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Electronic Supplementary Information

High-performance supercapacitor based on multi-structural CuS@polypyrrole composites prepared by in-situ oxidative polymerization

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Experimental details

Materials: Pyrrole monomer (Shanghai Chemical Works, China) was distilled under reduced pressure. *P*-toluenesulfonic acid (*P*-TSA) and glycol were purchased from Aladdin Ltd. (Shanghai, China), ammonium persulfate (APS, Tianjin Damao Chemical Co., China), Copper nitrate hydrate (Tianjin Kaixin Chemical Co., China), thiourea (Shandong Shuangshuang Chemical Co., China), polyving akohol (PVA, Shanghai Chemical Works, China). All chemical reagents were in analytical grade.

Synthesis of CuS microsphere: In a typical process, 0.241 g of copper nitrate hydrate (1 mmol) and 0.153 g of thiourea (2 mmol) were dissolved in 40 ml glycol under violent stirring. After stirring for 30 min approximately, the yellow-green solution was transferred into a 100 ml Teflon-lined stainless steel autoclave and heated at 150 °C for 24 h. After cooled to room temperature naturally, the resulting black precipitates of CuS were collected by filtration, washed with distilled water and absolute ethanol several times to remove the residue of the reactants, finally dried in vacuum at 60 °C for 24 h.

Synthesis of CuS@PPy composites: CuS@PPy composites were synthesized by in situ chemical oxidative polymerization of pyrrole in the presence of the CuS suspension. In a typical process, 0.10 g of CuS and 1.14 g of *P*-TSA were ultrasonic dispersed in 30 ml of deionized water at ambient temperature. Then, the solution was transferred into ice bath under violent stirring, and the solution cooled to below 5 °C. 0. 50 g of pyrrole monomer was dispersed in above solution. After stirring for 30 min, the 0.82 g of APS (dissolved in 10 ml deionized water) dropped into above solution. The polymerization was performed for at least 6 h at below 5 °C ice bath. Reaction product was collected by centrifugation and washed successively with deionized water and ethanol and then dried at 60 °C for 24 h under vacuum to obtain a black powder. The content of CuS in this composite is 16.7 wt%.

For comparison purpose, pure PPy without CuS was synthesized under the same conditions. CuS@PPy composites with various contents (wt%) of CuS is calculated from mass ratios of CuS to pyrrole monomer, such as 3.8%, 9.1% and 28.6% are added 0.02 g, 0.05 g and 0.2 g of CuS, respectively, and the other experimental conditions are the same as above.

Materials Characterization: The morphologies of the CuS and CuS@PPy products were examined with field emission scanning electron microscopy (FE-SEM, JSM-6701F Japan) at an accelerating voltage of 5.0 kV. The structure of the samples was characterized by a transmission electron microscopy (TEM, JEM-2010 Japan). X-ray diffraction (XRD) of samples was performed on a diffractometer (D/Max-2400, Rigaku) advance instrument using Cu Kα radiation (k =1.5418 Å) at 40 kV, 100 mA. The 2θ range used in the measurements was from 5 to 80°. The Brunauer-Emmett-Teller (BET) surface area (S_{BET}) of the powders was analyzed by nitrogen adsorption in a Micromeritics ASAP 2020 nitrogen adsorption apparatus (U.S.A.). All samples were degassed at 100 °C prior to nitrogen adsorption measurements.

Electrochemical measurements: The electrochemical test is conducted with a CHI 660D electrochemical workstation in an aqueous KCl solution (1 M) with a three-electrode cell where glassy carbon electrode with a diameter of 5 mm was used as the working electrode, platinum electrode serves as the counter electrode and a standard calomel electrode (SCE) as the reference electrode. The working electrodes were fabricated similar to our previous reported literature.[S1] Typically, 4 mg of CuS@PPy was ultrasonically dispersed in 0.4 mL of Nafion (0.25 wt%). The above suspension of 8 μL using a pipet gun was dropped onto the glassy carbon electrode and dried at room temperature.

Cyclic voltammograms were recorded from -0.8 to 0.5 V at scan rates of 25 mV s^{-1}. The galvanostatic charge/discharge property was measured at various current densities with cutoff voltage of -0.5 to 0.5 V. The cycle-life stability was performed using computer controlled cycling equipment (LAND CT2001A, Wuhan China). Electrochemical impedance spectroscopy (EIS) measurements were performed with the Autolab PGSTAT 128N equipped (Eco-chemie, Netherland) with FRA module, the frequency ranging from 10 mHz to 100 kHz and an impedance amplitude of ±5 mV at open circuit potential.

Two-electrode cell assembly and measurements: The capacitive performance of CuS@PPy samples was investigated using a two-electrode testing cell. The working electrode was prepared by mixing the CuS@PPy with polyvinylidene fluoride (PVDF) and commercial carbon black (8:1:1) in N-methyl-2-pyrrolidone (NMP) until homogeneous slurry. The slurry was coated on nickel foam with a working area of 1.0 cm^2 and the electrodes were dried at 120 ^{o}C for 12 h and then weighted and pressed into sheets under 20 MPa. The total mass was between 3 and 5 mg of each electrode and two electrodes with identical or very close weight were selected for the measurements.

PVA-KCl polymer electrolytes played role of separator and gel electrolyte. The PVA-KCl gel electrolyte was fabricated similar to the literature.[S2] Typically, 1 g KCl and 1 g PVA were added into 15 ml deionized water and thus heat up to 85 °C for 1 h under vigorous stirring became clear. For the construct supercapacitor, two pieces of the electrodes were immersed in a hot clear solution of gel electrolyte for 5 min. The resulting electrolyte-filled electrodes were solidified for 12 h at room temperature. Finally, as-prepared two electrodes were symmetrically assembled into sandwich-type cells. The cyclic voltammetry and galvanostatic charge-discharge tests of CuS@PPy composite with the potential from -0.5 V to 0.5 V.

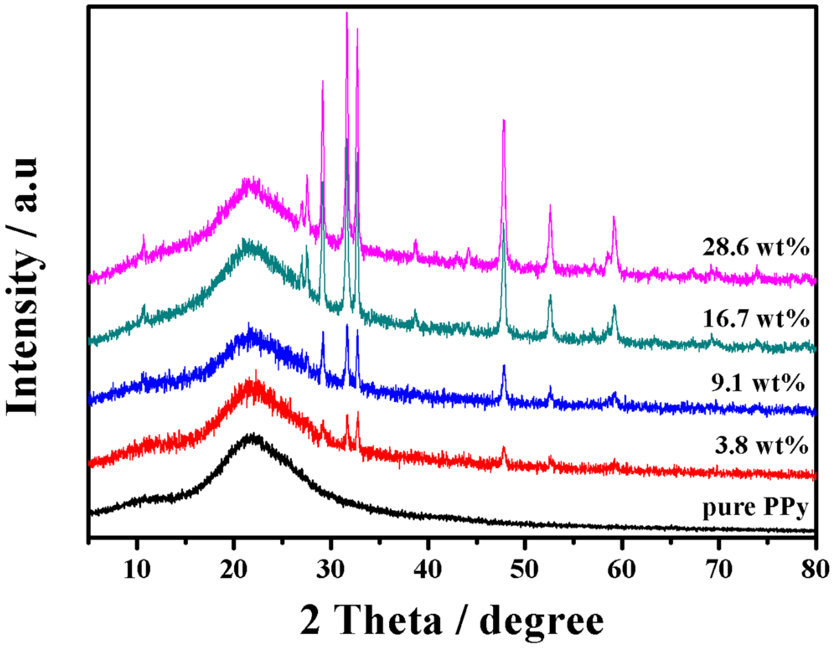

Fig. S1. XRD patterns of CuS@PPy composites with various contents (wt%) of CuS.

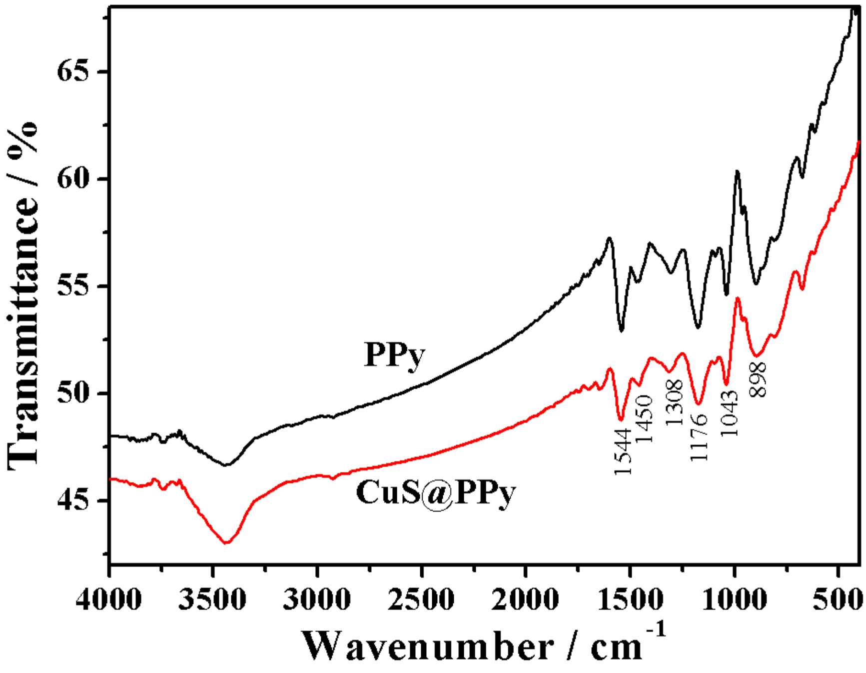

Fig. S2. FT-IR spectra of pure PPy and CuS@PPy composite (CuS content is 16.7 wt%)

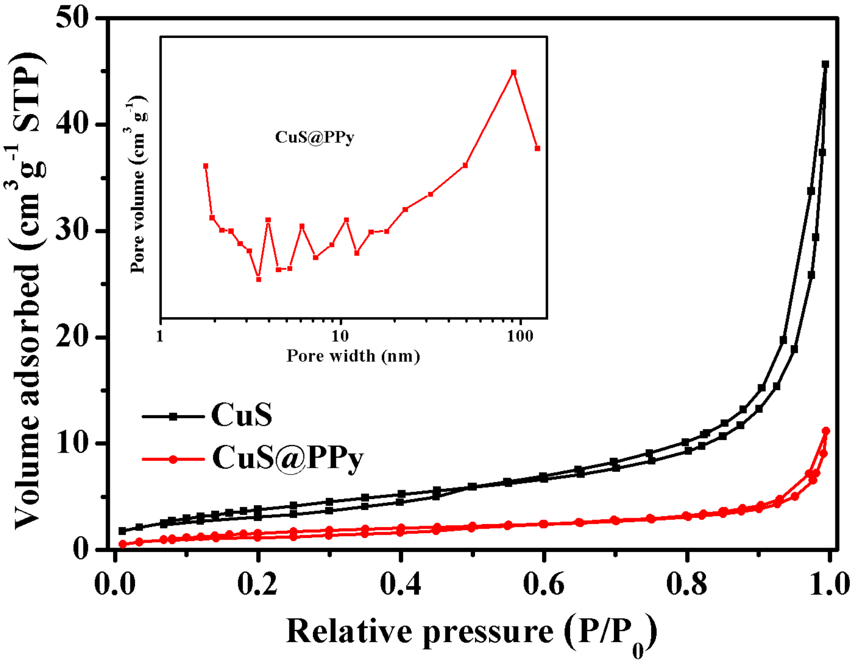

Fig. S3. Nitrogen adsorption-desorption isotherms of CuS and CuS@PPy composite (CuS content is 16.7 wt%). The inset shows the pore size distribution curve of CuS@PPy composite.

Table S1. The BET specific surface areas, average pore size, and pore volumes of CuS and CuS@PPy composite (CuS content is 16.7 wt%).

Samples	S_{BET} (m^2 g^{-1})	Average pore size (nm)	Pore volume (cm^3 g^{-1})
CuS	14.83	19.1	0.070
CuS@PPy	6.19	11.2	0.020

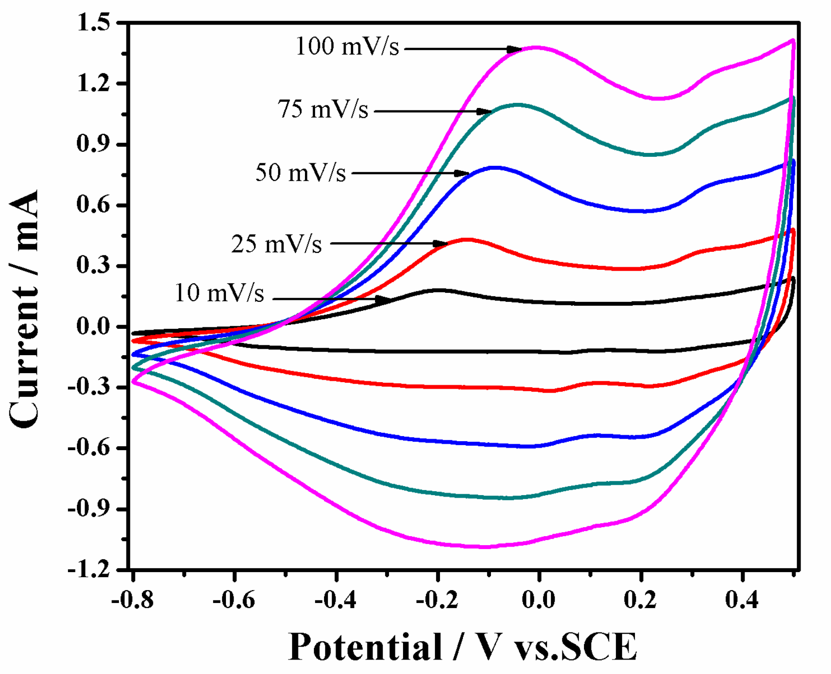

Fig. S4. CV curves of CuS@PPy composite (CuS content is 16.7 wt%) at various scan rates.

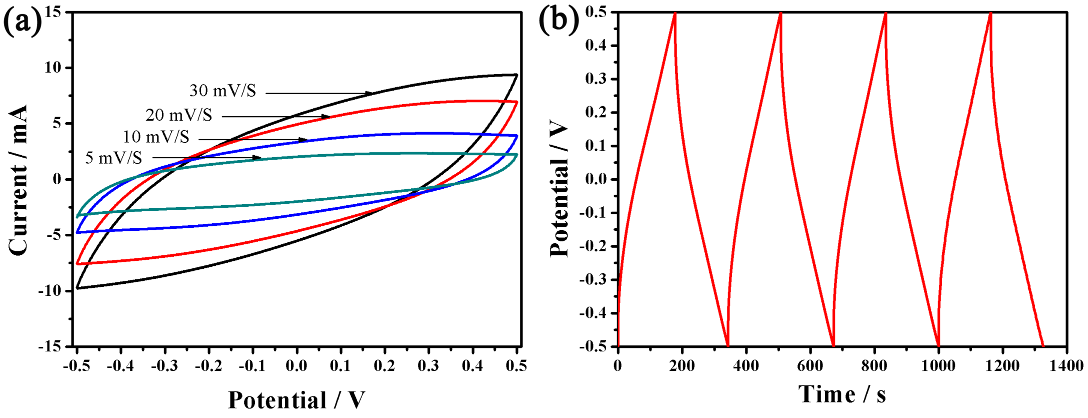

Fig. S5. (a) CVs of CuS@PPy composite (CuS content is 16.7 wt%) as a two-electrode cell configuration at various scan rates with the potential from -0.5 V to 0.5 V. (b) Galvanostatic charge-discharge curves of CuS@PPy composite (CuS content is 16.7 wt%) at the current of 3 mA. The total mass of active material of two electrodes is 9.0 mg.

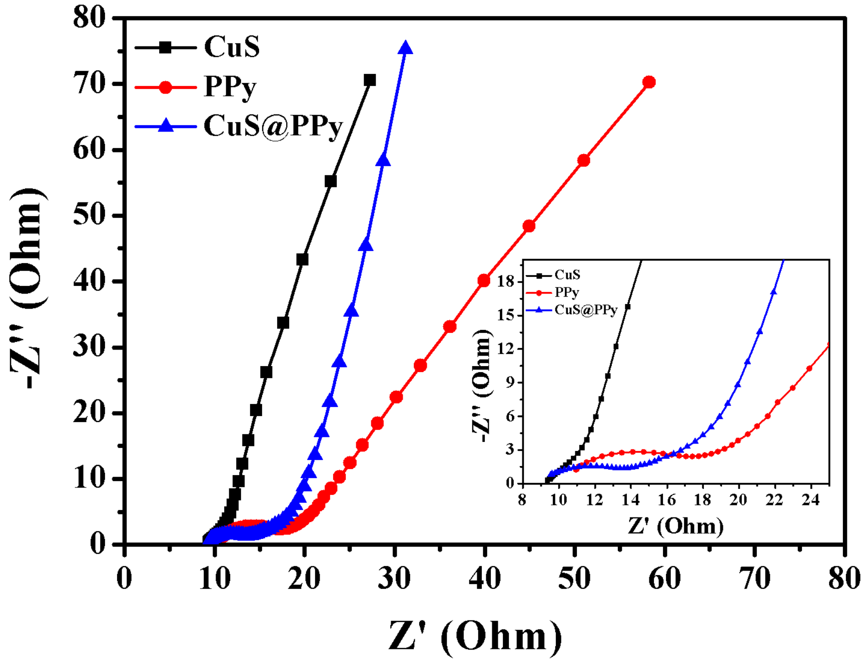

Fig. S6. Nyquist plots of CuS, PPy and CuS@PPy composite (CuS content is 16.7 wt%) in 1 M KCl. The inset shows the expanded high frequency region of the plot.

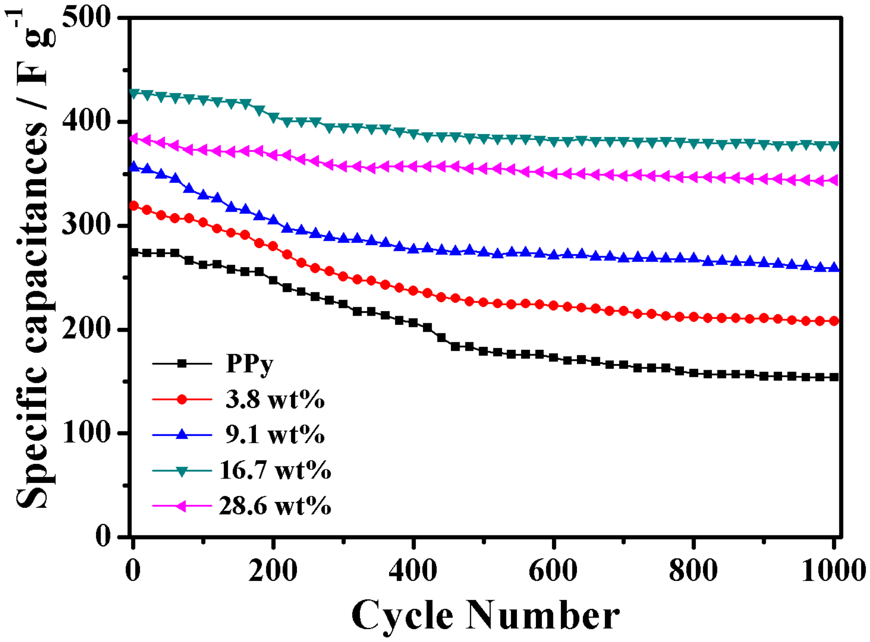

Fig. S7. The cycling stability of CuS@PPy composites with various contents (wt%) of CuS.

Table S2. Comparison of electrochemical performance of different PPy electrode materials.

Electrode material	**Preparation methods**	**Specific capacitance (Electrolyte)**	**Capacitance retention**	**Ref.**
PPy	Electrochemical deposition	354 F g^{-1} (1 mV s^{-1}) (Aqueous)	-	[S3]
PPy thin films	Chemical bath deposition	329 F g^{-1} (5 mV s^{-1}) (0.5 M H_2SO_4)	78% after 3000 cyclics	[S4]
PPy-CNT	In situ polymerization	282.4 F g^{-1} (1 mA cm^{-2}) (1 M KCl)	85% after 5000 cyclics	[S5]
Graphene/PPy	In situ polymerization	165 F g^{-1} (1 A g^{-1}) (1 M NaCl)	92% after 1000 cyclics	[S6]
GN/PPy/CNT	In situ polymerization	361 F g^{-1} (0.2 A g^{-1}) (1 M KCl)	96% after 2000 cyclics	[S7]
PPy/bacterial cellulose	In situ polymerization	316 F g^{-1} (0.2 A g^{-1}) (0.5 M KCl)	88.2% after 1000 cyclics	[S8]
PPy/RuO_2	Potentiostatically electropolymerized	302 F g^{-1} (0.5 mA cm^{-2}) (1 M H_2SO_4)	~ 90% after 300 cyclics	[S9]
PPy-covered MnO_2	Electrochemical polymerization	141.6 F g^{-1} (1 A g^{-1}) (1 M Na_2SO_4)	~ 50% after 500 cyclics	[S10]
MnO_2/PPy	In situ polymerization	294 F g^{-1} (1 A g^{-1}) (1 M Na_2SO_4)	92.6% after 1000 cyclics	[S11]
CuS@PPy	In situ polymerization	427 F g^{-1} (1 A g^{-1}) (1 M KCl)	88% after 1000 cyclics	This work

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