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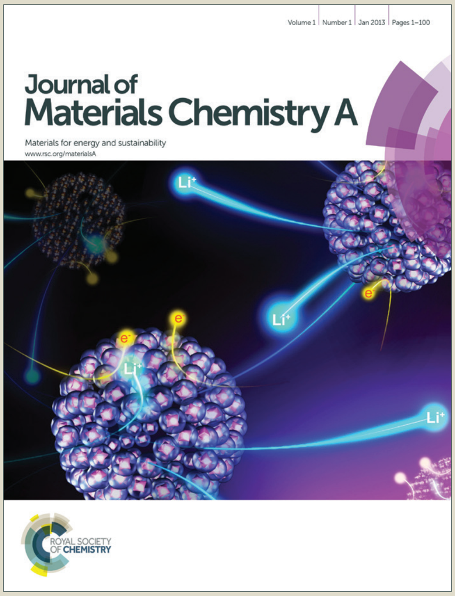

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COMMUNICATIONS

Nanostructured conductive polypyrrole hydrogels as high-performance, flexible supercapacitor electrodes

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Abstract. Electrochemically active conducting polymers are an important class of materials for applications in energy storage devices such as batteries and supercapacitors, owing to their advantageous features of unique three-dimensional (3D) porous microstructure, high capacitive energy density, scalable synthesis and light weight. Here, we synthesized a nanostructured conductive polypyrrole (PPy) hydrogel via an interfacial polymerization method. The simple synthesis chemistry offers the conductive hydrogel tunable nanostructures and electrochemical performance, as well as scalable processability. Moreover, the unique 3D porous nanostructure constructed by interconnected polymer nanospheres endows PPy hydrogels good mechanical property and high performance acting as supercapacitor electrodes with specific capacitance of ~380 F/g, excellent rate capability, and areal capacitance as high as ~6.4 F/cm^2 at mass loading of 20 mg/cm^2.

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Introduction

Flexible and portable electronics such as wearable electronic devices, flexible displays and bendable television screens, have been catching the eyes of developers and customers in the past decade.[1] Some novel conceptual products, such as Google Glass, Apple iWatch, next-generation transparent mobile phones and artificial electronic skins have been well known to the public.[2] The rapid development of portable electronic equipment requires the follow-up of flexible, lightweight and efficient energy storage devices.[3-5]

Electrochemical capacitors are widely recognized as an important class of energy storage devices of which charge storage mechanism is the reversible charge/discharge process involving only translation of electronic or ionic charges through electronically or ionically active materials.[6, 7] The development of flexible solid-state supercapacitors has been propelled by the prosperous advances in portable energy storage devices, because they can provide high power density, long cycle life and the potential to achieve relatively high energy density.[8] Several strategies for high-performance flexible supercapacitors have been demonstrated recently, including coating active materials, such as RuO_2,[9] MnO_2,[10, 11] V_2O_5,[12] NiOH,[13] graphene nanosheets[14, 15] onto conductive fibers by electrochemical deposition or casting and fabrication of hydrogel or aerogel films based on graphene. However, these methods suffer from high cost of noble metals or expensive carbon support materials, limited ionic/electronic conductivity, poor mechanical flexibility, and scalable electrochemical synthesis conditions, which could hinder their large-scale commercialization.

Electrically conducting polymers—such as polyaniline (PAni), polypyrrole (PPy), and their derivatives—are polymers that have intrinsic electronic conductivities. They provide the unique electrical properties of metals or semiconductors, as well as attractive properties associated with conventional polymers, such as ease of synthesis and flexibility in processing, thus becoming promising electrode materials for next-generation flexible energy storage devices. Recently, conducting polymers are simply mixed with or electrochemically deposited onto transition metal oxides to achieve high-performance hybrid electrode materials, such as RuO_2/PPy,[16] MnO_2/PPy[17] and three-dimensional (3D) conductive wrapping of graphene/MnO_2 nanostructures by PEDOT:PSS.[18] Improvements in terms of cycle life and rate capability have been presented in these works owing to the excellent electrochemical activity and additional pseudocapacitance of conducting polymers. However, conducting polymer wrapping on transition metal oxides may reduce the effective contact area between metal oxides and electrolytes. This will further impede alkali ions insertion into metal oxides and result in poor rate performance with lower specific capacitance. Due to the promising electrochemical activities of conducting polymers, a rational strategy will be using conducting polymers as active electrode materials directly and optimizing the performance by rational design of synthesis and control of the microscopic architectures.

3D hierarchically nanostructured hydrogels based on conducting polymers provide intrinsic conducting frameworks that promote the transport of charges, ions, and molecules and ideal interface between electronic-transporting and ionic-transporting phases, between biological and synthetic systems, as well as between soft and hard materials, thus becoming an ideal candidate for energy storage, molecular and bioelectronics and medical electrodes.[19] However, previously reported conductive hydrogels such as PAni hydrogel are interconnected nanofibers with relatively poor mechanical properties which hinder their application in flexible energy storage devices. And limited by the mechanical properties, thin film electrodes and thus relatively low mass loading of active materials are used in most studies, resulting in a low areal specific capacitance which is not desirable for practical applications.

In this paper, 3D nanostructured conducting PPy hydrogel with structure-derived elasticity was synthesized by a facile interfacial polymerization method in which the polymerization is carried out at an organic/aqueous biphasic interface.[20,21] The microstructure of PPy hydrogel and thus its mechanical and electrochemical properties could be tuned by controlling the ratio of phytic acid to pyrrole monomers in synthetic process. The mechanically robust, microstructured conductive hydrogel enables a physical dipping of the carbon cloth into PPy slurry which can result in a conformal coating of PPy hydrogel as well as high polymer loading on carbon fibers. The solid-state supercapacitor we obtained shows a specific capacitance of ~380 F/g, excellent rate capability, and areal capacitance as high as ~6.4 F/cm^2 at mass loading of 20 mg/cm^2.

Experimental

Synthesis of PPy hydrogel and fabrication of electrodes

Conducting PPy hydrogel was synthesized by a liquid phase interfacial reaction in a solution-based approach. Similar synthesis method had been mentioned in our previous publications.[22, 23]

During polymer synthesis, 0.274 g (1.2 mmol) of ammonium persulfate (98%, Sigma Aldrich) was dissolved in 0.5 mL deionized (DI) water, and labelled as solution A. 0.084 mL pyrrole (99%, Sigma Aldrich) was mixed into 0.5 mL isopropanol alcohol (IPA), followed by the addition of 0.184 mL phytic acid (50%, wt% in water, Sigma Aldrich), and labelled as solution B. After gentle shaking, solution B will become an ivory-white mixture. The solutions were rapidly cooled to roughly 0 ℃ using dry ice to slow down the rate of reaction. Right after mixing A and B solutions, a controllable time-dependent dip of a piece of carbon cloth (24-hour surface treatment in 8 M HNO_3, 10 mm × 20mm size) into the as-synthesized PPy hydrogel solution was conducted. Electrodes were naturally dried in fume hood at room temperature and purified by immersing them in DI water and IPA for 12 hours. Afterwards, another drying step in vacuum oven was conducted for electrochemical measurements. PPy hydrogels with different pyrrole: phytic acid (Py: PA) ratios of 5:1, 10:1 and 20:1 were synthesized for further optimization and electrochemical testing..

Assembly of solid-state supercapacitors

To make a solid-state supercapacitor, two pieces of as-synthesized PPy-coated carbon cloth electrodes were assembled together with Poly(vinyl alcohol) (PVA)-H_2SO_4 electrolyte sandwiched between. The PVA-H_2SO_4 electrolyte will infiltrate into the carbon cloth after an overnight drying process.

Characterizations of PPy hydrogel and electrochemical testing of supercapacitors

Fourier transform infrared spectroscopy (FT-IR) was used to confirm the chemical structure of PPy hydrogel. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were used to characterize micro-/nano-structures of the conducting PPy hydrogel.

Electrochemical performance of conducting hydrogel based supercapacitor electrodes with various PPy mass loadings and solid-state supercapacitors were examined through electrochemical impedance spectroscopy (EIS), cyclic voltammetry (CV), cycling performance, and galvanostatic charge/discharge tests. Different active electrode mass loadings from 1.8 mg/cm^2 to 20 mg/cm^2 are studied to systematically compare their electrochemical characteristics. CV tests were done with 5, 10, 20, 50, 100 mV/s scan rates in a potential window of -0.2—0.8 V vs Ag/AgCl reference electrode (RE), and 100 mV/s scan rate between 0.0—1.0 V with decreasing radius of curvature of ∞, 8mm, and 3mm, respectively. Galvanostatic charge/discharge measurement was performed for various current densities for different mass loadings. Specific capacitance (C_s) vs current density curves as well as the cycling stability were also plotted for both asymmetric supercapacitors and symmetric supercapacitors.

Results and discussion

The chemical structure of as-synthesized PPy hydrogel was analysed by the FT-IR spectra. (**Fig. 1a**) The absorption peak at 1552.4 cm^{-1} can be assigned to the in-ring stretching of C=C bonds in the pyrrole rings and the band at 1397.4 cm^{-1} was due to the vibrations of C–H bonds. The peak at 1296.2 cm^{-1} was attributed to the C-C stretching. The in-plane deformation of C-H bond and N-H bond showed its characteristic peak at 1045.1 cm^{-1}. The formation of PPy could be confirmed by these characteristic absorption peaks.[24] The structure of PPy hydrogel was also analysed by Raman spectra (Fig. S1).

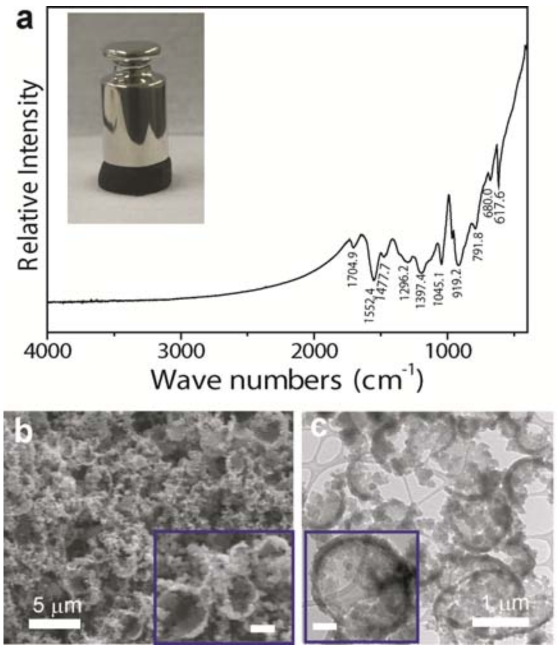

Fig. 1. Interconnected hollow sphere conducting PPy hydrogel. (a) The FT-IR spectrum of the as-synthesized conductive polypyrrole (PPy) hydrogel with peaks labelled. Inset, photograph showing a spongy PPy hydrogel sample placed under a balance weight of 100 g. (b) SEM image showing the microstructure of a piece of dehydrated hydrogel. Inset scale bar: 1 μm. (c) TEM image showing the top view. Inset, TEM image of dehydrated PPy hydrogel. Inset scale bar: 200 nm.

The inset photo in **Fig. 1a** shows the excellent mechanical property of obtained PPy hydrogel which is related to its microstructure. We used SEM and TEM to study the microstructure of our PPy hydrogel with Py: PA ratio of 10:1. SEM images (**Fig. 1b**) shows the three-dimensional porous morphology of PPy hydrogel. The foam-like microstructure is constructed by interconnected hollow spheres with diameters in range of 500 nm to 3 μm. The specific surface area of PPy hydrogel is ~36 m^2/g. Further investigation by TEM reveals that the shell thickness of PPy hollow spheres are of 50~100 nm (**Fig. 1c**). The structure of interconnected hollow spheres is induced by phytic acid which acts as crosslinkers and bi-phase synthesis. Such 3D hierarchical structures provide both large open channels between the branches and nanoscale porosities within the structure which facilitate the transport of electrons and ions. Our PPy hydrogel in dried state showed the conductivity of 0.5 S/cm when tested by four probe method. And the formation of spherical shell geometry with a structural hierarchy could overcome the inherent brittleness of PPy caused by its rigid polymer backbone consisting of sp^2 π–π bonding, thus endowing the PPy hydrogel with tunable effective elasticity which benefits the application in flexible solid-state supercapacitors.

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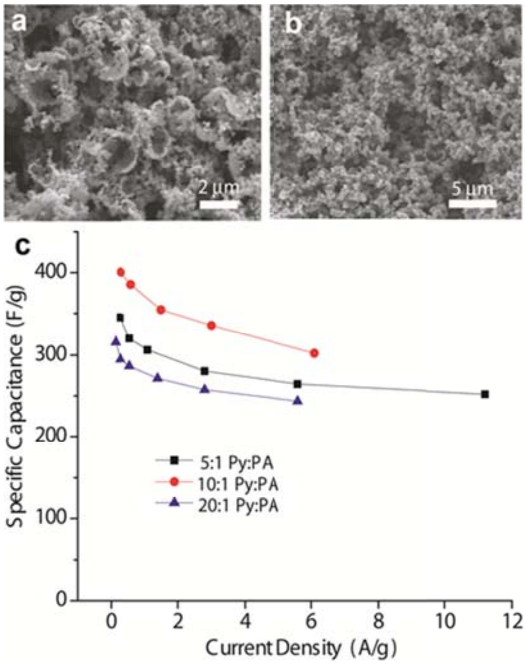

Fig. 2. Microstructures and capacitance performance of PPy hydrogels with different ratios of pyrrole (Py): phytic acid (PA). (a-b) SEM images of PPy hydrogel with Py: PA ratios of 5:1 and 10:1, respectively. (c) Specific capacitance vs current density profiles of PPy hydrogel electrodes with Py: PA ratios of 5:1, 10:1, and 20:1.

The microstructure of the PPy hydrogel could be tuned by adjusting the ratio of Py to PA. **Fig. 2a-b** shows the SEM characterizations of the microstructures of PPy hydrogel synthesized with Py: PA ratios of 5:1 and 20:1, respectively. It can be clearly seen from **Fig. 2a** that the PPy hollow spherical structures are actually dominant in PPy hydrogel with the Py:PA ratio of 5:1. Under higher Py: PA ratio of 20:1, *i.e.* lower concentration of crosslinker PA, PPy hollow spheres disappear but particle-like PPy dominate, which assemble into a hierarchically porous network structure. The electrochemical properties of PPy hydrogel electrode were in turn tuned with varying microstructures. **Fig. 2c** shows the summary plots of specific capacitance values for electrodes based on three different PPy samples at a series of current densities. It is observed that the one with medium PA content has the best capacitive performance compared to the other two at all current density. This could be explained by the following reasons. In the hollow spheres dominated hydrogel, although the broken hollow spheres can facilitate rapid ion/mass transport, big pore sizes could also decrease the specific active surface area of PPy hydrogel electrodes, resulting in a lower capacitance. As the ratio of Py: PA increases, the structures of resulting PPy transition from interconnected microstructured hollow spheres to smaller plate-like particles, which offers more 3D porous hierarchical nanostructure, but at expense of decreasing electronic conductivities (less crosslinking due to lower concentration of phytic acid). The competing factors of surface area, porosity and electronic conductivity of as-synthesized hydrogel material, lead to adjustable electrochemical performances of hydrogel based electrodes. In this work, we choose the PPy hydrogel electrodes synthesized with 5:1 Py: PA to further investigate the capacitive properties of PPy hydrogel with different mass loading.

To evaluate the electrochemical performance of 3D nanostructured PPy hydrogels as supercapacitor electrodes, we performed EIS, CV, and galvanostatic charge-discharge measurements in a conventional three-electrode system. **Fig. 3a** shows the EIS curves of PPy hydrogel based electrodes measured in a 1 M H_2SO_4 electrolyte with different PPy mass loadings: 1.8 mg/cm^2, 7.2 mg/cm^2 and 20 mg/cm^2. The small semicircles in higher frequency range indicate very small charge transfer

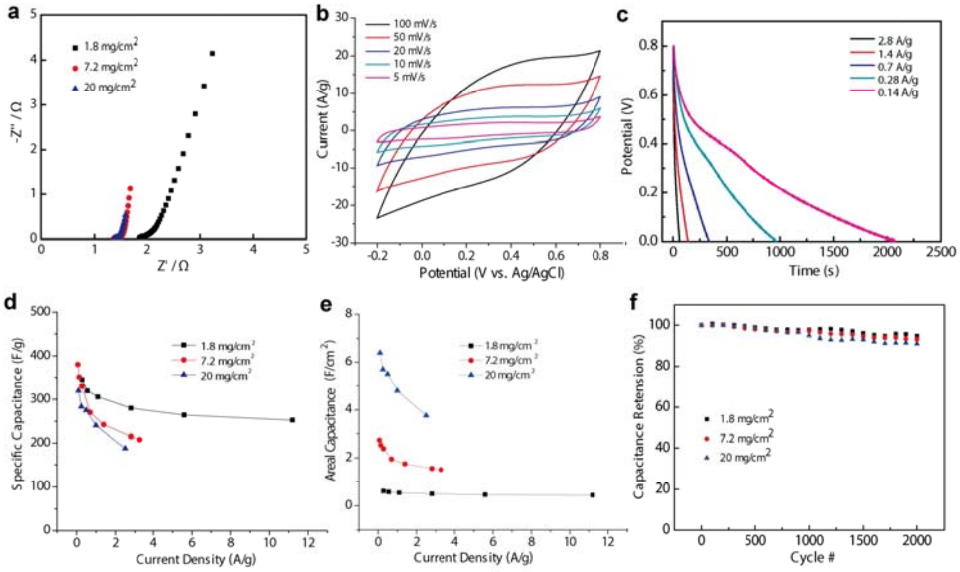

Fig. 3. Electrochemical performance of the PPy hydrogel based electrodes. (a) EIS curves of PPy electrodes with active material loadings of 1.8, 7.2 and 20 mg/cm^2. (b) Cyclic voltammograms of PPy electrode (7.2 mg/cm^2) at various scan rates of 5−100 mV/s. (c) Representative galvanostatic discharge curves of PPy electrodes at different current densities of 0.14−2.8 A/g. (d) Specific capacitance versus current density for PPy electrodes with different material loadings. (e) Corresponding areal capacitance versus current density with different active material. (f) Cycling performance of PPy hydrogel based electrodes with various active material loadings at current density of ~2.8 A/g.

resistance in electrode systems. Approximately vertical EIS curve tails in lower frequency range indicate nearly ideal capacitive behaviour. **Fig. 3b** exhibits the rate-dependent CV curves of the PPy hydrogel based supercapacitor electrodes. The current densities increase along with increasing scan rates, suggesting good rate performance. **Fig. 3c** shows the discharge profiles of the PPy hydrogel electrode at current densities of 0.14, 0.28, 0.7, 1.4, and 2.8 A/g, respectively. Specific capacitance vs current density profiles at various current densities (**Fig. 3d**) are compared for the hydrogel based electrodes with different active mass loadings of 1.8, 7.2, and 20 mg/cm^2. Specific capacitances as high as 300-400 F/g were achieved for all three samples at the low current density of ~0.2 A/g, revealing excellent capacitive performance even at relatively high mass loadings. Corresponding data were also shown in form of areal capacitance vs current density in **Fig. 3e**. Area-normalized capacitance values are significantly improved compared to previous reports.[25] The volumetric capacitance versus current density of PPy electrode with mass loading of 1.8 mg/cm^2 was showed in Fig. S2. To the best of our knowledge, this is among the best performance that has ever been reported in literatures for supercapacitors using conducting polymers as active electrode materials. In addition, cycle life is another criterion for evaluating supercapacitor performance. **Fig. 3f** shows the excellent cycling stability of the PPy hydrogel electrodes at current density of 2.8 A/g. After 2000 cycles, the capacitance degradations were less than 7% for all three samples. The exceptional performance could be attributed to the following reasons. Firstly, the synthesized conducting polymer hydrogel has an intrinsically good electric conductivity along the polymer backbones, providing a 3D continuous pathway for electron transport. The highly integrated conductive backbone of PPy hydrogel electrode ensures good electrochemical performance for supercapacitors. Secondly, PPy hydrogel electrode has micro-/nano- porous structures. The interspatial porosity offered by ruptured PPy hollow spheres allows fast ionic migration betwen the aqueous electrolyte and the electrode, favouring rapid adsorption/desorption redox process. Although PPy hydrogel layer will thicken proportionally with an increasing mass loading, its porous structure can be maintained by its structure-derived elasticity and support high-rate behavior of the supercapacitors, thus achieving excellent areal capacitance (F/cm^2) which is more important in practical utilities. Also, the hydrophilic property of PPy hydrogel can ensure a thorough wetting of the electrode by aqueous electrolyte. Moreover, the unique hydrogel viscosity provides good affinity to the carbon cloth fibers. No obvious active material peeling off from the carbon cloth substrate was observed during electrochemical tests. Most importantly, the rapidly charged/discharged redox-active sites incorporated on the polymer matrix can increase the overall capacitance of the supercapacitor under fast cycling rates.[26]

To pursue a highly flexible energy storage device, we assembled two pieces of dry PPy hydrogel electrodes sandwiched with a PVA-H_2SO_4 gel-like electrolyte to make an all-solid-state supercapacitor, as schematically illustrated in inset of **Fig. 4a**. The PVA-H_2SO_4 electrolyte is of high viscosity and environmentally stable under ambient conditions.[25] Also, PVA-H_2SO_4 electrolyte can permeate through the electrode materials due to the 3D porous structure of PPy hydrogel, ensuring a well wetted electrolytic environment for the electrodes.

A series of electrochemical measurements were carried out to examine the electrochemical properties of the flexible supercapacitor. **Fig. 4a** shows the EIS curve of the PPy hydrogel based flexible supercapacitor. The small semicircle on the real axis in the higher frequency range indicates good ionic conductivity of the PVA-H_2SO_4 electrolyte based supercapacitor. The nearly vertical tail in lower frequency range also implies ideal capacitive property of the all-solid-state supercapacitor.

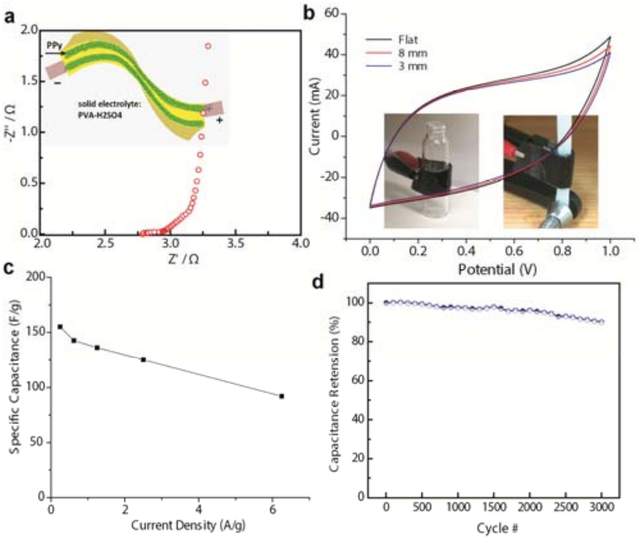

Fig. 4. Electrochemical characteristics of flexible PPy hydrogel based supercapacitors. (a) EIS curve of a full cell based on symmetric electrodes. Inset, schematic of the makeup of the flexible supercapacitor. (b) CV curves of the fabricated supercapacitor under different bending conditions at scan rate of 100 mV/s. (c) Specific capacitance of full cell as a function of current densities. (d) Cycling performance over 3000 charge-discharge cycles under bending curvature of 3 mm.

To study its capacitive properties under bending conditions (with radius of curvatures of ∞ (flat), 8 mm, and 3mm), CV data in potential window of 0.0−1.0 V vs Ag/AgCl at scan rate of 100 mV/ are plotted in **Fig. 4b**. The encircled areas in the closed CV curves remain almost the same (less than 3% decrease) as the curvature of the supercapacitor increases. Even at highly bended status, the capacitance change is still negligible compared to that of a flat one. This can be attributed to the mechanical flexibility of the sponge-like PPy network, which is composed of crosslinked PPy hollow nanospheres. The porous space enclosed in PPy network will largely accommodate the deformation of PPy backbone during bending. Insets in **Fig. 4b** show the flexible solid-state supercapacitor in testing with different bending curvatures. Radii of curvature of the samples are 8 mm and 3 mm on the left and right, respectively. To test the flexibility-related rate performance of PPy hydrogel based solid-state supercapacitor, we carried out galvanostatic charge/discharge tests at various current densities. Specific capacitance was calculated and plotted vs current density in **Fig. 4c**. The specific capacitance retains ~81% and ~61% of the initial value when current density is increased by ~10× and ~25×, respectively. Cycling performance was further tested for the flexible solid-state supercapacitor by 3000 charge/discharge electrochemical cycles in the potential range of 0.0−1.0 V vs Ag/AgCl. A capacitance

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retention of ~90% was finally achieved, indicating good electrochemical stability and cyclability of the assembled supercapacitor device.

Conclusion

In summary, we developed a facile and scalable synthesis route for conductive PPy hydrogel with tunable 3D microstructures as electroactive materials for high-performance flexible solid-state supercapacitors. Flexible symmetric PPy hydrogel supercapacitors were also fabricated using PVA-H_2SO_4 as the electrolyte, and demonstrated promising capacitive properties and good electrochemical stability during long-term cycling. Even with high PPy loading and at bending/folding states, the electrodes can still offer good rate capabilities and high specific capacitance. The combination of excellent electrochemical performance with mechanical flexibility is based on: (1) intrinsically good conductivity of PPy hydrogel, (2) 3D hierarchical porous structure enabling fast charge carrier transfer during electrochemical processes, (3) strong adhesion between PPy hydrogel and carbon cloth substrate, (4) structure-derived good mechanical property of hydrogel itself. The structure-controlled conductive hydrogels with tunable electrochemical properties and mechanical flexibility represent a promising material platform for emerging flexible energy storage devices.

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Notes and references

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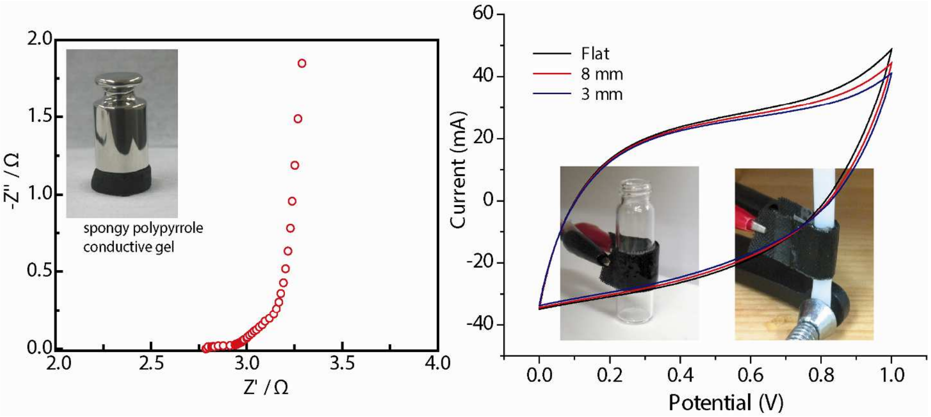
A spongy polypyrrole based conductive hydrogel with chemically tunable structures and electrochemical characteristics was developed for highly flexible solid-state supercapcitors.



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