ORIGINAL PAPER

Electrodeposition of hybrid film of polyaniline/silica and its pseudocapacitive properties

Xiao-Xia Liu · Ya-Bing Li · Li-Jun Bian ·
Yu-Qian Dou · Yu-Qiu Huo

Abstract Electrodeposition of hybrid film of polyaniline (PANI) and nanoparticles of silica (SiO_2) was conducted through electrochemical surface polymerization of aniline, which hydrogen-bonded onto surfaces of SiO_2 particles. The hybrid film showed a 3D structure that facilitated the contact of electroactive material with electrolyte. PANI/SiO_2 displayed a capacitance of 558 mF•cm^{-2} in 0.5 M H_2SO_4 when charged–discharged at 1.5 mA•cm^{-2}, which is 2.5 times of that of similarly prepared PANI film. The capacitance of the hybrid film kept essentially constant when charging–discharging under current densities up to 24 mA•cm^{-2}.

Keywords Polyaniline · Silica · Electrodeposition · Hybrid film · Pesudocapacitive properties

Introduction

The study of organic–inorganic composite materials is a recent but very fruitful enterprise, as the merits of organic and inorganic moieties can be combined in the composites. Polyaniline (PANI) has been widely studied, as it has promising applications in a variety of technologic fields, such as electrochemical supercapacitors, batteries, sensors, and corrosion inhibitors, etc. [1]. The properties of PANI can be improved by incorporating other functional materials, including oxides, polyacidic anions, etc. [2–5]. Supercapacitor

X.-X. Liu (✉) · Y.-B. Li · L.-J. Bian · Y.-Q. Dou · Y.-Q. Huo
Department of Chemistry, Northeastern University,
Shenyang 110004, China
e-mail: xxliu@mail.neu.edu.cn

has attracted significant attention because of its promising applications as high pulse-power devices in energy-storage systems [6]. The capacitance of electrochemical super-capacitor arises mainly from the Faradaic reactions at the interface of electrode material and electrolyte, so most of the charges are stored at the surface or in the bulk near the surface of the solid electrode material. Hence, in this case, the contact of the electrode material with the electrolyte plays an important role for the device to display improved capacitance [6]. Incorporation of oxide nanoparticles into PANI film will facilitate the contact of electrode material with electrolyte, thus, representing an opportunity for the design of materials with improved properties.

Among those inorganic moieties in the organic–inorganic composites, silica (SiO_2) has received great attention because of their unique properties and wide applications [7]. Nano- and mesoporous silica particles have been included in the composites through many ways, including surface polymerization of aniline adsorbed onto silica surfaces [8, 9], in-situ hydrolysis and condensation of tetraethoxysilane (TEOS) in PANI solutions or on solid PANI surfaces [10, 11], etc. Although silica is insulating, some of the composites were in the same conductivity level as that of PANI [11], and some even displayed enhanced conductivity [10], providing potential applications of the composites in electrochemistry and related fields.

Electrodeposition is an effective way to produce composite films with a large variety of tunable parameters, and so the advantage of convenient film control. Therefore, electrode-position of the hybrid film of PANI and silica is conducted in this paper through electrochemical surface polymerization. The morphology of the film was investigated by scanning electron microscope (SEM). The pseudocapacitive properties of the resulting PANI/SiO_2 composite were studied by means of chronopotentiometry (CP).
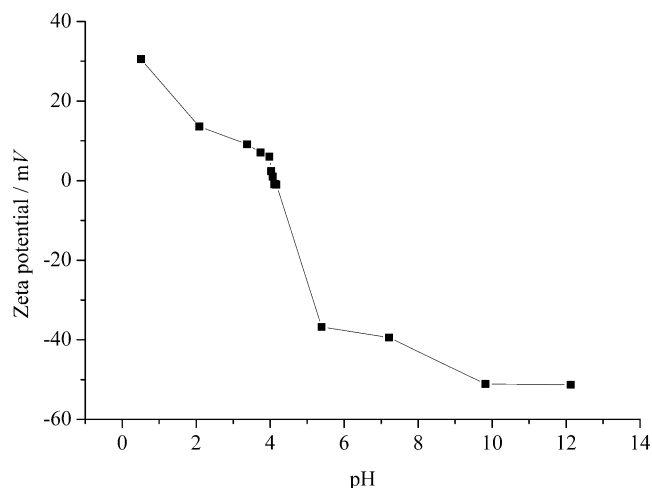
Fig. 1 Zeta potentials of silica nanoparticles in the presence of 0.1 M aniline at different pH

Experimental

Aniline was distilled under reduced pressure before use. Other chemicals were of analytical grade and used as received. Nanoparticles of silica (average 160 nm) were prepared by literature method [12]. The solution and silica nanoparticle containing suspension were prepared from distilled water. The pH value of the media were adjusted by HNO_3 or KOH.

Electrochemical experiments were performed on electrochemical analyzer, CHI 660B, under ambient condition. Potentials were measured and reported versus saturated calomel electrode (SCE). Platinum wire was used as counter electrode. Electrodeposition was conducted on carbon cloth electrode. Before use, the carbon cloth was cleaned by acetone and distilled water, and then pretreated by three cyclic voltammetric scans during $-2.0\sim2.0$ V at 200 $mV\cdot s^{-1}$ in 2.0 M H_2SO_4. Electropolymerization of aniline was conducted in 0.1 M aniline at pH 1 in the presence of silica nanoparticles (0.75 $g\cdot l^{-1}$) to afford PANI/SiO_2 hybrid film through 100 successive cyclic voltammetric scans in the potential range of $-0.3\sim0.9$ V at a scan rate of 50 $mV\cdot s^{-1}$. The film of PANI was obtained through similar potential dynamic scans containing 0.1 M Na_2SO_4 (at pH 1) as supporting electrolyte.

The films were cyclic voltammetric scanned in 0.5 M H_2SO_4 at 5 or 50 $mV\cdot s^{-1}$ to study their electroactivities.
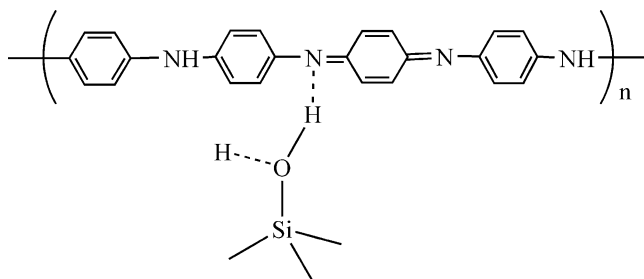

Fig. 2 Illustration of incorporation of SiO_2 into PANI
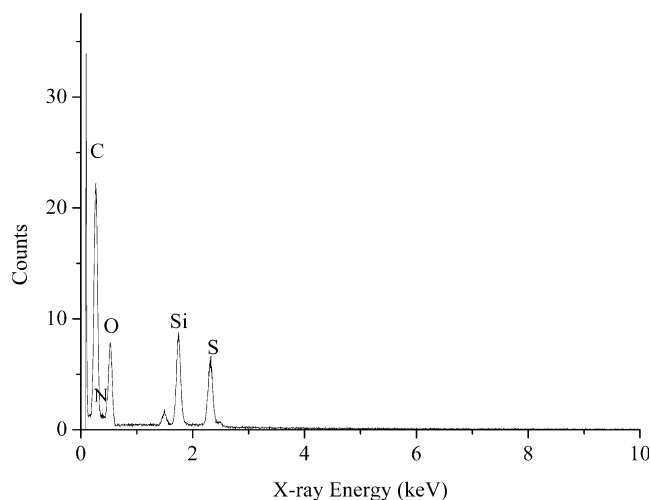

Fig. 3 EDX spectrum of PANI/SiO_2 (see Fig. 4)

Pseudocapacitive property studies were performed in the same solution by CP.

Zeta-potentials of silica nanoparticles in the suspension containing 0.1 M aniline were measured by using Malvern Nano ZS Nanosizer. The morphology of and the existence of silica in the hybrid film were inspected by SEM and energy dispersive X-ray diffraction (EDX) on Shimadzu SSX-550 SEM.

Results and discussion

Eletrodeposition and electroactivities of PANI/SiO_2 hybrid film

Figure 1 shows the Zeta potentials of silica nanoparticles in the presence of 0.1 M aniline at different pH. The isoelectric point of SiO_2 in this media is 4.1 based on Fig. 1. Therefore, silanols on the surfaces of the particles
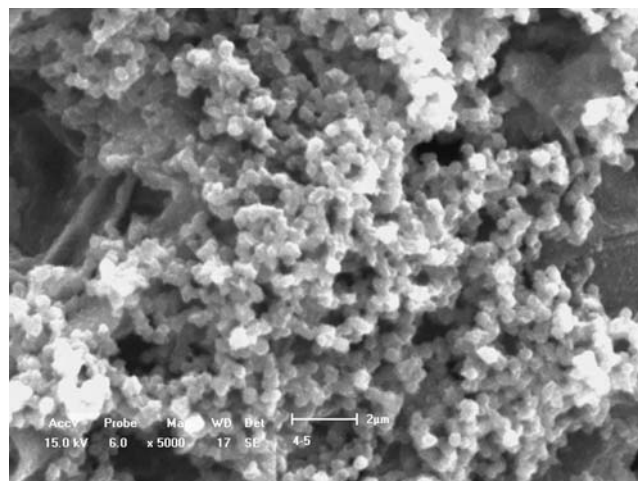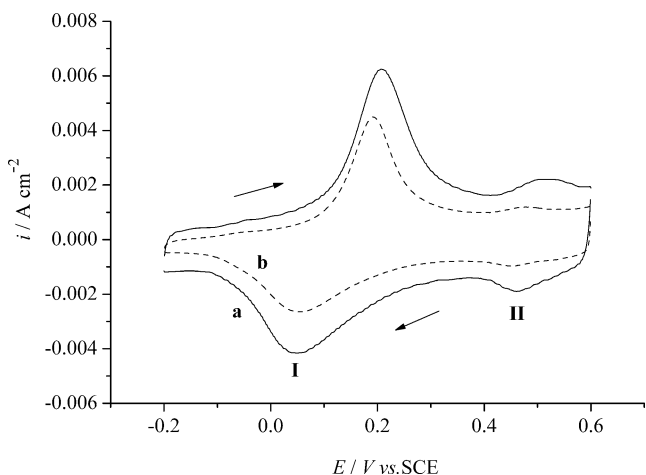

Fig. 4 SEM images of PANI/SiO_2

Fig. 5 Cyclic voltammograms in 0.5 M H_2SO_4 of PANI/SiO$_2$ (**a** *solid line*) and similarly prepared PANI film from solution containing 0.1 M Na$_2$SO$_4$ as supporting electrolyte (**b** *dash line*); SCE reference electrode; scan rate, $\nu = 5$ mV·s^{-1}

Fig. 7 Chronopotentiograms in 0.5 M H_2SO_4 at 1.5 mA·cm^{-2} of PANI/SiO$_2$ (**a** *solid line*) and similarly prepared PANI film from solution containing 0.1 M Na$_2$SO$_4$ as supporting electrolyte (**b** *dash line*); SCE reference electrode

will be protonated at pH 1 to produce (SiOH$_2^+$) group [13]. And aniline monomers in the medium will be bonded onto the particles through hydrogen-bonding between the amine group of aniline and the (SiOH$_2^+$) group on the surfaces of silica. Therefore, the local concentration of aniline at surfaces of silica particles is considerably high. Then, silica particles will be incorporated into PANI during cyclic voltammetric scans for the electropolymerization of aniline and enveloped into the polymer through hydrogen-bonding action, as illustrated in Fig. 2. Wang's group reported the in situ hydrolysis and condensation of TEOS in PANI solution. The hydrogen bonding between the organic and inorganic components assured a well-dispersed structure of PANI in silica matrix, resulting in an improved electrical conductivity of the hybrid material [10]. The hybrid of PANI and silica in our work should also be conductive enough to prolong the surface electropolymerization to
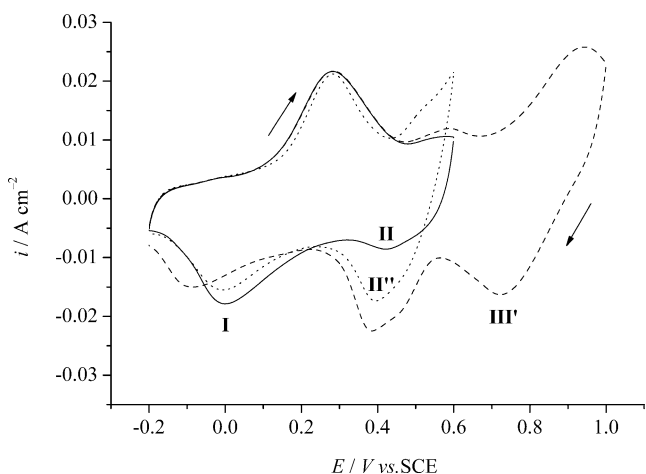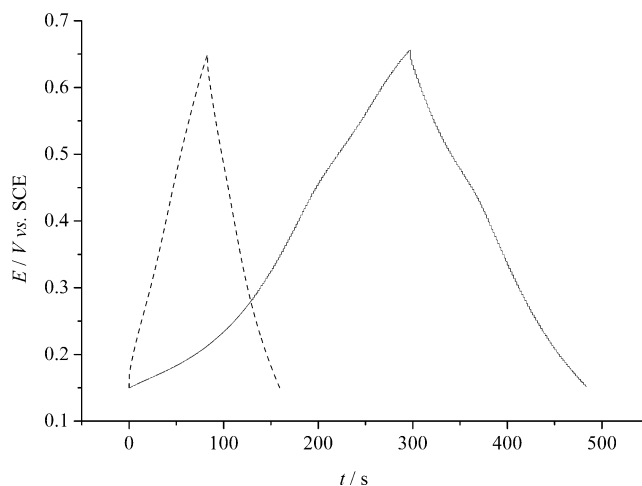
produce bulk hybrid film. The existence of silica in PANI/SiO$_2$ is confirmed by EDX analysis of the film (Fig. 3).

Figure 4 shows the SEM images of the PANI/SiO$_2$ hybrid film. A globular 3D structure that may be caused by a nanoparticle template-guiding polymerization process is observed [14]. This open structure will provide effective contact for electrolyte with active sites of the film and so facilitate the redox of the polymer chain. Therefore, current densities on the cyclic voltammogram of the hybrid film in 0.5 M H_2SO_4 are higher (Fig. 5a, solid line) than those of similarly prepared PANI from solution containing 0.1 M Na$_2$SO$_4$ instead of SiO$_2$ (Fig. 5b, *dash line*).

There are two redox pairs on the cyclic voltammogram of the hybrid film (Fig. 6a). The first one (I; at 0.28 V for anodic peak and 0.00 V for cathodic peak) can be ascribed to the redox between the emeraldine and leucoemeraldine states of PANI [15]. To investigate the second redox pair (II), cyclic voltammetry is conducted from −0.2 to 1.0 V

Fig. 6 Cyclic voltammograms of PANI/SiO$_2$ in the potential range of −0.2 to 0.6 V (**a** *solid line*), −0.2 to 1.0 V (**b** *dash line*) and −0.2 to 0.6 V again (**c** *dot line*) in 0.5 M H_2SO_4 solution; SCE reference electrode; scan rate, $v = 50$ mV·s^{-1}
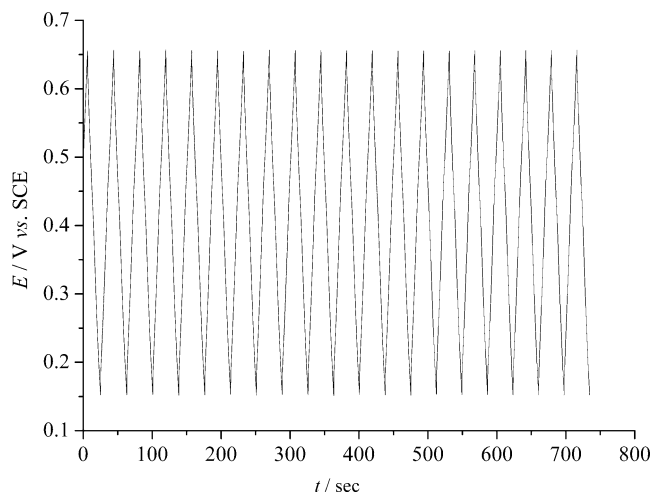

Fig. 8 Multi-step chronopotentiogram of PANI/SiO$_2$ in 0.5 M H_2SO_4 at 15 mA·cm^{-2}

(Fig. 6b) and then from −0.2 to 0.6 V again (Fig. 6c). The third redox pair III′ on Fig. 6b may be because of the exchange between the pernigraniline and emeraldine states of PANI [15]. After cyclic voltammetry to higher potential (1.0 V in this experiment) is conducted on the hybrid film in monomer-free acidic solution, the current of the redox pair increases obviously from that on Fig. 6a (II) to that on Fig. 6c (II″). Therefore, this redox pair should be ascribed to the hydrolysis products of PANI [16].

Pseudocapacitive properties of PANI/SiO$_2$ composite film

Pseudocapacitive properties of PANI/SiO$_2$ hybrid film are studied by charge–discharge through CP experiment at 1.5 mA•cm^{-2} in 0.5 M H$_2$SO$_4$ (Fig. 7a). Figure 7b is the chronopotentiogram of PANI. The average capacitance of the film can be deduced from the discharge curve based on Eq. 1 [17]

$$C = i \cdot \Delta t / \Delta E \qquad (1)$$

Where i and Δt are the discharge current density and time, respectively. ΔE is the discharge potential window. From Fig. 7a, the average capacitance of the hybrid film is 558 mF•cm^{-2}, which is 2.5 times of that of PANI made under similar condition (225 mF•cm^{-2}, from Fig. 7b). Although silica is nonconductive, the conductivity of PANI and silica composites may be similar to or even higher than that of PANI [10, 11], and the incorporation of SiO$_2$ into PANI film could increase the effective surface area of the material [18]. Therefore, the contact of electrode-active material with electrolyte can be modified upon inclusion of silica into PANI, which enhances the charge storage of the film.

To test the high-power property of PANI/SiO$_2$, the charge–discharge behavior of the film is examined by CP in 0.5 M H$_2$SO$_4$ at relatively high current densities. The measured capacitance keeps essentially constant under a charge–discharge current density up to 24 mA•cm^{-2}, which is quite high for Faradaic supercapacitors, providing the hybrid film potential usage in high pulse power energy storage devices. However, the capacitance decreases when measured under higher current densities that can be predicted from kinetic point of view similar to other systems. Figure 8 is the typical chronopotentiometric result measured at 15 mA•cm^{-2} for the hybrid film. The charging curves are symmetric to the corresponding discharging counterparts, indicating that the PANI/SiO$_2$ hybrid film exhibits capacitive-like behavior in this medium.

Conclusions

Electrodeposition is a convenient route to prepare organic–inorganic composite films. Hybrid film of PANI and nanoparticles of silica was obtained through electrochemical surface polymerization of aniline hydrogen-bonded onto surfaces of silica nanoparticles. Incorporation of silica into PANI film facilitated the effective contact of the electrolyte and the active materials of the film. As a result, the hybrid film displayed a capacitance of 558 mF•cm^{-2} at 1.5 mA•cm^{-2}, which is 2.5 times that of PANI film, and the capacitance of the hybrid film kept essentially constant when charging–discharging under a current density up to 24 mA•cm^{-2}, providing the hybrid film potential usage in high-pulse-power energy storage devices.

References

1. Inzelt G, Pineri M, Schultze JW, Vorotyntsev MA (2000) Electrochim Acta 45:2403
2. Liu XX, Bian LJ, Zhang L, Zhang LJ (2007) J Solid State Electrochem 11:1279
3. Gurunathan K, Amalnerkar DP, Trivedi DC (2003) Mater Lett 57:1642
4. Gomez-Romero P, Chojak M, Cuentas-Gallegos K, Asensio JA, Kulesza PJ, Casan-Pastor N, Lira-Cantu M (2003) Electrochem Commun 5:149
5. Fusalba F, Belanger D (2000) Electrochim Acta 45:3877
6. Burke A (2000) J Power Sources 91:37
7. Liu P, Liu WM, Xue QJ (2004) Mater Chem Phys 87:109
8. Feng XM, Yang G, Liu YG, Hou WH, Zhu JJ (2006) J Appl Polym Sci 101:2088
9. Jang J, Ha J, Lim B (2006) Chem Commun 1622
10. Wang Y, Wang X, Li J, Mo Z, Zhao X, Jing X, Wang F (2001) Adv Mater 13:1582
11. Niu Z, Yang Z, Hu Z, Lu Y, Han CC (2003) Adv Funct Mater 13:949
12. Sadasivan S, Rasmussen DH, Chen FR, Kannabiran RK (1998) Colloids Surf A Physicochem Eng Aspects 132:45
13. Curran MD, Stiegman AE (1999) J Non-Cryst Solids 249:62
14. Kulkarni MV, Viswanath AK, Khanna PK (2006) J Macromol Sci A Pure Appl Chem 43:759
15. Huang WS, Humphrey BD, MacDiarmid AG (1986) J Chem Soc Faraday Trans 1(82):2385
16. Duic L, Mandic Z, Kovac S (1995) Electrochim Acta 40:1681
17. Park JH, Park OO (2002) J Power Sources 111:185
18. Dutta K (2007) Phys Lett A 361:141