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†Electronic Supporting Information

Highly Rate and Cycling Stable Electrode Materials constructed from Polyaniline/Cellulose Nanoporous Microspheres

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Experimental Section

Preparation of cellulose microspheres: All chemicals were analytical grade and were used without further purification. The cellulose solution was prepared according to the previous method.¹ A solution of LiOH/urea/H₂O (4.6/15/81.4, by weight) was pre-cooled to -12 °C, and then 8.4 g of cellulose was immediately dispersed into the solvent (200 mL) under vigorous stirring for 3 min at ambient temperature to obtain a transparent cellulose solution, which was degassed by centrifugation at 8000 rpm for 10 min at 5 °C. The obtained cellulose solution was dropped in the solution of Span 85 in isooctane within 1 h and stirred in a scheduled stirring speed. The suspension in the vessel was stirred at the same speed and temperature for an additional 3 h to form the regenerated cellulose microspheres. Subsequently, the suspension was allowed to stand until it was separated into two layers. The bottom layer aqueous phase containing cellulose microspheres were rinsed with deionized water and washed with anhydrous ethanol to dry.

Construction of PANI/PA/CM via phytic acid "bridge": The PANI/PA/cellulose microspheres were prepared according to our method² as follows. The PANI/PA/cellulose microspheres were fabricated through the aniline oxidative polymerization by using ammonium persulfate (APS) as oxidant. Acidic solutions of APS and aniline were prepared with 10 wt% phytic acid solution and concentrations of 0.1 mol·L⁻¹ APS and aniline. Briefly, 1 g cellulose microspheres were dispersed into 100 ml of 0.1 mol·L⁻¹ aniline solution under stirring for 10 min. Subsequently, 0.1 mol·L⁻¹ APS was added into the above suspension under stirring at 0 °C for 6 h to obtain PANI/phytic acid/cellulose microspheres, coded as PANI/PA/CM. Finally, the microsphere were collected, and then washed with deionized water several times. The absorbed water in the composite microspheres were exchanged to tertiary butyl alcohol, and then by the freeze-dried method to obtain PANI/PA/cellulose microspheres products.

Preparation of the electrodes: Unless otherwise specified, the electrodes were composed of 80 wt. % PANI/PA/CM, 10 wt.% acetylene black (Alfa Aesar, 99.9 %), and 10 wt. % poly (tetrafluoroethylene) (PTFE) as a binder. The PTFE was dispersed

in about 30 mL of ethanol before the addition of PANI/PA/CM and acetylene black. The resulting solution was homogenized by stirring overnight, and ethanol was evaporated in oil bath at 80 °C until the formation of a rubber like paste, which was roll-pressed into a 40-µm-thick film on a flat glass surface. The reference electrodes were fabricated in the same way with working electrode. The ratio between active carbon (YP50) and PTFE is 95%/5%. Before electrochemical characterization, the electrodes were dried overnight at 60 °C and were subsequently immersed in the material bulk.

Characterization

The morphology and structure of the composite microspheres were determined by field-emission scanning electron microscopy (FE-SEM, Zeiss, SIGMA), transmission electron microscopy (TEM, JEOL JEM-2010), The preparation method of TEM slice as follows: The imbibed water of the PANI/PA/CM was exchanged to acetone, and then the microspheres were embedded with epoxy resin Epon812 (Shanghai Bioscience, Shanghai, China). After that, the embedded specimen was sectioned by a Leica Ultracut-E using a diamond knife to prepare approx 80 nm-thick sections. X-ray diffraction using the Cu K α radiation ($\lambda = 1.5418$ Å) (XRD, D8-Advance, Bruker, USA), thermal gravimetric analysis (TGA) (STA449C, 31MFC, G Jupiter, German) and X-ray photoelectron spectroscopy (XPS, XSAM800). Surface area and pore size distribution were evaluated using N2 adsorption (Micromeritics, AsAp2020 USA), and the specific surface area was calculated from the N2 adsorption isotherm using the Branauer-Emmett-Teller (BET) equation. Solid-state ¹³C NMR and ¹³P NMR spectra (BRUKER AVANCE III spectrometer) and FTIR spectra with the KBr disk method (1600, Perkin-Elmer Co., MA) were used to study the hydrogen bonding interaction between PANI, PA and cellulose. The electrochemical properties of the materials were investigated with cyclic voltammetry (CV) and chronopotentiometry measurements employing a CHI 660D electrochemical workstation (Chenhua, Shanghai) and Autolab PGSTAT302N, and the electrochemical impedance spectroscopy (EIS) was measured by an Autolab PGSTAT302N at a frequency ranging from 100 mHz to 10 kHz with a potential amplitude of 10 mV, and the sheet resistance measurements were tested by four-point probe method (RTS-8, China).



Figure S1. Preparation Process of the PANI/PA/CM: cellulose microspheres were prepared via emulsifier from the cellulose solution (First step); then PANI were generated in situ polymerization of aniline on cellulose microspheres (Second step).



Figure S2. The photographs of the flexible circular electrodes (a) and winding electrodes (b) of the PANI/PA/CM. The electrode materials prepared from the PANI/PA/CM microspheres displayed flexibility repeated bending (Figure S2b).



Figure S3. Optical photomicrographs of the cellulose microsphere (CM) (a) and PANI/PA/CM (b) as well as the TEM image of the edge (c) and inside (d) of PANI/PA/CM.



Figure S4. ³¹P fast-MAS NMR spectrum of the phytic acid (PA) (a)³ and Solid-state ³¹P fast-MAS NMR spectrum of the PANI/PA/CM (b) as well as the chemical structure of the phytic acid (PA).



Figure S5. XPS patterns of the cellulose microspheres (CM), PANI/PA/CM, PANI powder (a); XPS spectra of N1s (b), C1s (c) and P2p (d) for the PANI/PA/CM.



Figure S6. XRD patterns (left) of the cellulose microspheres (CM) (a), PANI/PA/CM (b) and pure PANI powder (c), and TG curves (right).



Figure S7. EIS spectrum of the pure PANI



Figure S8. The specific capacitance versus current density



Figure S9. Ragone plot of the device.

The Ragone plot shown in **Figure S9** evaluates the performance of the device in terms of its energy density and power density, which can be estimated using the following equations:

 $C_m = (I\Delta t)/(M\Delta V)$ $E = 0.5C_m(\Delta V)^2$ $P = E/\Delta t$

Where C_m , I, Δt , M and ΔV represents the specific capacitance (F/g) of the device, the discharge current (A), the discharge time (s), the total mass of electrode materials (g) and the device voltage (V) after the IR drop, respectively.

No apparent degradation of PANI/PA/CM could be observed after 12000 cycles with high coulombic efficiency of aroud 100 %. This excellent cycling stability was much larger than the common values of PANI, PANI/CNT/cellulose films, PANI/Graphene or PANI/carbon composite electrodes (see **Table S1**). Table S1 lists the comparison of cycling stable performance of PANI-based supercapacitors.

Materials	Electrolytes	Cycling stable capablity	Sources
PANI	1 M H ₂ SO ₄	45.7 % retention after 1000 cycling	Ref. 4
SWCNT/PANI films	1 M LiClO4	85 % retention after 1000 cycling	Ref. 5
BC-MWCNTs-PANI ₁₀ paper	1 M H ₂ SO ₄	99.8% retention after 1000 cycling	Ref. 6
Graphene/PANI nanofibers	$1 \text{ M Et}_4\text{N}^+ \bullet \text{BF}_4/\text{PC}$	73.7 % retention after 1000 cycling	Ref. 7
3DOMC-P ANI composite	1 M H ₂ SO ₄	85 % retention after 1000 cycling	Ref.8
Graphene/PANI paper	1 M H ₂ SO ₄	82 % retention after 1000 cycling	Ref. 9
PANI/CNT/cellulose films	1 M H ₂ SO ₄	81 % retention after 1000 cycling	Ref. 10
Cloth-SWCNT-PANI	1 M H ₂ SO ₄	90 % retention after 3000 cycling	Ref. 11
3D-RGO/PANI	1 M H ₂ SO ₄	88 % retention after 5000 cycling	Ref. 12
PANI/PA/CM	1 M H ₂ SO ₄	no apparent capacitance degradation after 12000 cycling	This work

Table S1. Comparison of the cycling stable performance of PANI-based supercapacitors.

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