

Electrochemical capacitance performance of polypyrrole–titania nanotube hybrid

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Abstract In this study, the polypyrrole–titania nanotube hybrid has been synthesized for an electrochemical supercapacitor application. The highly ordered and independent titania nanotube array is fabricated by an electro-oxidation of titanium sheet through an electrochemical anodization process in an aqueous solution containing ammonium fluoride, phosphoric acid and ethylene glycol. The polypyrrole–titania nanotube hybrid is then prepared by electrodepositing the conducting polypyrrole into well-aligned titania nanotubes through a normal pulse voltammetry deposition process in an organic acetonitrile solution containing pyrrole monomer and lithium perchlorate. The morphology and microstructure of polypyrrole–titania nanotube hybrid are characterized by scanning electron microscopy, infrared spectroscopy and Raman spectroscopy. The electrochemical capacitance performance is determined by cyclic voltammetry and charge/discharge measurement. It indicates that the polypyrrole film can be uniformly deposited on both surfaces of titania nanotube walls, demonstrating a heterogeneous coaxial nanotube structure. The specific capacitance of polypyrrole–titania nanotube hybrid is determined to be 179 F g^{-1} based on the polypyrrole mass. The specific energy and specific power are 7.8 Wh kg^{-1} and 2.8 kW kg^{-1} at a constant charge/discharge current of 1.85 mA cm^{-2} , respectively. The retained specific capacitance still keeps 85% of the initial capacity even after 200 cycle numbers.

This result demonstrates the satisfying stability and durability of PPy–TiO₂ nanotube hybrid electrode in a cyclic charge/discharge process. Such a composite electrode material with highly ordered and coaxial nanotube hybrid structure can contribute high energy storage for supercapacitor applications.

Keywords Polypyrrole · Titania · Nanotube hybrid · Electrodeposition · Supercapacitor

Introduction

Electrochemical supercapacitors are attracting much interest on account of their high specific capacitance in energy storage [1, 2]. It is known that the general electrode materials used in supercapacitors are porous carbon materials, transition metal oxides and conducting polymers [3–5]. Porous carbon materials show a low electrochemical double-layer capacitance. Some noble metal oxides, such as hydrous ruthenium dioxide, contribute very high electrochemical Faradic capacitance. However, the high cost of these noble metals limits their application. In recent years, electronically conducting polymers have been considered as one of the most promising supercapacitor electrode materials because of its low cost, good environmental stability, easy synthesis and high electrical conductivity [4, 6]. Various nanocomposites based on conducting polymers have been synthesized for energy storage [7, 8]. Herein, the conducting polypyrrole (PPy) with well-designed nanostructure and high surface area can be regarded as suitable electrode materials of electrochemical supercapacitors [9]. The highly ordered titania (TiO₂) nanotube array can be applied as a substrate material of electrodes owing to its high surface area and chemical/electrochemical stability [10, 11]. The

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well-aligned TiO₂ nanotube array with the controlled morphologies can be fully fabricated by an electrochemical anodization method. The conducting polymer/metal oxide nanocomposites can be prepared by either wet chemical or electrochemical synthesis method [12–15].

In this study, an electrochemical deposition method is adopted to prepare polypyrrole–titania (PPy–TiO₂) nanotube hybrid based on the substrate of TiO₂ nanotubes [16]. This kind of PPy–TiO₂ can supply highly ordered nanopore structure to promote a short diffusion path for reactive ions and then improve electron transfer effectiveness in a reversible redox reaction, consequently resulting in a high capacitance performance in a continuous charge/discharge process.

Experimental

Synthesis of PPy–TiO₂ nanotube hybrid

PPy–TiO₂ nanotube hybrid was prepared through an electrochemical synthesis route. Firstly, TiO₂ nanotube array was directly formed on Ti sheet by a potentiostatic anodization process at 30 V for 2 h in water and ethylene glycol mixture solution (volume ratio, 50/50) containing 0.2 M ammonium fluoride and 0.5 M phosphoric acid. A calcination treatment at 450 °C for 2 h was used for crystallization of TiO₂ nanotube array from amorphous phase to anatase phase. Then, a normal pulse voltammetry deposition method was adopted to prepare PPy–TiO₂ nanotube hybrid in a three-electrode system using TiO₂/Ti as a working electrode, Pt as a counter electrode and Hg/Hg₂Cl₂ as a reference electrode in an organic acetonitrile solution containing 0.15 M pyrrole monomer and 0.1 M lithium perchlorate (LiClO₄) supporting electrolyte. The pulse potential was increased from 0.7 to 1.1 V with a pulse potential increment of 0.004 V. The pulse width is 0.06 s and the pulse period is 20 s. As-formed PPy–TiO₂ was repeatedly washed with deionized water and finally dried at room temperature. Additionally, Fig. 1a shows the applied pulse potential curve in the pulse voltammetry deposition process. Since the electropolymerization reaction is a kinetics-controlled process, a very short pulse width of 0.06 s and much long pulse period of 20 s have been applied for this electrochemical synthesis reaction. It is believed that this applied pulse potential can benefit a sufficient molecule diffusion of pyrrole monomer. Figure 1b shows the responding current curve when synthesizing PPy–TiO₂ nanotube hybrid. The current increment is only 1.125 nA when the initial electrode potential increases from 0.7 to 0.85 V. Actually, the electrochemical polymerization reaction of pyrrole monomer occurs predominately at an anodic potential above 8.0 V vs. saturated calomel electrode (SCE). The current response is very low in this initial reaction period. A quick enhancement of current

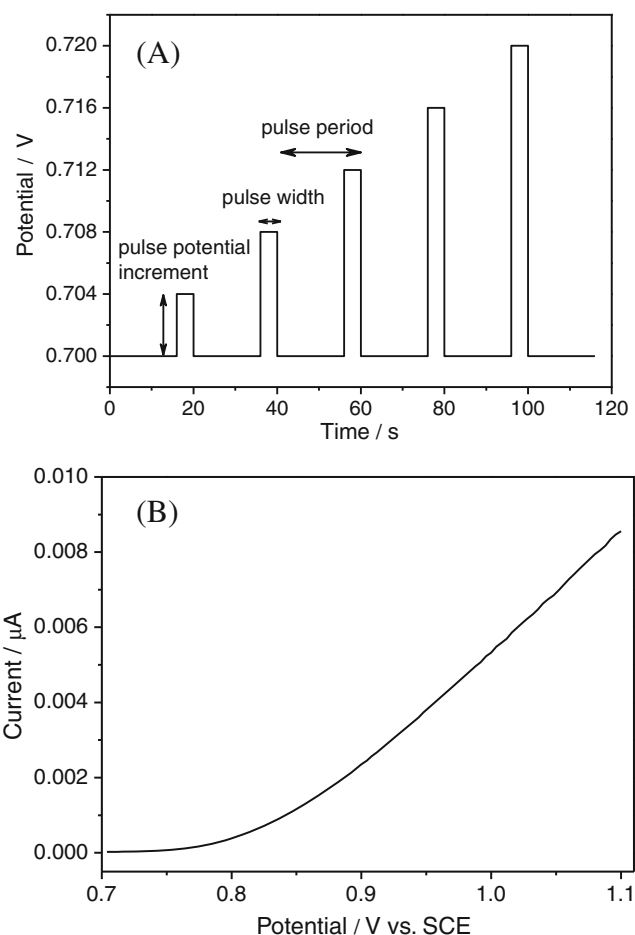


Fig. 1 (A) The applied pulse potential curve and (B) the responding current curve in a normal pulse voltammetry deposition process to synthesize PPy–TiO₂ nanotube hybrid

response can be then achieved when the electrode potential is further raised from 8.5 to 1.1 V. It indicates that the specific resistance of as-formed PPy–TiO₂ gradually decreases along with the continual deposition of polypyrrole on TiO₂ nanotube array. Therefore, the electroactive PPy has been well formed on the substrate of TiO₂ nanotube array in this normal pulse voltammetry deposition process, which can well promote the electrical conductivity of TiO₂ substrate. Therefore, PPy–TiO₂ nanotube hybrid can act well as a conducting electrode material for supercapacitor applications.

Characterization and electrochemical measurement of PPy–TiO₂ nanotube hybrid

The surface morphology and microstructure of bare TiO₂ nanotube array and PPy–TiO₂ nanotube hybrid were investigated using scan electron microscopy (SEM, Hitachi S-3000, Japan). To identify the chemical structure of TiO₂ nanotube array and PPy–TiO₂ nanotube hybrid, Infrared spectroscopy was performed using Fourier transform infrared spectrometer (FTIR, NICOLET-5700, USA) in the range

of 400–4,000 cm^{-1} . Moreover, Raman spectroscopy was performed using Raman spectrometer (Raman, Renishaw Invia Reflex System, UK) in the range of 0–2,000 cm^{-1} . This device was equipped with a He–Ne laser beam operating at a wavelength of 785 nm. The cyclic voltammetry measurement was carried out using an electrochemical workstation (CHI760C, CH Instruments, USA) in 1.0 M H_2SO_4 electrolyte solution. A conventional three-electrode system was established using Pt sheet as a counter electrode, KCl-saturated calomel electrode as a reference electrode and PPy–TiO₂ nanotube hybrid as a working electrode. The galvanostatic charge/discharge measurements were conducted in 1.0 M H_2SO_4 electrolyte solution under a controlled current density, potential window and charge/discharge time by using a charge/discharge testing system (IM6e ZAHNER Elektrik, Germany).

Results and discussion

Morphology characterization

The scanning electron microscopy was used to characterize microstructure of TiO₂ nanotube array and PPy–TiO₂ nanotube hybrid. SEM images of bare TiO₂ nanotube array are shown in Fig. 2. Obviously, each nanotube has its own wall and is separated from each other. The inner diameter of TiO₂ nanotubes is 120–150 nm and the wall thickness is 10–20 nm. The interspace between the neighboring tubes is 35–60 nm. The total length of TiO₂ nanotubes is approximate 800–950 nm. Highly ordered and vertically oriented TiO₂ nanotube array offers a high surface area of nanotube walls without a concomitant decrease in geometric and structural order. Such an independent nanotube structure is beneficial to deposit the polypyrrole inside these tubes and in the interspace between these tube walls. It is helpful to fill these TiO₂ nanotubes with more conducting polymers.

SEM images of PPy–TiO₂ nanotube hybrid are shown in Fig. 3. Obviously, the PPy–TiO₂ exhibits an ordered array and heterogeneous coaxial nanotube structure. The tube mouths still keep open. However, all these tube walls are inclined to bond together. The nanotube wall thickness increases up to 50–80 nm after PPy is loaded into TiO₂ nanotubes. The nanotube inner diameter is 30–90 nm. The total length is 920–1,020 nm, which is close to or a little higher than the length of bare TiO₂ nanotubes. It indicates that PPy has been mostly encapsulated inside TiO₂ nanotubes rather than outside that. The controlled electropolymerization process becomes a feasible approach to deposit PPy on both surfaces of TiO₂ nanotube walls to form PPy–TiO₂ nanotube hybrid. It is believed that such an ordered and coaxial nanotube structure contributes highly effective interface area to shorten the ion diffusion path and

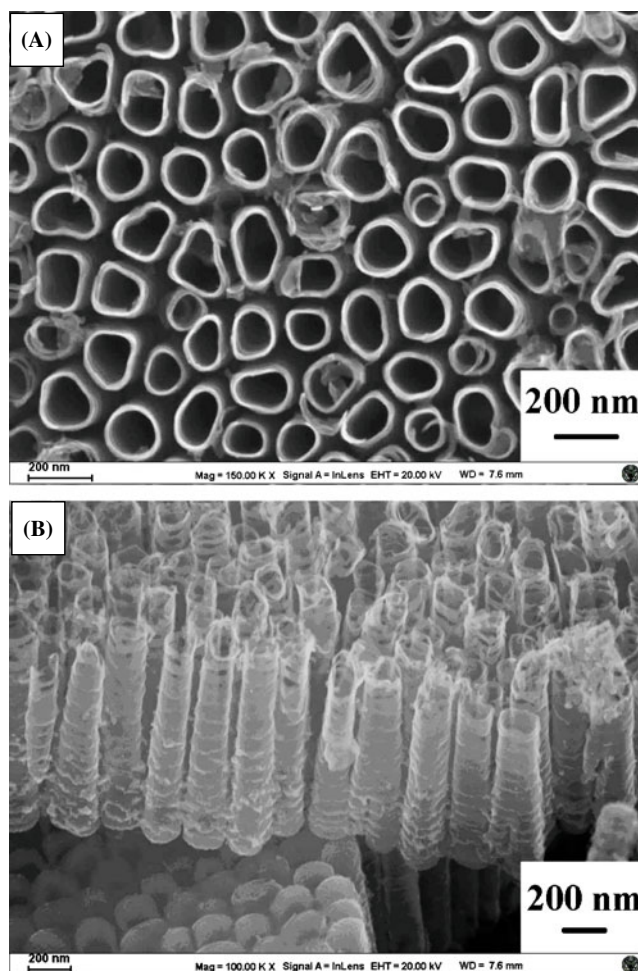


Fig. 2 SEM images of (A) top surface view and (B) cross-section view of TiO₂ nanotube array

electron transfer path, consequently improving the electrochemical capacitance performance.

FTIR spectroscopy analysis

FTIR spectroscopy measurement is carried out for the determination of the PPy electrodeposition on TiO₂ nanotube array. The FTIR spectra of TiO₂, PPy and TiO₂–PPy have been analysed and discussed in detail, which are shown in Fig. 4.

Regarding the FTIR spectrum of TiO₂ nanotube array (see curve A), both the strong characteristic peak at 681 cm^{-1} and the weak peak at 798 cm^{-1} are ascribed to Ti–O stretching vibration. Concerning the FTIR spectra of bare PPy film and PPy–TiO₂ nanotube hybrid (see curve B and C), the absorption bands at 1,577 cm^{-1} of PPy and 1,540 cm^{-1} of PPy–TiO₂ are assigned to C=C antisymmetric/symmetric stretching vibration in the pyrrole ring. The absorption bands at 1,424 cm^{-1} of PPy and 1,480 cm^{-1} of PPy–TiO₂ are assigned to C–C stretching vibration. The

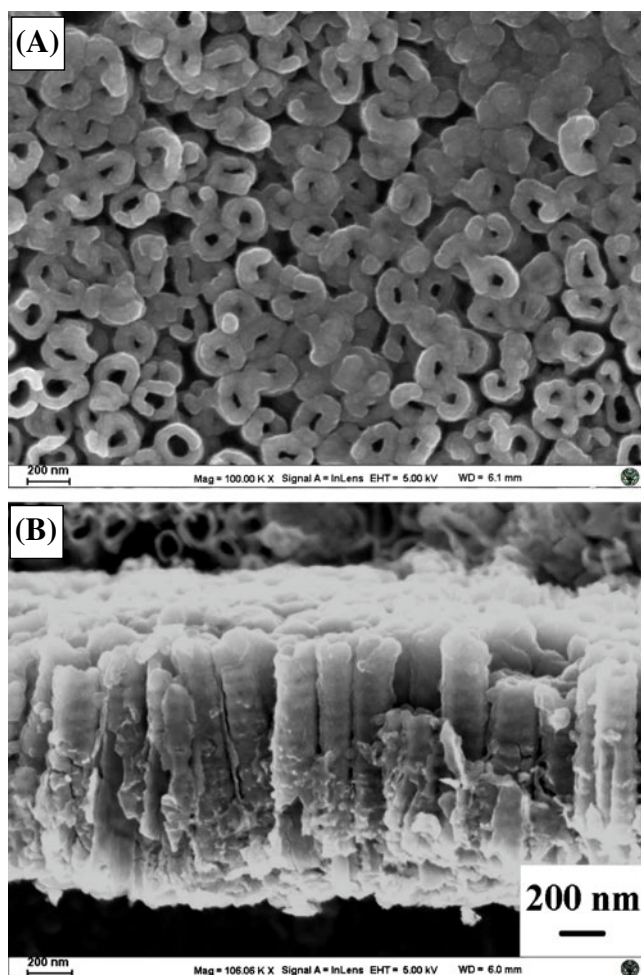


Fig. 3 SEM images of (A) top surface view and (B) cross-section view of PPy-TiO₂ nanotube hybrid prepared by a normal pulse voltammetry deposition method

absorption bands at 1,040 cm⁻¹ of two samples are assigned to C-H and N-H in-plane deformation vibration. The absorption bands at both 1,290, 1,212 cm⁻¹ of PPy and 1,288, 1,190 cm⁻¹ of PPy-TiO₂ are all assigned to C-N stretching vibration in the pyrrole ring. The bands at 920, 766 and

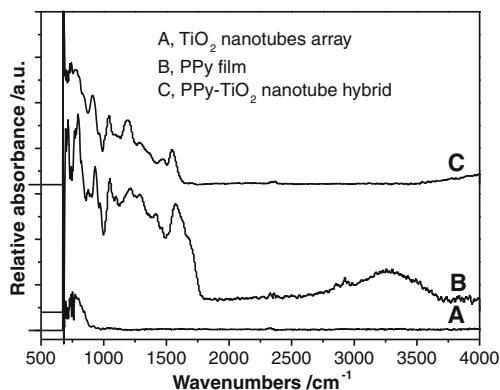


Fig. 4 FTIR spectra of (A) TiO₂ nanotube array, (B) PPy film and (C) PPy-TiO₂ nanotube hybrid

675 cm⁻¹ are assigned to C-H in-plane and out-of-plane vibration. Additionally, the broad absorption band at 3,000–3,500 cm⁻¹ of PPy film is attributed to N-H and C-H stretching vibration of polypyrrole [13, 17, 18]. Comparatively, both PPy and PPy-TiO₂ samples have similar characteristic absorption bands. It proves that PPy has been fully coated on TiO₂ nanotubes to form PPy-TiO₂ nanotube hybrid.

Raman spectroscopy analysis

Raman spectroscopy measurement is also carried out for TiO₂ nanotube array, PPy film and PPy-TiO₂ nanotube hybrid to confirm the electrodeposition effect of the conducting polymer of PPy. The corresponding Raman spectra of TiO₂, PPy and TiO₂-PPy are shown in Fig. 5.

Regarding the Raman spectrum of TiO₂ nanotube array (see curve A), two characteristic peaks at around 147 and 640 cm⁻¹ are ascribed to O-Ti-O symmetric deformation vibration and Ti-O stretching vibration, respectively. Regarding the Raman spectra of bare PPy film and PPy-TiO₂ nanotube hybrid (see curve B and C), both samples have similar characteristic absorption peaks. Obviously, the strong absorption peak at 1,598 cm⁻¹ is ascribed to C=C stretching vibration. The absorption peaks at 1,470 and 1,376 cm⁻¹ are assigned to C-C and C-N stretching vibration, respectively. The absorption peak at 1,242 cm⁻¹ is caused by C-H in-plane bending vibration. The absorption peaks at 1,087 and 936 cm⁻¹ are owed to C-H ring deformation vibration [17, 18]. The determination of characteristic peaks of C=C double bond and C-N single bond structure have proven the formation of PPy film supported on TiO₂ nanotube array through an electro-polymerization deposition process.

In general, the incompatibility of conducting polymer/TiO₂ heterojunction causes a poor connection using a physical interface adsorption. The bifunctional anchoring molecules or functional polymers with hydroxylic groups are

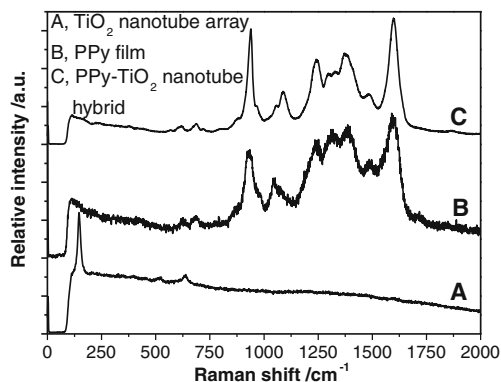


Fig. 5 Raman spectra of (A) TiO₂ nanotube array, (B) PPy film and (C) PPy-TiO₂ nanotube hybrid

usually applied to form a strong chemical bond connection between TiO_2 and PPy. On the base of above FTIR and Raman spectrum analysis, the characteristic absorption peaks of TiO_2 -PPy nanotube hybrid are very similar to that of PPy film. Other new characteristic peaks assigned to new chemical groups bonding PPy and TiO_2 are not observed at all. Herein, PPy film could fully coat on the both surfaces of TiO_2 nanotube walls. Considering the absence of bifunctional anchoring molecules and functional groups of polymer molecules to connect TiO_2 and PPy using chemical bonds, the interaction between PPy film and TiO_2 nanotube array is mostly ascribed to a physical linking rather than a chemical bonding [19, 20].

Electrochemical measurement

The cyclic voltammetry measurement of TiO_2 nanotube array and PPy- TiO_2 nanotube hybrid electrodes has been carried out to investigate the electrochemical reaction properties. The cyclic voltammetry curve of TiO_2 nanotube array exhibits a symmetrical characteristic at the axis of zero current, and do not shows any redox peak in the applied potential range of 0–0.6 V vs SCE (see Fig. 6a). Figure 6b shows a cyclic voltammetry curve of PPy- TiO_2 nanotube hybrid electrode. The reduction reaction peak occurring at 0.25 V vs SCE is ascribed to the insertion of protons into

PPy in an acidic H_2SO_4 electrolyte solution. The de-insertion of protons from the doped PPy occurs at the potential of 0.4–0.6 V. Comparatively, the reduction peak at 0.25 V vs SCE do not appear in a neutral Na_2SO_4 electrolyte solution. This characteristic peak at 0.25 V vs SCE is observed again when H_2SO_4 is added into Na_2SO_4 electrolyte solution (this result is not shown here.). Therefore, the revisable redox reaction of PPy- TiO_2 nanotube hybrid must have been involved in H_2SO_4 electrolyte solution, which represents the doping and de-doping process of hydrogen ion on PPy. Therefore, TiO_2 nanotube array can only contribute an electric double-layer capacitance in supercapacitor applications. However, the PPy- TiO_2 nanotube hybrid can well conduct a highly reversible redox reaction to contribute an electrochemical Faradic capacitance.

The galvanostatic charge/discharge measurement of TiO_2 nanotube array and PPy- TiO_2 nanotube hybrid electrodes has been carried out in 1.0 M H_2SO_4 solution to investigate the electrochemical capacitance performance [10, 21]. The charge/discharge curves are showed in Fig. 7. Their specific capacitance (C), specific energy (E) and specific power (P) can be calculated according to the following equations.

$$C = (I \times \Delta t) / (\Delta V \times m) \quad (1)$$

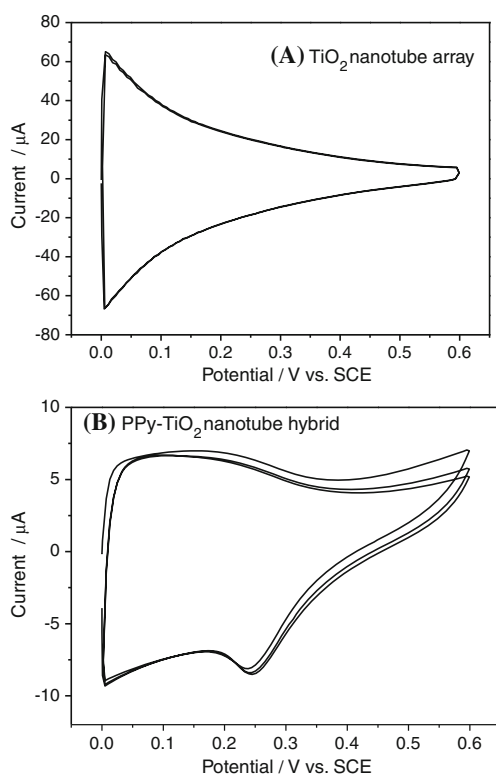


Fig. 6 Cyclic voltammetry curves of (A) TiO_2 nanotube array and (B) PPy- TiO_2 nanotube hybrid testing in 1.0 M H_2SO_4 electrolyte solution at a scan rate of 20 mV s^{-1}

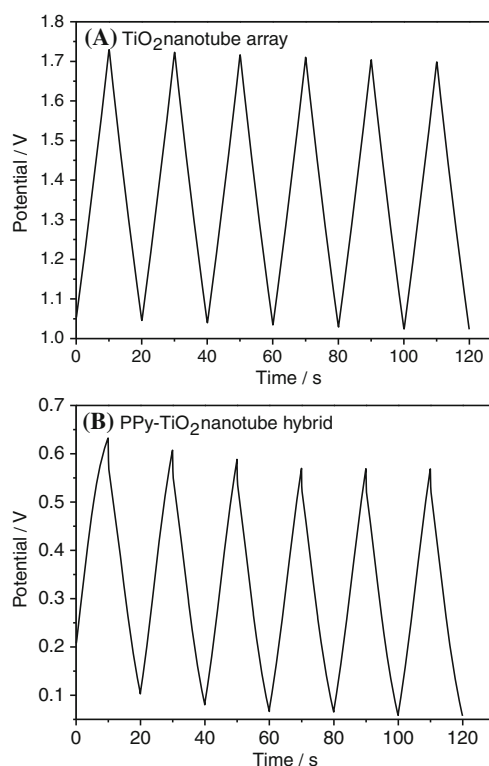


Fig. 7 Galvanostatic charge/discharge curves of (A) TiO_2 nanotube array testing at $30 \mu\text{A cm}^{-2}$ and (B) PPy- TiO_2 nanotube hybrid testing at 1.85 mA cm^{-2} in 1.0 M H_2SO_4 electrolyte solution

$$E = (I \times \Delta V \times \Delta t) / 2m = \left[C \times (\Delta V)^2 \right] / 2 \quad (2)$$

$$P = (I \times \Delta V) / 2m \quad (3)$$

Where I , Δt , ΔV and m denote the charge/discharge current, charge/discharge time, potential window and the active material mass of PPy or the apparent area of PPy–TiO₂ nanotube hybrid electrode, respectively.

According to the galvanostatic charge/discharge curves as shown in Fig. 7, the electric double-layer capacitance of TiO₂ nanotube array is determined to be 0.4524 mF cm⁻² when testing at a constant current of 30 μ A cm⁻². Comparatively, the electrochemical Faradic capacitance of PPy–TiO₂ nanotube hybrid is determined to be 33.1 mF cm⁻² when testing at a constant current density of 1.85 mA cm⁻². Obviously, a significant improvement of electrochemical capacitance has been achieved for TiO₂ nanotube array through PPy modification. Moreover, on the basis of the loading mass of PPy on TiO₂ nanotube array, the specific capacitance of PPy–TiO₂ hybrid is determined to be 179 Fg⁻¹. The specific power and specific energy of PPy–TiO₂ nanotube hybrid are accordingly determined to be 7.8 Wh kg⁻¹ and 2.8 kW kg⁻¹, respectively. This PPy–TiO₂ electrode material can keep a high-energy density. Meanwhile, its power density is even close to that of the conventional carbon electrode material. It is believed that the fast redox reaction is likely to occur in the charge/discharge process. The above results indicate that PPy–TiO₂ nanotube hybrid can act well as a superior electrode material for supercapacitor applications. The highly ordered TiO₂ nanotube array provides high surface area and excellent tubular channels. The well-designed PPy–TiO₂ keeps an ordered and coaxial nanotube hybrid structure, which contributes a short diffusion path of reactive ions in the electrolyte solution and effective electron transfer path along with the space charge layer of tube walls. The fast and reversible redox reaction is probably achieved in a cyclic charge/discharge process. Consequently, a high electrochemical capacitance performance has been obtained for PPy–TiO₂ nanotube hybrid acting as supercapacitor electrode material.

The electrochemical stability of the electrode interface is of high importance for the supercapacitor system. Herein, the specific capacitance performance is analysed and discussed to evaluate the electrochemical stability of PPy–TiO₂ nanotube hybrid electrode in a cyclic charge/discharge process. The specific capacitances performance with respect to the charge/discharge cycle numbers is measured as shown in Fig. 8. The specific capacitance of PPy–TiO₂ nanotube hybrid electrode declines obviously from 179 to 160 Fg⁻¹ during the first 100 cycles, presenting 89% retention of

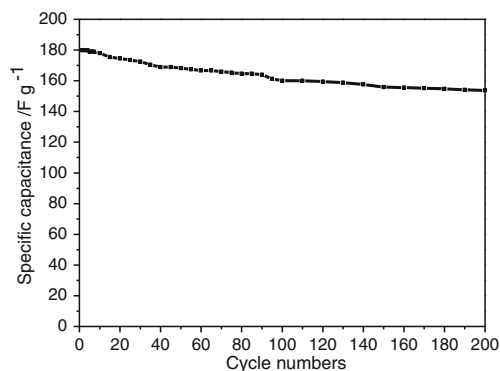


Fig. 8 Specific capacitance performance of PPy–TiO₂ nanotube hybrid with respect to cycle numbers

initial capacity. We believe that the capacitance decay during the initial charge/discharge cycles is related to the segmental detachment of PPy layer from the top surface of TiO₂ nanotubes. The retained specific capacitance still keeps 85% of the initial capacity even after 200 cycle numbers. It is noteworthy that the PPy–TiO₂ electrode material exhibits the satisfying stability and durability in a cyclic charge/discharge process. Such a cyclic stability also indicates that the coaxial nanotube strategy of PPy layer coating on TiO₂ nanotube walls is a feasible way for the advanced supercapacitor electrode application.

Conclusions

The PPy–TiO₂ nanotube hybrid has been fabricated by the controlled electrochemical synthesis route for the application of supercapacitor electrode material. The conducting PPy can be well incorporated into well-aligned TiO₂ nanotube array through a normal pulse voltammetry deposition method. The obtained PPy–TiO₂ has a highly ordered and coaxial nanotube structure. Such a nanostructure with a high surface area and tubular channels contributes a short diffusion path and effective electron transfer path, leading to the promoted reversible redox reaction in a charge/discharge process. The specific capacitance of PPy–TiO₂ nanotube hybrid is 179 Fg⁻¹ in 1.0 M H₂SO₄ electrolyte solution. The corresponding specific power and specific energy are 7.8 Wh kg⁻¹ and 2.8 kW kg⁻¹, respectively.

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