Anthraquinone on Porous Carbon Nanotubes with Improved Supercapacitor Performance

Xiao Chen, Huanwen Wang, Huan Yi, and Xuefeng Wang*
Department of Chemistry, Tongji University, Shanghai 200092, China

Xingru Yan and Zhanhu Guo*
Integrated Composites Laboratory (ICL), Dan F. Smith Department of Chemical Engineering, Lamar University, Beaumont, Texas 77710, United States

*Supporting Information

ABSTRACT: Anthraquinone (AQ) molecules were selected to decorate the lab-made hierarchical porous carbon nanotubes (HPCNTs) to obtain electrode materials (AQ-HPCNTs) for supercapacitors, which showed a remarkable capacitance increment in comparison with pure HPCNTs when tested in 1 M H2SO4 aqueous solution. At a current density of 1 A g⁻¹, the AQ-HPCNTs (mass ratio 7:5) electrode showed an ultrahigh specific capacitance of 710 F g⁻¹, which is much larger than that of the unmodified HPCNTs (304 F g⁻¹). Even at a high discharge current density of 20 A g⁻¹, the specific capacitance of the AQ-HPCNTs (mass ratio 7:5) electrode was still as high as 419 F g⁻¹, indicating an excellent rate capability. Furthermore, all the AQ-HPCNTs electrodes exhibited a long cycle life. Electrochemical behaviors of AQ on the HPCNTs’ surface showed a double pair of redox peaks, which are appropriate for two types of π−π stacking interactions supported by infrared spectra. The excellent capacitive behaviors of the AQ-HPCNTs electrode materials are due to a strong positive synergistic effect between AQ and HPCNTs on the improvement of electrochemical performances.

1. INTRODUCTION

Recently, supercapacitors have received much attention because of their high power density, long cycle life, and low maintenance cost.¹⁻⁴ According to the charge storage mechanism, supercapacitors can be classified into two types: electrical double-layer capacitors depending on the separation of charges and pseudocapacitors via redox reactions.³,⁴ Apparently, the strategy of introducing redox materials into carbonaceous materials provides a chance to merge the merits of these two kinds of mechanisms, which can effectively enhance the capacitance performance of supercapacitors. Therefore, major attention has been devoted to fabricate composite materials,⁵⁻²³ such as carbon−transition metal oxides,⁹⁻¹¹,¹⁶,¹⁷ and carbon−conducting polymers.¹²⁻¹⁴,¹⁸,¹⁹,²²,²³

There are some organic molecules with reversible electrochemical redox couples that could produce pseudocapacitance. For instance, one of the redox-active small organic molecules, anthraquinone (AQ), has been introduced into some carbonaceous materials to obtain promising composite electrode materials for supercapacitors. For example, Pickup and co-workers reported AQ-modified carbon fabrics by a diazonium coupling method with a 40% higher average capacitance.²⁴ Meanwhile, asymmetric supercapacitors assembled with these AQ-modified carbon fabrics as the negative electrode have been reported to possess an improved energy and power density.²⁵,²⁶ Furthermore, Bélanger and co-workers synthesized AQ-modified activated carbon via the spontaneous reduction of the diazonium derivative of AQ by the activated carbon in acetonitrile. With these attached anthraquinone groups, the capacitance of the modified activated carbon was almost doubled (195 F g⁻¹) as compared to that of the unmodified carbon (100 F g⁻¹) in 0.1 M H2SO4.²⁷ Similarly, Wu and co-workers used the 2-aminoanthraquinone (AAQ) to modify graphene hydrogels for supercapacitors, which showed a specific capacitance of 258 F g⁻¹ at 0.3 A g⁻¹.²⁸ Anjos et al. selected three kinds of quinones (1,4-naphthoquinone, 9,10-phenanthrenequinone, and 4,5-pyrenedione) to decorate carbon onions. A maximum capacitance of 264 F g⁻¹ was obtained for 4,5-pyrenedione-modified carbon onions at 1.3 A g⁻¹.²⁹ All of these literatures have demonstrated that AQ modification is an effective way to enhance the capacitive performance of carbonaceous materials. However, further enhancement in the structures with larger specific surface area is still needed to enlarge the AQ loading and to increase...
the portion of pseudocapacitor contribution for practical supercapacitor applications.

In this paper, hierarchical porous carbon nanotubes (HPCNTs) with an ultrahigh surface area (2080 m² g⁻¹) were synthesized and selected to serve as a scaffold. Through solvothermal reaction, AQ molecules were adsorbed onto the surface of HPCNTs with π−π stacking interactions. The redox reactions between hydroquinone and quinone occurred on the surface and then dried at 60 °C overnight. The products were denoted as AQ-HPCNTs (see Table 1 for description, the products were denoted as AQ-HPCNTs). For example, AQ-HPCNTs 3:5 corresponds to the composite material prepared with 0.06 g of AQ and 0.1 g of HPCNTs. The AQ-HPCNTs materials show much enhanced capacitive performance in serving as hybrid electrode materials for supercapacitor applications.

2. EXPERIMENTAL SECTION

2.1. Synthesis of HPCNTs. HPCNTs were prepared by carbonization and activation of polypyrrole (PPy) nanotubes. The PPy nanotubes were obtained by a reactive self-degraded template method revealed in the literature.30 Briefly, 0.405 g (1.5 mmol) of FeCl₃·6H₂O was dissolved in 30 mL of 5 mM methyl orange deionized water solution (0.15 mmol) and then 105 μL (1.5 mmol) of pyrrole monomers was added into the mixture that was stirred for 24 h and then filtrated and dried to obtain PPy nanotubes, which were further annealed at 850 °C for 1.5 h under a nitrogen atmosphere. After cooling down to room temperature, the solid was physically mixed with KOH in a mass ratio of 1:3 and then activated at 850 °C for 1.5 h under a nitrogen atmosphere. The final products, namely, HPCNTs, were washed with 0.1 M HCl and deionized water several times and then dried at 60 °C overnight.

2.2. Synthesis of AQ-HPCNTs. AQ was introduced into HPCNTs by a solvothermal reaction. Typically, a certain amount of AQ was dissolved in 70 mL of dimethylformamide (DMF) and then 0.1 g of HPCNTs was added under vigorous stirring. The mixture was ultrasonically agitated for 60 min, and the stirring was continued for another 2 h to form the well-dispersed solution. Finally, the dark homogeneous solution was transferred into a 100 mL Teflon-lined stainless steel autoclave and heated at 180 °C for 12 h. The products, namely, AQ-HPCNTs, were washed with deionized water several times and then dried at 60 °C for 24 h. For the convenience of description, the products were denoted as AQ-HPCNTs x:y to indicate the mass ratio of AQ (x) to HPCNTs (y). For example, AQ-HPCNTs 3:5 corresponds to the composite material prepared with 0.06 g of AQ and 0.1 g of HPCNTs. The whole process for the preparation of AQ-HPCNTs is shown in Figure 1.

2.3. Characterization. The morphologies of PPy nanotubes, HPCNTs, and AQ-HPCNTs were investigated by field emission scanning electron microscopy (FESEM; Hitachi S-4800, Japan) and transmission electron microscopy (TEM; JEOL, JEM-2010, Japan). The nitrogen adsorption–desorption isotherms of HPCNTs and AQ-HPCNT 5:5 were measured at 77 K by an automatic adsorption instrument (Tristar3000, Micromeritics), and XPS measurement of HPCNTs was tested by a PerkinElmer PHI 6000C ECSA system with monochromatic Al Kα (1486.6 eV) irradiation. The FT-IR spectra of AQ-HPCNTs were recorded at 0.5 cm⁻¹ resolution on a Bruker Vertex 70 V with 0.1 cm⁻¹ accuracy using a three-reflection attenuated total reflection (ATR) accessory with a ZnSe internal reflection element (Harrick Scientific Products). Raman spectra were collected using a 514 nm laser with RM100 under ambient conditions with a laser spot size of about 1 mm.

2.4. Electrochemical Measurement. The electrochemical capacitive behaviors of the AQ-HPCNTs and HPCNTs electrodes were measured on a CHI660D electrochemical workstation (CHI Instruments, Austin, TX, USA). The working electrodes were fabricated by adding a few drops of ethanol to the mixture of 75 wt % active materials, 15 wt % acetylene black, and 10 wt % polytetrafluoroethylene (PTFE) to form homogeneous slurry. Then, the slurry was coated onto the graphite current collector and dried at 60 °C for 12 h. Finally, each working electrode containing about 0.4 mg of electroactive materials was tested in 1 M H₂SO₄ solution using a saturated calomel electrode (SCE) and a platinum electrode as reference and counter electrodes. Cyclic voltammetry (CV), galvanostatic charge–discharge (GC), electrochemical impedance spectroscopy (EIS) measurement, and cycle-life stability tests were employed. CV tests were performed at scanning rates ranging from 2 to 20 mV s⁻¹ over a voltage range of −0.4 to 0.4 V (vs SCE). GC tests were carried out between −0.3 and 0.4 V (vs SCE) at various current densities. EIS measurements were conducted by applying an ac voltage with 5 mV amplitude in a frequency range from 0.1 Hz to 100 kHz at −0.1 V. Finally, the cycle-life stability tests were carried out between −0.3 and 0.4 V (vs SCE) at a charging and discharging current of 10 A g⁻¹ for up to 1000 cycles.

3. RESULTS AND DISCUSSION

3.1. Materials Characterization. A schematic representation of the synthesis of AQ-HPCNTs is shown in Figure 1. HPCNTs were first prepared through the carbonization and chemical activation of the PPy nanotubes. Subsequently, AQ molecules were adsorbed onto the surface of HPCNTs through π−π stacking interactions in the solvothermal process. Figure 2 illustrates the FESEM and TEM images of PPy nanotubes, HPCNTs, and AQ-HPCNTs 5:5, which show tubular structures with a smooth surface and a diameter of 100–400 nm, and the wall thickness of the hollow PPy nanotubes is about 40 nm (Figure 2a,b). Furthermore, in the FESEM images of HPCNTs nanotubes (Figure 2c,d), it can be seen that some part of HPCNTs is broken and unzipped after the carbonization and activation processes. On the whole, HPCNTs still maintain a one-dimensional tubular structure with a slightly rougher surface and a smaller diameter of 90–300 nm. The TEM image (inset of Figure 2d) further demonstrates the hierarchical porous structure of HPCNTs, and the wall thickness of HPCNTs is around 30 nm. The FESEM images of AQ-HPCNTs 5:5 (Figure 2e,f) remain almost the same as that of the precursor HPCNTs. However, on the basis of the results of BET data and FT-IR spectra, which will be described below, it is clear that AQ molecules have been successfully adsorbed on the surface of HPCNTs.

Figure 1. Schematic diagram for the preparation of AQ-HPCNTs.
As shown in Figure 3a, nitrogen adsorption–desorption isotherms of HPCNTs have a distinct type IV hysteresis loop, illustrating a characteristic mesoporous feature. Furthermore, the pore size distribution of the HPCNTs (inset of Figure 3a) is derived from the desorption isotherm using the Barrett–Joyner–Halenda (BJH) method. Obviously, the micropores peaked at 1.9 nm and the mesopores peaked at 3.7 nm are prominent, indicating that the micropores and small mesopores are abundant and concentrated in the HPCNTs. Notably, the BET specific surface area and pore volume of samples are up to 2080 m² g⁻¹ and 1.23 cm³ g⁻¹, respectively. In contrast, nitrogen adsorption–desorption isotherms of the AQ-HPCNTs 5:5 (Figure 3b) exhibit a characteristic type V isotherm. Notice that the BET surface area has sharply decreased to 50 m² g⁻¹, which should be attributed to the adsorption of AQ molecules into the micropores and mesopores of HPCNTs. The pore-size distribution derived using BJH is also given in the inset, from which a declined pore volume is observed, especially in the micropore and small mesopore ranges. That is to say, the AQ modification causes the disappearance of most micropores and small mesopores. As a result, the total pore volume of AQ-HPCNTs 5:5 is only 0.13 cm³ g⁻¹, which is about 10 times smaller than that (1.23 cm³ g⁻¹) of HPCNTs. More surface area and pore structure parameters of HPCNTs and AQ-HPCNTs 5:5 are provided in the Supporting Information (Table S1).

XPS (Figure 4) of HPCNTs demonstrates a predominant C 1s peak at around 284.8 eV, a weak O 1s peak near 532 eV, and a pronounced N 1s peak located at about 400 eV, with atomic concentrations of 87.81, 9.7, and 2.5%, respectively. Without evidence of impurities, the presence of the N 1s peak verifies the doping of N atoms within HPCNTs. The N 1s spectrum (Figure 4b) can be fitted by three peaks located at 401.5, 400.3, and 398.3 eV, which are assigned to quaternary, pyrrolic, and pyridinic nitrogen, respectively. This demonstrates that the N atoms within the pentagonal ring of PPy are partly converted into quaternary or pyridinic nitrogen during the carbonization process.

This ultrahigh specific surface area and hierarchical porous structure are beneficial for AQ adsorption. The presence of AQ...
molecules on the HPCNTs surface can be confirmed by the FT-IR reflectance spectra (Figure 5). As can be seen in Figure 5a, the characteristic peaks of AQ-HPCNTs 1:5 are observed at 698, 1282, 1591, and 1672 cm\(^{-1}\), which are consistent with the adsorptions of pure AQ, strongly confirming the presence of AQ onto HPCNTs. The peak at 1672 cm\(^{-1}\) is due to the C=O stretching vibrations of AQ, while the peaks at 1282 and 698 cm\(^{-1}\) are originating from the aromatic skeleton stretching vibration and C–H out-of-plane deformation vibration, respectively.\(^{32-35}\) Notice that, for the pure AQ sample, the characteristic peaks are observed at 693, 1284, and 1675 cm\(^{-1}\). Apparently, for the AQ-HPCNTs 1:5 sample, the C=O and aromatic skeleton stretching vibrations show red shifts, while the C–H out-of-plane deformation mode exhibits a blue shift, suggesting strong \(\pi-\pi\) stacking interactions between AQ and HPCNTs. With introducing more AQ molecules on the surface of HPCNTs, for example, AQ-HPCNTs 7:5, the absorptions become broader and the peaks move closer to that of pure AQ (Figure 5b).

The chemical structures of HPCNTs and AQ-HPCNTs 5:5 are further analyzed by Raman spectra. As illustrated in Figure 6, the well-known D-band peak at 1339 cm\(^{-1}\) and G-band at 1588 cm\(^{-1}\) occur in both Raman curves of HPCNTs and AQ-HPCNTs 5:5. It is generally accepted that the D-band is assigned to the presence of structure defects and disorders in
the carbon systems, while the G-band is attributed to the stretching vibration of any pair of sp² sites inside the graphitic pattern. Therefore, the intensity ratio between the D-band and G-band (I_D/I_G) gives an indicator of the degree of disorder within the samples. The I_D/I_G values of HPCNTs and AQ-HPCNTs 5:5 are about 0.88 and 0.85, respectively. This indicates that HPCNTs possess a high degree of graphitization and a small amount of defects, while the similarity of these two values reflects the intimate interaction between AQ and HPCNTs. Moreover, the same peak positions and similar peak shapes for both curves also indicate that AQ modification does not disrupt the sp² structure of HPCNTs.

3.2. Electrochemical Characterization. Electrochemical behaviors of all the electrodes were measured with a three-electrode system in an electrolyte of 1 M H₂SO₄. Figure 7a illustrates the CV curves of AQ-HPCNTs 1:5, 3:5, 5:5, and 7:5, unmodified HPCNTs, and pure AQ electrodes in the potential range from −0.4 to 0.4 V at a scan rate of 10 mV s⁻¹. Apparently, the current density of each AQ-HPCNTs electrode is much higher than that of HPCNTs and pure AQ. As expected, the CV curve for HPCNTs displays a rectangular-like shape, which is characteristic of EDLC behavior, whereas a pair of redox peaks is observed in the CV curve for AQ, indicating that the specific capacitance primarily originates from Faradaic capacitance. Comparatively, after AQ modification, the resultant AQ-HPCNTs electrodes possess both Faradaic capacitance and EDLC, which lead to a higher electrochemical capacitance than HPCNTs and pure AQ electrodes. Notably, the background currents of all the AQ-HPCNTs electrodes are a little smaller than that of the unmodified HPCNTs. This may be attributed to the decreased specific surface area after AQ modification (see more details in the Supporting Information, Table S1), since the amplitude of the background current attenuation has a positive correlation with AQ content. Nevertheless, the capacitance increment from the surface redox reaction for each AQ-HPCNTs electrode is much more obvious than the capacitance decrement from the decreased specific surface area.

From the previous literature, the CV curve of AQ shows a single redox couple corresponding to the conversion between AQ and 9,10-dihydroxyanthracene (AQH₂) in the unbuffered acidic aqueous solution. This redox reaction can be described as a two-electron and two-proton reaction (see this equation in the Supporting Information, Figure S1). In our work, the dosage of AQ definitively influenced the electrochemical behavior of the composited materials. As shown in Figure 7a,b, it can be seen that a pair of redox peaks are observed for AQ-HPCNTs 1:5 and 3:5 electrodes, with peak potential separations of 46 and 102 mV, respectively. These values are smaller than that of the pure AQ electrode (164 mV), indicating that the electron transfer between AQ and HPCNTs is a fast process. Figure 7b further reveals the CV curves of AQ-HPCNTs 3:5 at different scan rates. No obvious distortion can be observed from the CV curves as the scan rate increases from 2 to 20 mV s⁻¹, suggesting an excellent capacitance behavior and small equivalent series resistance (ESR). However, in the cases of AQ-HPCNTs 5:5 and 7:5 (Figure 7a,c), unusual electrochemical behaviors are observed. The CV curves show double pairs of redox peaks with one pair overlapped in the oxidation region and two peaks separated in the reduction region. Such a phenomenon is quite rare, which can be explained by the π–π stacking interactions between AQ and HPCNTs. When the number of AQ molecules is small (in the cases of AQ-HPCNTs 1:5 and AQ-HPCNTs 3:5), monolayer AQ molecules adsorb on the surfaces of HPCNTs, forming AQ-HPCNTs π–π stacking interactions. However, when the number of AQ molecules is large enough (in the cases of AQ-HPCNTs 5:5 and AQ-HPCNTs 7:5), another layer of AQ molecules is adsorbed on the HPCNTs, causing a weaker type of interaction that is probably originated from AQ–AQ π–π stacking interactions. Therefore, AQ molecules with two types of π–π stacking interactions exist in the cases of AQ-HPCNTs 5:5 and 7:5, which give them two redox couples. Apparently, two oxidation peaks are too close to be distinguishable in the CV curves of AQ-HPCNTs 5:5 and 7:5; however, two sequential reduction peaks can be clearly observed. Moreover, it can be seen from Figure 7c that the shape of the CV curves at different scan rates for AQ-HPCNTs...
5:5 is stable and almost unchanged for the entire sweep, indicating a fast diffusion of electrolyte ions into the electrode.

The presence of two types of π–π stacking interactions is strongly supported by the FT-IR spectra (Figure 5). For the AQ-HPCNTs 1:5 sample, the characteristic peaks for AQ shift obviously from the absorptions for pure AQ, suggesting strong π–π stacking interactions. However, for the AQ-HPCNTs 7:5 sample, the characteristic peaks for AQ become broader and move closer to the absorptions for pure AQ, demonstrating another layer of AQ molecules absorbed on the surface of HPCNTs with weak interactions.

Figure 8a presents the galvanostatic charge−discharge (GC) curves of AQ-HPCNTs 1:5, 3:5, 5:5, and 7:5, HPCNTs, and pure AQ electrodes within a potential window of −0.3 to 0.4 V at 1 A g⁻¹. Obviously, the charging and discharging time of all the AQ-HPCNTs electrodes is much longer than that of HPCNTs and pure AQ, which is due to the combination of EDLC and Faradaic capacitance. Moreover, the GC curves of AQ-HPCNTs 5:5 and 7:5 electrodes show one charge voltage plateau and two discharge voltage plateaus, whereas one charge−discharge voltage plateau is observed for AQ-HPCNTs 1:5 and 3:5 and pure AQ electrodes. This is in agreement with the aforementioned results of AQ-HPCNTs' CV curves. Comparatively, the GC curves of HPCNTs exhibit a nearly linear shape, which is another typical characteristic of EDLC.

The specific capacitance (C) of the electrode can be calculated from the discharge curves according to eq 1

\[ C = \frac{I\Delta t}{m\Delta V} \]

where I is the current density, Δt the discharge time, m the mass of the active material, and ΔV the voltage drop during the discharge process. The specific capacitance of AQ-HPCNTs 1:5, 3:5, 5:5, and 7:5 is calculated to be 414, 650, 663, and 710 F g⁻¹ at 1 A g⁻¹, respectively. Apparently, these values are much higher than those of the pristine HPCNTs (304 F g⁻¹ at 1 A g⁻¹) and pure AQ (42 F g⁻¹ at 1 A g⁻¹). This remarkable capacitance improvement can be attributed to the additional pseudocapacitance of AQ and the strong positive synergistic effects between AQ and HPCNTs. Moreover, there is a clear trend that, with increasing the mass ratio of AQ to HPCNTs, the capacitance value increases monotonically. However, when the mass ratio of AQ to HPCNTs further increased (in the cases of AQ-HPCNTs 9:5 and 11:5), a specific capacitance decrement appears. More specifically, the specific capacitances of AQ-HPCNTs 9:5 and 11:5 are 641.4 and 588.6 F g⁻¹, respectively (Supporting Information, Figure S2), which are lower than that of AQ-HPCNTs 7:5. That is to say, 7:5 is the optimal composition in terms of specific capacitance.

Moreover, the GC curves of AQ-HPCNTs 3:5 at various current densities are presented in Figure 8b. These curves show typical pseudocapacitance characteristics, and the specific capacitance of 454 F g⁻¹ is still obtained at a high current density of 10 A g⁻¹, suggesting the excellent rate capability. No obvious iR drop is observed for any of the curves, meaning that the electrode has a low internal resistance once again. Similarly,
the GC curves of AQ-HPCNTs 5:5 at various current densities are presented in Figure 8c. These curves show one charge voltage plateau and two discharge voltage plateaus at low current density (1 and 2 A g\(^{-1}\)). At a specific current of 10 A g\(^{-1}\), the specific capacitance of the AQ-HPCNTs 5:5 is 436 F g\(^{-1}\), 65.8% of that at 1 A g\(^{-1}\) (663 F g\(^{-1}\)). Furthermore, the calculated specific capacitances of AQ-HPCNTs and HPCNTs at different current densities are shown in Figure 8d. The specific capacitance of HPCNTs decreased from 304 to 169 F g\(^{-1}\) with current density increasing from 1 to 20 A g\(^{-1}\). In other words, at a higher current density of 20 A g\(^{-1}\), HPCNTs hold 55.6% specific capacitance of that at 1 A g\(^{-1}\). Similarly, the capacitance retention of AQ-HPCNTs 1:5, 3:5, 5:5 and 7:5 is 78.3, 64.6, 60.1, and 59.1%, respectively. Obviously, the capacitance retention of AQ-HPCNTs materials progressively decreases with increasing the AQ content. This tendency can be explained by the ion diffusion and electron transport resistance increment caused by the presence of double-layer or multilayer adsorption of AQ. With further increasing the AQ loading (in the cases of AQ-HPCNTs 9:5 and 11:5), the capacitance retentions are even lower than that of HPCNTs (Supporting Information, Figure S3). However, the rate capability of each AQ-HPCNTs electrode with a mass ratio less than or equal to 7:5 is still superior to that of HPCNTs, suggesting that AQ-HPCNTs composite materials possess a rapid current response, which is highly desirable to be applied in supercapacitors.

Electrochemical impedance tests were carried out at −0.1 V with a frequency range from 0.1 to 10\(^8\) Hz to evaluate the charge transfer and electrolyte diffusion in AQ-HPCNTs 3:5 and 5:5, HPCNTs, and pure AQ electrodes. A semicircle in the high-frequency region and a straight line in the low-frequency region are observed for each electrode (Figure 9). In contrast with AQ-HPCNTs 3:5 and 5:5 and pure AQ electrodes, the slope of HPCNTs’ impedance plot is almost vertical, reflecting the nearly ideal capacitive behavior. From the enlarged view in the inset of Figure 9, each electrode is observed to have its respective diameter of the semicircle in the high-frequency region, which corresponds to the charge-transfer resistance caused by the Faradaic reaction on the electrode surface.\(^{42,43}\) The charge-transfer resistance of the AQ-HPCNTs 3:5 and 5:5 electrodes is about 0.26 and 0.40 ohm, respectively. This value is between that of the HPCNTs electrode (0.18 ohm) and the AQ electrode (0.56 ohm), which further indicates that the combination of AQ and HPCNTs facilitates the charge transfer during the redox process of AQ. Another difference observed in the inset of Figure 9 is the high-frequency intercept along the x axis, which corresponds to the internal resistance, including the electrolyte resistance, the intrinsic resistance of the active material, and the contact resistance at the active material/current collector interface.\(^{43}\) The pure AQ electrode shows the largest internal resistance of 2.80 ohm, and HPCNTs electrode shows the smallest one of about 1.83 ohm, whereas the values of AQ-HPCNTs 3:5 (2.16 ohm) and AQ-HPCNTs 5:5 electrode (2.29 ohm) are among them. Apparently, the intrinsic resistances of AQ-HPCNTs are still a little larger than that of HPCNTs, but a significant improvement has already been achieved when compared with pure AQ.

Furthermore, the cycle tests of AQ-HPCNTs 3:5 and 5:5 and HPCNTs were measured. As shown in Figure 10, after 1000 cycles at 10 A g\(^{-1}\), the capacitance retentions of AQ-HPCNTs 3:5 and 5:5 and HPCNTs are 96.45, 93.75, and 92.31%, respectively. These high values illustrate that the noncovalent modification of HPCNTs through AQ molecules does not sacrifice the cycle-life stability of HPCNTs. The excellent cycle performance of AQ-HPCNTs indicates that a stable energy storage process is repeated during the long cycle service and the charge–discharge process does not induce microstructural changes in the HPCNTs. Notice that the cycle performance of AQ-HPCNTs 3:5 is superior to that of AQ-HPCNTs 5:5, which is due to the loss of AQ molecules during the long-term test. For the same reason, the capacitance retentions of AQ-HPCNTs 9:5 and 11:5 decreased to 84.68% and 81.52%, respectively, (Supporting Information, Figure S4). The introduction of AQ (especially in low AQ content) results in an enhanced rate capability and cycle performance as compared to the pristine HPCNTs. This may be due to the high reversibility of AQ on HPCNTs through AQ molecules does not sacrifice the cycle-life stability of HPCNTs. The excellent cycle performance of AQ-HPCNTs indicates that a stable energy storage process is repeated during the long cycle service and the charge–discharge process does not induce microstructural changes in the HPCNTs. Notice that the cycle performance of AQ-HPCNTs 3:5 is superior to that of AQ-HPCNTs 5:5, which is due to the loss of AQ molecules during the long-term test. For the same reason, the capacitance retentions of AQ-HPCNTs 9:5 and 11:5 decreased to 84.68% and 81.52%, respectively, (Supporting Information, Figure S4). The introduction of AQ (especially in low AQ content) results in an enhanced rate capability and cycle performance as compared to the pristine HPCNTs. This may be due to the high reversibility of AQ on HPCNTs. The π–π stacking interactions between AQ and HPCNTs lead to ultrafast redox reactions between AQ and AQH\(_2\). The positive synergetic effect in tert-butyldihydroquinone-decorated graphene nanosheets has also

![Figure 9. Nyquist plots of AQ-HPCNTs 3:5 and 5:5, HPCNTs, and pure AQ electrodes with the enlarged view of the high-frequency region in the inset.](Image)

![Figure 10. Cycling performance of AQ-HPCNTs 3:5 and 5:5 and HPCNTs at a current density of 10 A g\(^{-1}\).](Image)
been reported with an enhanced rate capability and good cycle performance.14

4. CONCLUSIONS
In this paper, we have demonstrated that AQ molecules are adsorbed onto the surface of HPCNTs by a solvothermal reaction and the electrochemical performances of the AQ-HPCNTs are improved obviously when compared with those of HPCNTs. After AQ modification, ultrahigh specific capacitances of 650, 663, and 710 F g⁻¹ are obtained, respectively, for AQ-HPCNTs 3:5, 5:5, and 7:5 electrodes at a current density of 1 A g⁻¹, which are much higher than those of the unmodified HPCNTs (304 F g⁻¹) and pure AQ (42 F g⁻¹). The AQ modification also results in an excellent rate capability and improved cycle life. Unusual electrochemical behaviors of AQ on the surface of HPCNTs are observed, which are originated from the two types of π–π stacking interactions, i.e., AQ-HPCNTs and AQ-AQ π–π stacking interactions. Therefore, AQ-modified HPCNTs promise to be a desirable electrode material for supercapacitors.

ASSOCIATED CONTENT

Supporting Information
The reaction equation between AQ and AQH₂ and the surface area and pore structure parameters of HPCNTs and AQ-HPCNTs 5:5 are provided, as well as the detailed electrochemical test results of samples AQ-HPCNTs 9:5 and 11:5. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Authors
*E-mail: xfwang@tongji.edu.cn.
*E-mail: zhanhu.guo@lamar.edu.

Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (Nos. 21173158 and 21373152).

REFERENCES

(28) Wu, Q.; Sun, Y. Q.; Bai, H.; Shi, G. Q. High-Performance Supercapacitor Electrodes Based on Graphene Hydrogels Modified


