**α-Fe₂O₃@PANI Core–Shell Nanowire Arrays as Negative Electrodes for Asymmetric Supercapacitors**

Xue-Feng Lu, Xiao-Yan Chen, Wen Zhou, Ye-Xiang Tong, and Gao-Ren Li*

MOE Laboratory of Bioinorganic and Synthetic Chemistry, KLGHEI of Environment and Energy Chemistry, School of Chemistry and Chemical Engineering, Sun Yat-sen University, Guangzhou 510275, China

Supporting Information

**ABSTRACT:** Highly ordered three-dimensional α-Fe₂O₃@PANI core–shell nanowire arrays with enhanced specific areal capacity and rate performance are fabricated by a simple and cost-effective electrodeposition method. The α-Fe₂O₃@PANI core–shell nanowire arrays provide a large reaction surface area, fast ion and electron transfer, and good structure stability, which all are beneficial for improving the electrochemical performance.

Here, high-performance asymmetric supercapacitors (ASCs) are designed using α-Fe₂O₃@PANI core–shell nanowire arrays as anode and PANI nanorods grown on carbon cloth as cathode, and they display a high volumetric capacitance of 2.02 mF/cm³ based on the volume of device, a high energy density of 0.35 mWh/cm³ at a power density of 120.51 mW/cm³, and very good cycling stability with capacitance retention of 95.77% after 10,000 cycles. These findings will promote the application of α-Fe₂O₃@PANI core–shell nanowire arrays as advanced negative electrodes for ASCs.

**KEYWORDS:** α-Fe₂O₃@PANI, hybrid, core–shell nanowire, negative electrode, supercapacitor

1. **INTRODUCTION**

Supercapacitors have mainly been employed as energy sources for back-up power devices, hybrid electronic vehicles, and renewable energy systems due to their high power density, long cycling life, safety, and low maintenance costs. However, in order to meet the increasing energy density demands for next-generation electronic devices, the energy density of supercapacitor electrodes needs to be further improved. Compared with symmetric supercapacitors (SCCs), the asymmetric supercapacitors (ASCs) demonstrate better performance because of their much wider voltage windows and thus the increased energy density. The ASC devices typically consist of a cathode as the energy source and an anode as the power source. Due to their large surface area, excellent electrical conductivity, and outstanding stability, carbon-based materials have been widely used as anodes for ASCs. However, the low specific capacitance (C_{sp}) of carbon materials severely limits the energy density of ASCs according to the equation of 1/C = 1/C_{an} + 1/C_{cat} (C_{an} capacitance of anode; C_{cat} capacitance of cathode).

In order to improve the energy density of ASCs, it is highly desirable to explore new anode materials with high capacitance and conductivity. In this regard, some new negative electrodes, such as MoO₃, Fe₂O₃, and some metal nitrides, have been developed for ASCs. Among these negative electrodes, hematite (α-Fe₂O₃) holds great promise for ASCs because of its high theoretical C_{sp} suitable potential window, low cost, abundance, and nontoxicity. However, due to its poor electrical conductivity, its electrochemical performance is mostly inferior. Tremendous efforts have been devoted to address this issue, including two main directions: nanostructures and composites. The unique nanostructures, such as nanoparticles, nanotubes, and nanofibers, provide a short transport path for ions, a highly active contact area, and an effective buffer during charge–discharge processes. Another strategy is to combine these nanostructures with conductive materials including carbon-based materials and conducting polymers. However, carbon coatings, which are realized usually by thermal decomposition of carbon precursors, usually cause environmental problems because of the formation of volatile organic compounds, CO and CO₂, and sometimes lead to the inferior reconstruction of materials.

Herein, we first fabricated α-Fe₂O₃ nanowire arrays on carbon cloth by electrodeposition followed by an annealing process in air. Subsequently, a thin PANI was electrodeposited on the α-Fe₂O₃ nanowires and finally the highly ordered 3D α-Fe₂O₃@PANI core–shell nanowire arrays were obtained. Compared with pure α-Fe₂O₃ electrode, the α-Fe₂O₃@PANI electrode has better electrochemical performance with a twice increase in C_{sp} from 33.93 to 103 mF/cm². In addition, a high-

**Received:** April 19, 2015  
**Accepted:** June 19, 2015  
**Published:** June 19, 2015
performance ASC was designed with $\alpha$-Fe$_2$O$_3@$PANI nanowires grown on carbon as anode and PANI nanorods grown on carbon cloth as cathode, and it displayed a high volumetric capacitance of 2.02 mF/cm$^3$, a high energy density of 0.35 mWh/cm$^3$ at the power density of 120.51 mW/cm$^3$ based on volume of the whole device, and very good stability with $C_{sp}$ retention of 95.77% after 10 000 cycles.

2. EXPERIMENTAL SECTION

2.1. Fabrication of Electrode Materials. All the chemical reagents used in this study were of analytical grade (AR). The electrodeposition was carried out in a simple two-electrode cell via galvanostatic electrolysis, and the graphite electrode was used as a counter electrode (spectral grade, 1.8 cm$^2$). Carbon cloth (0.5 × 2 cm$^2$) was used as the working electrode for electrodeposition, and it was washed with ethanol and water, successively, in an ultrasonic bath.

2.1.1. Synthesis of Negative Electrode. First, metal Fe nanowire arrays were electrodeposited in a solution of 9 g/L FeCl$_3$·6H$_2$O + 14 g/L (NH$_4$)$_2$C$_2$O$_4$·H$_2$O at a current density of 4 mA/cm$^2$ at room temperature for 40 min. Then, $\alpha$-Fe$_2$O$_3$ nanowire arrays were obtained by calcining Fe nanowires at 500 °C for 2 h in air with a speed of 3 °C/min. Finally, a thin PANI film was electrodeposited on the $\alpha$-Fe$_2$O$_3$ nanowires in a solution 0.01 M aniline + 0.1 M H$_2$SO$_4$ with a current density of 2 mA/cm$^2$ at room temperature for 5 min.

2.1.2. Synthesis of Positive Electrode. PANI nanorods was electrodeposited on carbon cloth in a solution 0.1 M aniline +1.0 M H$_2$SO$_4$ with a current density of 2 mA/cm$^2$ at room temperature for 20 min.

2.2. Fabrication of ASC. The ASC device was assembled using $\alpha$-Fe$_2$O$_3@$PANI electrode (0.35 cm$^2$) and PANI electrode (0.35 cm$^2$).
with a separator (NKK separator; Nippon Kodoshi Corporation, Kochi, Japan) sandwiched between the two electrodes. A Na2SO4 (1.0 M) aqueous solution was used as the electrolyte. To avoid leakage of the electrolyte, the entire device was sealed by two pieces of PET membranes with a small part of electrode kept outside.

2.3. Material Characterization and Electrochemical Measurements. The morphologies, microstructures, and compositions of products were characterized by field-emission scanning electron microscopy (FE-SEM, JSM-6330F), X-ray diffractometry (XRD, D-MAX 2200 VPC), transmission electron microscopy (TEM, Tecnai G2 F30), photoelectron spectroscopy (XPS, ESCA Lab250) and Raman spectroscopy (Nicolet NXR 9650).

The electrochemical measurements of the electrodes were carried out in a standard three-electrode electrolytic cell in a 1.0 M Na2SO4 aqueous solution. A graphite electrode was used as a counter electrode. A saturated calomel electrode (SCE) was used as the reference electrode. The cyclic voltammometry and chronopotentiometric measurements were performed on a CHI 760 E electrochemical workstation (CH Instruments, Inc.) to determine the electrochemical properties. The EIS was conducted in the frequency range between 0.01 Hz and 100 kHz with an amplitude of 5 mV at the open-circuit potential.

3. RESULTS AND DISCUSSION

The α-Fe2O3@PANI core–shell nanowire arrays on carbon cloth were achieved by electrodeposition, as illustrated in Scheme 1, and the electrodeposition has been proven an efficient method for synthesis of nanomaterials. SEM images of α-Fe2O3 nanowire arrays before and after coating a thin film of PANI show that the nanowire arrays were uniformly grown on the surface of carbon fiber (Figure 1a,b). The core–shell nanostructure of α-Fe2O3@PANI was confirmed by TEM. As shown in Figure 1c,d, the PANI is uniformly coated on the surface of α-Fe2O3 nanowire. The length of the core–shell nanowire is ~375 nm. The diameter of Fe2O3 nanowire is ~20.3 nm, and the thickness of PANI shell is ~8.3 nm. The lattice spacing of 0.25 nm corresponds to the (110) crystal plane of α-Fe2O3, and a clear twin plane is seen in Figure 1d.

The selected-area electron diffraction (SAED) pattern in the

Figure 2. (a) XRD patterns of the prepared Fe, α-Fe2O3, and α-Fe2O3@PANI; (b) Raman spectrum of the prepared α-Fe2O3, PANI, and α-Fe2O3@PANI.

Figure 3. XPS spectra of the prepared α-Fe2O3@PANI: (a) survey, (b) Fe 2p, (c) O 1s, and (d) N 1s.
The peaks of air at 500 °C electrodeposition (PDF of benzenoid rings), 1497 cm−1 can be assigned to the stretching vibrations of C–H bonding of benzenoid rings, 1497 cm−1 (C═N stretching of the quinoid rings), and 1595 cm−1 (C–C stretching of benzenoid rings).34,35 In addition, two distinct peaks at 1323 and 1395 cm−1 can be assigned to the stretching vibrations of C–N fragments, indicating the emeraldine salt of PANI, which is a highly electrical conductive form.34 These results reveal that PANI is coated on the surface of α-Fe2O3 nanowires. Figure 3a presents XPS survey of α-Fe2O3@PANI nanowire arrays, which shows four elements (Fe, O, N, and C) existing in the sample. The fine XPS spectra of Fe 2p, O 1s, and N 1s are displayed in Figure 3b–d. As shown in Figure 3b, except for two shakeup satellites at ~718.9 and 732.4 eV, two major peaks centered at around 711.0 eV for Fe 2p1/2 and 724.6 eV for Fe 2p3/2, with a spin energy separation of 13.6 eV, which is in good agreement with the reported value for α-Fe2O3.12,36 The O 1s spectrum shown in Figure 3c can be deconvoluted into three components. The bands at 529.8, 531.3 and 533.1 eV can be assigned to the oxygen bond of Fe–O, Fe–O−H, and H–O–H, respectively.12,37 The N 1s spectrum shown in Figure 3d shows that most of the nitrogen atoms are in the form of amine (−NH−) centered at 400.04 eV in benzenoid amine or amide groups. Two small additional peaks suggest that some nitrogen atoms exist as imine (−N═) form centered at 399.3 eV and positively charged nitrogen (N+) form centered at 401.08 eV.38,39 Therefore, the PANI is coated on the surface of Fe2O3 nanowire arrays successfully, and this is in line with the results of XRD and Raman.

The electrochemical studies of α-Fe2O3 nanowire arrays and α-Fe2O3@PANI core−shell nanowire arrays on carbon cloth were conducted by cyclic voltammetry (CV), galvanostatic charge/discharge (GCD), and electrochemical impedance spectroscopy (EIS) in a three-electrode system in 1.0 M Na2SO4 electrolyte. As shown in Figure 4a, the α-Fe2O3@PANI core−shell nanowires electrode shows better capacitance than pure α-Fe2O3 nanowire electrode, and the summary plot of areal Csp versus different scan rates was displayed in Figure 4b. In addition, the improvement of Csp is also confirmed by the GCD curves, which were displayed in Figure 4c. The summary plot of Csp versus different current density was displayed in Figure 4d, and the corresponding GCDs were displayed in Figure S1c,d. (SI). The highest Csp of α-Fe2O3@PANI is 103 mF/cm², which is twice that of pure α-Fe2O3 (33.93 mF/cm²). The improvement of Csp is attributed to the coating of PANI, which is highly conductive and thus enhances the electrical conductivity of the overall electrode. This can be seen more clearly in EIS spectrum in Figure 4e. Compared with pure α-Fe2O3 electrode, the α-Fe2O3@PANI electrode has much
smaller charge-transfer resistance ($R_{ct}$) at high frequency, suggesting the fastest charge transfer and transport process.\(^{40}\) Moreover, the low frequency line shows more vertical shape for $\alpha$-Fe$_2$O$_3@PANI$ electrode, indicating the faster ion diffusion behavior.\(^{41}\) Besides, the coated PANI is helpful for improving the stability, which can be seen in Figure 4f. After 2500 cycles testing, the $C_{sp}$ retention of $\alpha$-Fe$_2$O$_3@PANI$ is almost 100% while the retention of pure $\alpha$-Fe$_2$O$_3$ is just 93%.

Therefore, such high electrochemical performance of $\alpha$-Fe$_2$O$_3@PANI$ electrode can be attributed to the synergistic effect of $\alpha$-Fe$_2$O$_3$ and PANI. Moreover, the carbon cloth can act as conductivity framework, and the active materials were grown directly on its interconnected carbon fibers, which ensure a good electric contact and consequently enhances the rate capability.\(^{42}\) In additional, the hierarchical 3D core–shell nanowire arrays structure provides large reaction surface area, fast ion and electron transfer, and good structural stability.\(^{43}\) Significantly, the excellent capacitive behaviors demonstrate that the prepared $\alpha$-Fe$_2$O$_3@PANI$ will be a promising candidate as a negative electrode for ASCs.

To fabricate ASCs using $\alpha$-Fe$_2$O$_3@PANI$ core–shell nanowires as the negative electrode, we select PANI as the positive electrode because of its high capacitance (theoretical value: 3407 F/g) and easy synthesis. Moreover, PANI has high hydrogen evolution overpotential and large operational potential.\(^{44,45}\) In our experiments, PANI nanorods were electrodeposited on carbon cloth by a similar method for coating PANI on $\alpha$-Fe$_2$O$_3$. The morphology and its electrochemical performance in three-electrode system were displayed in Figure S2 (SI). Obviously, there is a pair of redox peaks, which are attributed to the redox transitions of PANI (i.e., the leucoemeraldine/emeraldine transitions and the emeraldine/...
Figure 5a shows the schematic illustration of the structure of our ASC, which is sealed by two thin pieces of PET membranes. To determine the best operating potential of the ASC device, the CVs of α-Fe2O3@PANI electrode (black curve) and PANI (red curve) electrode were measured in a 1.0 M Na2SO4 solution, respectively, as shown in Figure 5b. Figure 5c (SI) displays the CVs and GCD curves of the prepared ASC device collected in different potential windows, which indicates that the potential window of the fabricated ASC can be as large as 1.5 V (vs SCE).

Figure 6a shows the CV of the ASC at different scan rates from 5 to 100 mV/s. The current intensity increases as the scan rate increases, but the shape is well retained, indicating its ideal pseudocapacitive nature. Figure 6b shows the volume capacitance as a function of scan rate, and the volume capacitance increases from 0.78 to 2.02 F/cm3 with the scan rate from 100 to 5 mV/s. Figure 6c shows the GCD test, which was performed at different current densities in the potential window of 0–1.5 V (vs SCE). The linear voltage versus time profiles, the symmetrical charge/discharge characteristics, and a quick I–V response represents good capacitive characteristics for the ASC. Figure 6d compares the volumetric power density and energy density of the ASC device to the values reported for other supercapacitors. The maximum energy density of the prepared ASC is 0.35 mWh/cm3 at a power density of 120.51 mW/cm3. These values are superior to the previously reported supercapacitor systems, including graphene-based SCs (0.06 mWh/cm3, 135 mW/cm3),17 TiN-based SCs (0.05 mWh/cm3, 120 mW/cm3),18 TiO2@C-based SCs (0.01 mWh/cm3, 19 mW/cm3),49 ZnO@MnO2/rGO-based SCs (0.234 mWh/cm3, 5 mW/cm3),50 and even comparable to the values of MnO2//Fe2O3-based SCs (0.4 mWh/cm3, 60 W/cm3),11 VO2//VN-based SCs (0.6 mWh/cm3, 80 mW/cm3),12 and TiO2@MnO2//TiO2@C-based SCs (0.3 mWh/cm3, 190 mW/cm3).51 In addition, the ASC exhibits good cycling stability, which is one of the most critical factors in supercapacitor operations. The cycling test of the ASC shows ~95.77% Csp retention over 10 000 cycles at a scan rate of 50 mV/s (Figure 6e), which is significantly better than those reported in previous work (typically 70–85% retention over 1000 cycles).51,52 To show the practical application, we assembled three ASCs in series. As shown in Figure 6f, the ASCs can light a 50 cm long commercial red (2.0 V) or green (2.5 V) LED soft rope light, indicating high power and energy characteristic of the ASCs device.

4. CONCLUSIONS

In summary, we fabricated highly ordered α-Fe2O3@PANI core–shell nanowire arrays by a simple and cost-effective electrodeposition method and first used them as negative electrodes for supercapacitors. This unique core–shell nanowire array structure enables a high areal Csp of 103 mF/cm2 and outstanding cycling performance (2500 cycles without any loss), which are superior to pure α-Fe2O3 nanowire arrays. Additionally, a high-performance ASC device based on α-Fe2O3@PANI core–shell nanowire arrays as anode and PANI nanowire arrays as cathode was prepared. The α-Fe2O3@PANI//PANI ASC device achieved a maximum energy density of 0.35 mWh/cm3 and a maximum power density of 301.19 mW/cm3 with a good cycling stability of 95.77% Csp retention after 10 000 cycles. These findings will open up the possibility of α-Fe2O3@PANI core–shell nanowire arrays as anodes for the applications in ASCs with large potential window and high energy and power densities to meet the diverse demands in the modern industry development.

ASSOCIATED CONTENT

Supporting Information

Calculations of specific capacitance, power density, and energy density; CVs, galvanostatic data, and SEM image. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.5b03126.

AUTHOR INFORMATION

Corresponding Author

E-mail: ligaoren@mail.sysu.edu.cn. Fax: 86-20-84112245. Tel: 86-20-84110071.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by NSFC (51173212 and J1103305), Natural Science Foundation of Guangdong Province (S2013020012833), Fundamental Research Fund for the Central Universities (13lgps51), SRF for ROCS, SEM ([2012]1707), the Project of High Level Talents in Higher School of Guangdong Province, and Open-End Fund of Key Laboratory of Functional Inorganic Material Chemistry (Heilongjiang University), Ministry of Education.

REFERENCES

(11) Lu, X.; Zeng, Y.; Yu, M.; Zhai, T.; Liang, C.; Xie, S.; Balogun, M. S.; Tong, Y. Oxygen-Deficient Hematite Nanorods as High-Perform-


