

***In situ* synthesis of cabbage like polyaniline@hydroquinone nanocomposites and electrochemical capacitance investigations**

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ABSTRACT: A Cabbage like polyaniline@hydroquinone composite microsphere was synthesized using *in situ* polymerization and the electrochemical performance was investigated. The core template, p-benzoquinone, is demonstrated working as an oxidizing agent for the *in situ* polymerization of PANI, and to be reduced to 1, 4-hydroquinone after reaction. The morphology and microstructure of samples were examined by field emission scanning electron microscopy, transmission electron microscope, X-ray photoelectron spectrometer, thermo gravimetric, and Fourier transform infrared spectra. The cyclic voltammetry, impedance and galvanostatic charge/discharge analysis demonstrates that PANI contributes electronic conductive channels for hydroquinone, and hydroquinone works as a pseudocapacitance component. The prepared PANI@hydroquinone nanocomposite exhibits brilliant electrochemical properties of a specific capacitance of 126.0 F g^{-1} at a scan rate of 5 mV s^{-1} and enhanced stability of about 85.1% of initial capacitance retained after 500 cycles scanning at a current density of 1 A g^{-1} . © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 42290.

KEYWORDS: composites; conducting polymers; electrochemistry; nanostructured polymers

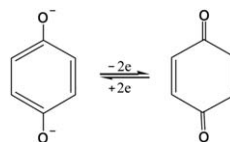
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INTRODUCTION

The increasing demands of portable energy storage devices have made electrochemical supercapacitors receive great attentions owing to their high power density, long cycle life, wide range of operating temperature, and low emissions.^{1–4} Various structured materials have been investigated as electrode for supercapacitors so far, such as core-shell structured particles,⁵ nanowire arrayed nanocomposites,⁶ nanotubes,⁷ acicular structured composites,⁸ and so on. Among them, Core-shell structured particles coating with conductive polymers as wrappings have attracted increasing attentions because of their properties that originate the new cooperative effects between the cores and shells. As a nanostructured conjugated polymer, polyaniline (PANI) own strong competitiveness because of its sound environmental stability, excellent electrical conductivity, low cost, and high flexibility.^{9–11} Core-shell structured conducting PANI@inorganic nanocomposites have been studied extensively, such as metallic oxide, silica, and carbon nanotube.

However, to the best of our knowledge, there are no reports on core-shelled structured PANI@organics nanocomposites. Hydroquinone, an electrochemically active compound, could offer pseudocapacitance because of the oxygenic groups which would afford the charge/discharge pathway as followed:¹²



Unfortunately, its poor cycling stability impedes its wide application in supercapacitors. Herein, we first report a core-shell structured polyaniline@hydroquinone which looks like a cabbage. In our previous work, we found p-benzoquinone appears negative charge when the pH of the aqueous solutions approaches five as tested by the Zeta potential measurements. As is known, L-lysine contains amidogen which is positively charged in acid aqueous solution and lipophilic groups. Hence, L-Lysine can be used as a linker either for p-benzoquinone nanoparticles or aniline that has lipophilic groups on its surface via electrostatic interactions, thus aid the adsorption of monomers, and facilitates the *in situ* oxidation polymerization.^{13,14} The reaction mechanism sketch is shown in Figure 1. First of all, p-benzoquinone nanocores were made, and then L-Lysine was added in the prepared solution. After electrostatic interactions, L-Lysine was adsorbed on the surfaces of nanocores successfully. Then added the aniline monomer, owing to the lipophilic groups in L-Lysine, aniline could gather on the surfaces of p-benzoquinone nano-cores. Because of the higher oxidative potential of p-benzoquinone, PANI was synthesized after *in*

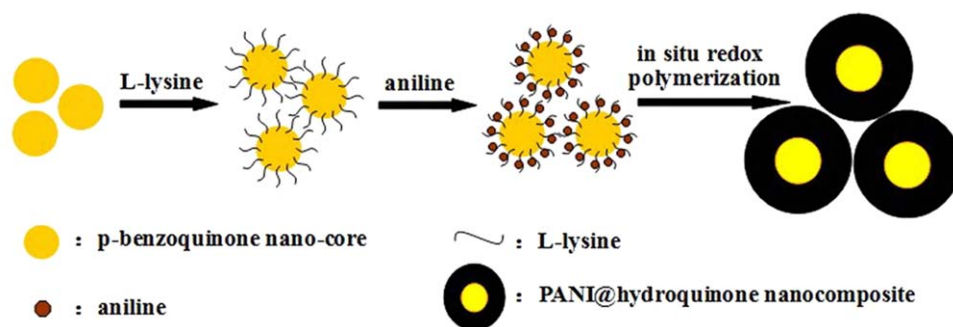


Figure 1. Schematic illustration for the synthesis mechanism of the PANI@hydroquinone nanocomposites. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

situ polymerization and p-benzoquinone was reduced to hydroquinone.

EXPERIMENTAL

Synthesis of Polyaniline@Hydroquinone Composite

In a typical progress, 0.04 g dioctyl sodium sulfosuccinate (AOT) was dissolved in 40 mL deionized water, then, 4 mL p-benzoquinone/acetone solution (0.25 g/ mL) was added to this solution under constant stirring to get the p-benzoquinone nanocores. Then, 0.1 g L-Lysine was dissolved in 30 mL deionized water and the PH of this resulting solution was adjusted to 5 using dilute HCl. Next, measuring 10 mL prepared p-benzoquinone nanocores solution into the L-Lysine solution and transferring this mixed solution into a flask under ultrasonic agitation for 20 mins. Finally, the aniline monomer (25 μ L) was injected into the mixture and the polymerization was carried out under ice water bath and magnetically stirring for 6 h. The product was washed with deionized water twice, and collected

by centrifugation then the cabbage structured polyaniline@hydroquinone composite microspheres were prepared after vacuum drying at 40°C for 24 h.

Characterization

The materials were analyzed by transmission electron microscope (TEM, H800), field emission scanning electron microscopy (FESEM, SU8020), X-ray photoelectron spectrometer (XPS, ESCALAB250), and fourier infrared spectrometer (FT-IR, Nicolet 67).

Electrochemical Investigation

Working electrode was prepared by mixing 80 wt % of polyaniline@hydroquinone composite, 10 wt % of sodium carboxymethylcellulose (CMC) and 10 wt % of acetylene black to form slurry, then the slurry was spread on a piece of platinum net. Then the working electrode was dried in a vacuum oven at 60°C for 12 h before further use. Electrochemical tests for supercapacitor were performed on a CHI660 electrochemical

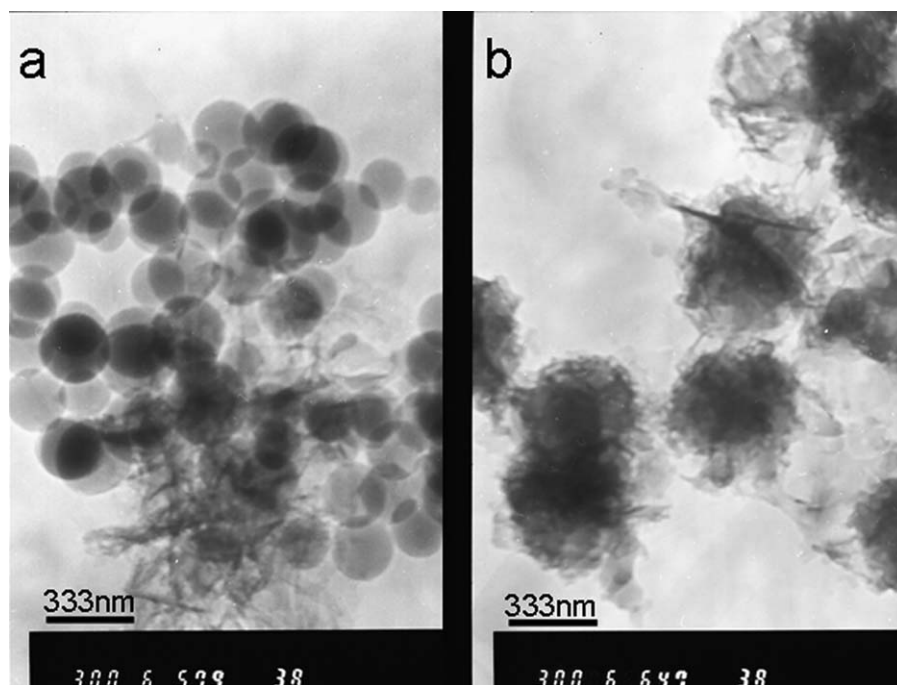


Figure 2. (a) TEM images of (a) p-benzoquinone nanocores and (b) PANI@hydroquinone nanocomposites.

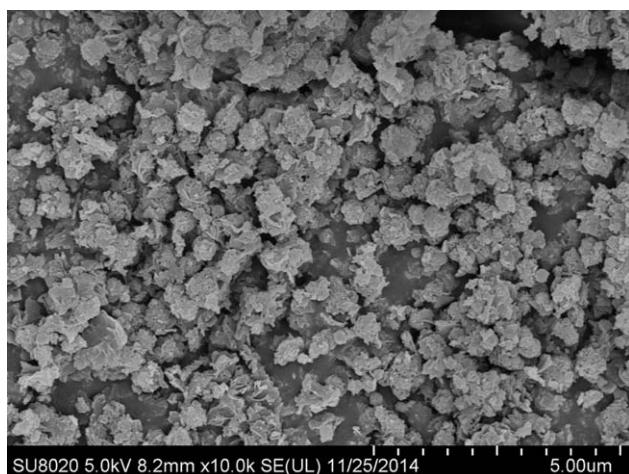


Figure 3. FESEM image of cabbage like PANI@hydroquinone nanocomposites.

workstation system. The electrolyte was 1M H₂SO₄ solution and the three-electrode system was equipped with a platinum foil counter electrode and a saturated calomel reference electrode.

RESULTS AND DISCUSSION

The morphologies of p-benzoquinone and PANI@hydroquinone nanocomposite were investigated by TEM and FESEM. Figure 2(a) shows the TEM image of p-benzoquinone nanocores. From the image, it is observed that the pure p-benzoquinone nanoparticles are well dispersed and are of spherical shape with average diameter in the range of 250 to 300 nm. For PANI@hydroquinone nanocomposite, as shown in Figure 2(b), it is clear that the dark shell structure PANI is successfully coated on the surface of spherical hydroquinone with around of 350 nm in overall diameter. The spherical hydroquinone core could hardly be found because the outer PANI was dark enough that covered the light shaded hydroquinone spheres. The FESEM (the accelerating voltage is 5.0 kV) image of the PANI@hydroquinone core-shell nanoparticles was shown in Figure 3. From Figure 3, many-fold shapes on the surface of nano-

beads, which demonstrate the *in situ* oxidation polymerization of PANI.

The FT-IR spectra of pure PANI, hydroquinone, and PANI@hydroquinone nanocomposite are given in Figure 4(a). Main characteristic bands of pure PANI are as follows. A broad band at 3450 cm⁻¹ is ascribed to the N-H stretching mode of benzenoid ring. The bands at 1579 and 1507 cm⁻¹ are attributed to C=N and C=C stretching mode of vibration for the quinonoid and benzenoid units of PANI.⁵ The peak at 1296 cm⁻¹ is the characteristic of the conducting protonated form of PANI. All these characteristic bands of pure PANI are also followed by PANI@hydroquinone. However, compared with pure PANI, the spectrum of PANI@hydroquinone nanocomposite reveals another strong absorption located at 3234 cm⁻¹ because of the -OH vibration, which corresponding to the spectrum of hydroquinone.

Thermogravimetric (TG) curves of PANI@hydroquinone and hydroquinone are shown in Figure 4(b), respectively. The curve of PANI@hydroquinone presents four distinct weight loss processes under nitrogen atmosphere. The initial region of weight loss (3.5%) before 110°C is because of the removal of water molecules physically absorbed on the external surface of the materials, and the second weight loss region from 160°C to 240°C is believed to be because of the evaporation of hydroquinone (as shown in the inset). The third weight loss region from 250°C to 360°C is because of polymer degradation. The last region of weight loss starting from 360°C is attributed to the decomposition of PANI chains with high molecular weights. The decomposition process ends at 800°C with observed 43% residue corresponds to amorphous carbon which is the transitions from PANI. Calculated by TG curves, the content of the polyaniline in the composite is 54%.

XPS is a significant method to analyze the composition of each element as well as the functional groups. Figure 5(a,b) show the full spectrum of PANI@hydroquinone and the high-resolution of C1s, respectively. From the spectrum of PANI@hydroquinone, the atomic ratio of C/O/N is 78.13/15.02/6.85, which demonstrates the existence of PANI. From the high resolution of C1s, four main peaks can be fitted. The peaks around 284.7,

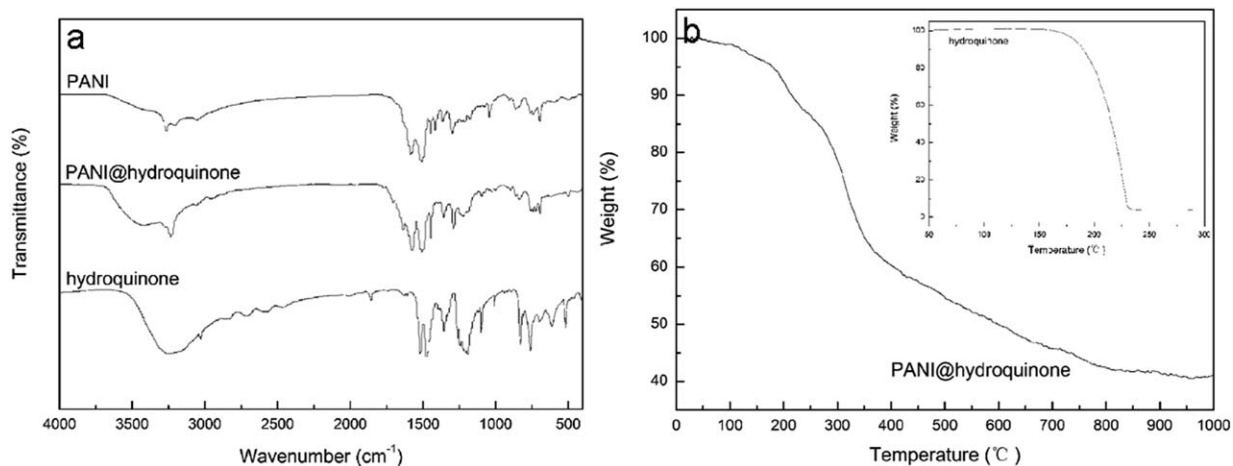


Figure 4. (a) FT-IR spectra of PANI, hydroquinone and PANI@hydroquinone nanocomposites and (b) TG curves of PANI@hydroquinone and hydroquinone.

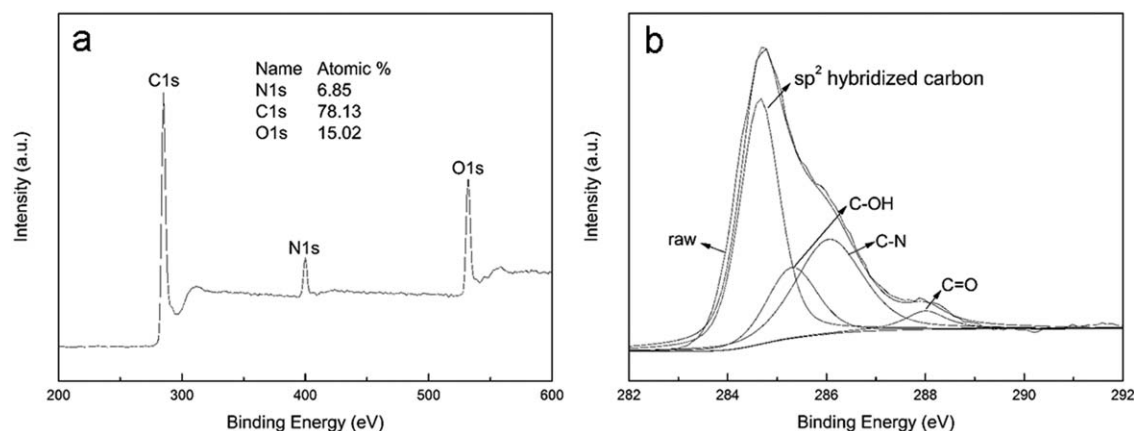


Figure 5. X-ray photoelectron spectra of PANI@hydroquinone (a) full spectrum and (b) high-resolution of C1s.

285.3, 286.1, and 288.0 eV assigned to the sp^2 hybridized carbon, C-OH, C-N, and C=O configurations, respectively.^{15,16} The area of C-OH is larger than that of C=O gives a broad hint that most p-benzoquinone molecules participated in the polymerization of aniline.

Cyclic voltammetry (CV) is performed to estimate the electrochemical performance of the as prepared electrode at different scan rates with the voltage range from -0.2 to 1.0 V. The results are shown in Figure 6(a). The CV curves of polyaniline@hydroquinone composite shows several well-defined

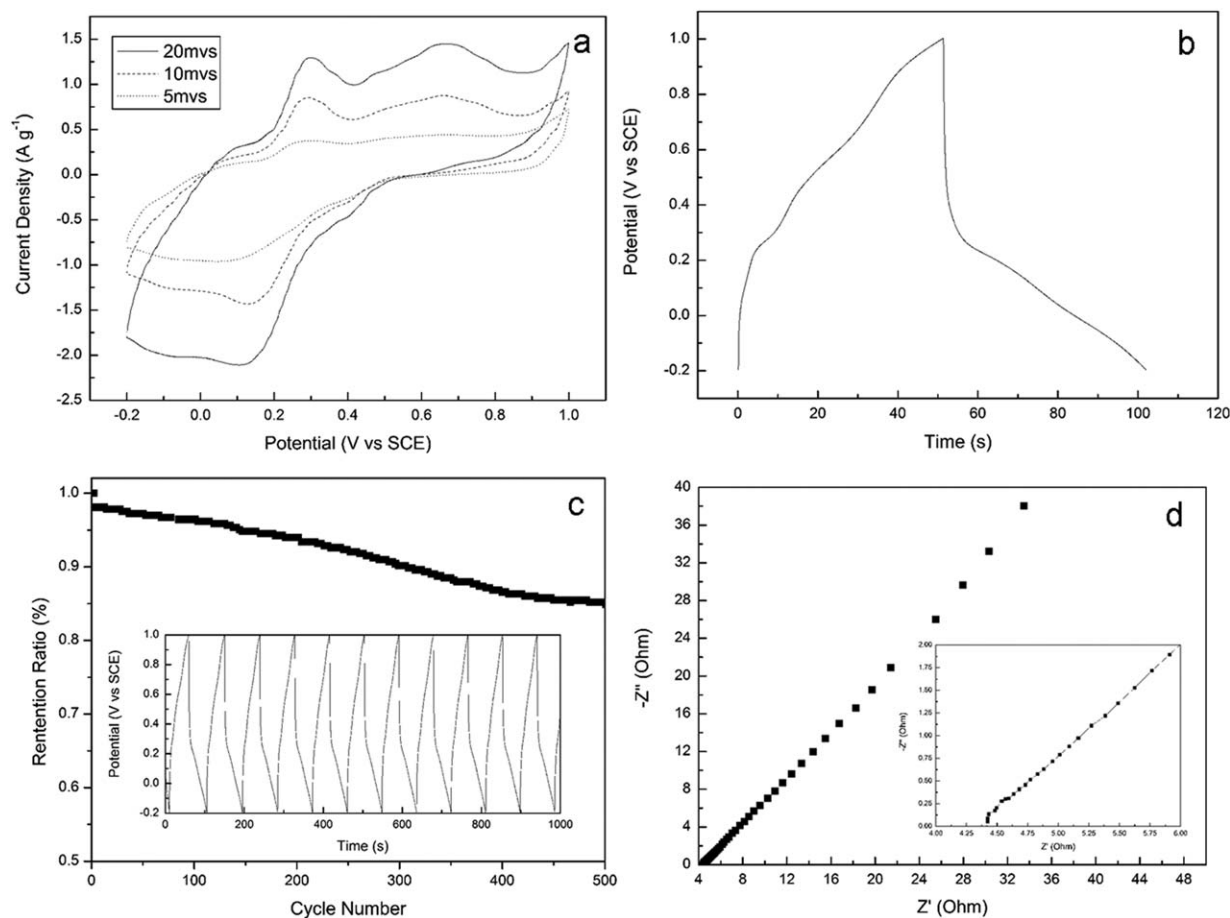


Figure 6. (a) CV curves of PANI@hydroquinone nanocomposites at different scan rates of 5, 10, and 20 mV s⁻¹; (b) galvanostatic charge/discharge curves at current density of 1 A g⁻¹; (c) cycling stability at current density of 1 A g⁻¹; and (d) impedance spectra of PANI@hydroquinone nanocomposites.

quasireversible redox peaks and a pair of symmetric broad peaks centered at 0.15 and 0.3 V corresponding to the oxidation of hydroquinone to p-benzoquinone and reduction of p-benzoquinone to hydroquinone, respectively.¹⁷ As is known to all, the redox progresses have great contribution to enhance the specific capacitance as pseudocapacitance. The specific capacitance of PANI@hydroquinone nanocomposite are 126.0, 94.1, and 72.7 F g⁻¹ at scan rates of 5, 10, and 20 mV s⁻¹, respectively. However, the electrochemical performance is not high values because the inner center hydroquinone core has not been fully utilized for the contribution to pseudocapacitance. The advantage of this kind of core-shelled structure is that PANI has better conductivity which favors for electronic conductive channels for hydroquinone. Also the porous structure can accommodate the volume change during cycling, which would improve the stability of the capacitor. A typical galvanostatic charge/discharge curve of the supercapacitors at a current density of 1 A g⁻¹ is shown in Figure 6(b). The charge/discharge curve shows a deviation from the ideal triangle shape because of the contribution of pseudocapacitance, which is in agreement with the cyclic voltammetry result. The electrochemical stability of the composite is presented in Figure 6(c) at the current density of 1 A g⁻¹. Excitingly, the capacitance retention is about 85.1% of initial capacitance after 500 charge/discharge cycles. This phenomenon reveals the PANI@hydroquinone-based supercapacitor that has excellent electrochemical cycle stability. The electrochemical impedance of the PANI@hydroquinone nanocomposite was measured by electrochemical impedance spectroscopy (EIS) method in 1M H₂SO₄ solution in the frequency ranging from 0.01 Hz to 100 kHz. EIS is a very effective method for characterization of the internal resistance, charge transfer in the electrode materials and electrolyte, and ion diffusion process of electrochemical devices. Figure 6(d) shows the nyquist plot which consists of small semicircle regions and a straight line in the low-frequency region reflect the fast rapid charge transfer process and the capacitors diffusive resistance of the electrolyte and the ion diffusion in the host materials, respectively.

CONCLUSIONS

In conclusion, a cabbage like PANI@hydroquinone nanocomposite was successfully prepared via an *in situ* chemical oxidative polymerization procedure using p-benzoquinone nanoparticles as oxidant. The method was very simple in comparison with others. The as prepared composite was characterized by FESEM, TEM, FT-IR, and XPS, and the particular structure has been confirmed. The electrochemical properties were measured by CV, galvanostatic charge/discharge analysis and EIS. It demonstrates that PANI has better conductivity which favors the electronic conductive channels for hydroquinone, and hydroquinone works as a pseudocapacitance component. The CV showed specific capacitance of 126.0 F g⁻¹ at a scan rate of 5 mV s⁻¹.

The specific capacitance retained 85.1% of initial capacitance after 500 cycles at a current density of 1 A g⁻¹.

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