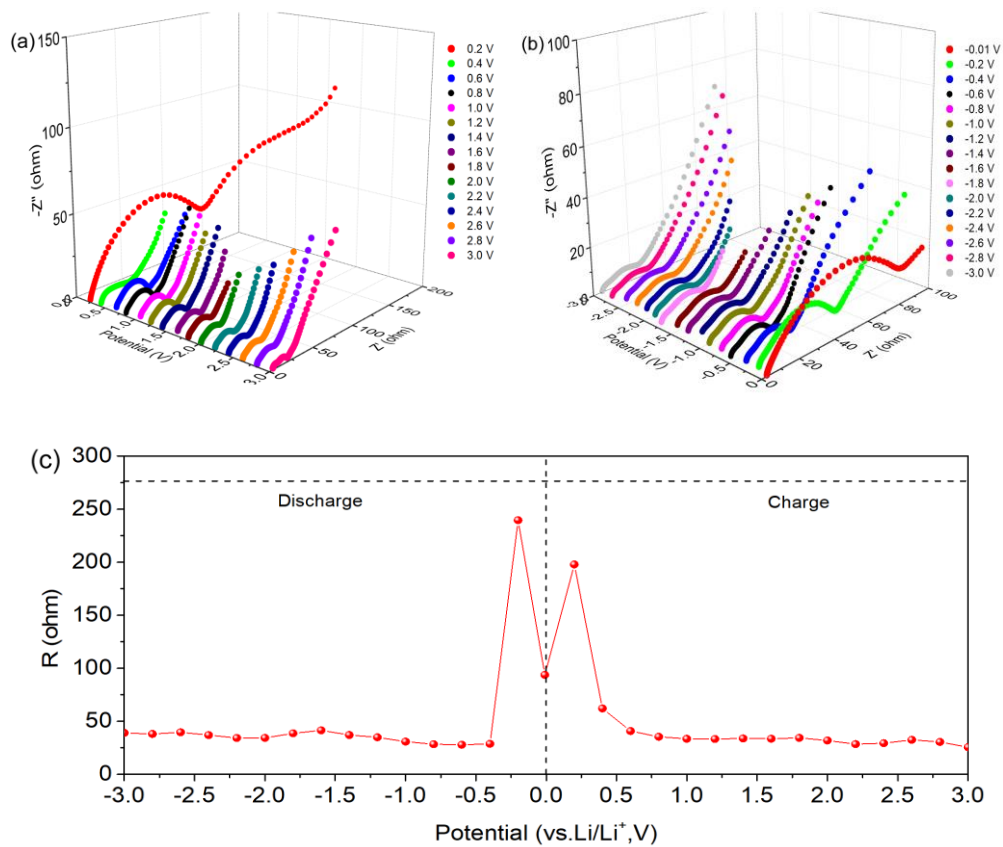


Fig. S15 EIS Nyquist plots of the CS-QDs/CNTs microcapsules within one cycle of (e) charge and (f) discharge. (g) Total resistance vs potential.