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Controlled synthesis of polyaniline inside mesoporous carbon for electroanalytical sensors

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A novel electroanalytical system was developed using polyaniline (PANI) functionalized ordered mesoporous carbon (CMK-3). Hydrophilic surface modification of CMK-3 is necessary and enables monomers to penetrate the pore channels of CMK-3, which makes it possible for the formation of PANI layers inside the pores of CMK-3 via in situ polymerization. The structures of the surface-modified ordered mesoporous carbon (m-CMK-3) and the PANI functionalized composites (CMK-PANIs) were characterized by X-ray diffraction, thermal gravimetric analysis, Fourier transform-infrared spectroscopy, transmission electron microscopy, and N₂ adsorption measurements. The catalytic effect of the resultant CMK-PANI composite electrodes with various PANI loadings on the hydroquinone/quinone (H₂Q/Q) redox reaction, was investigated. It was found that the CMK-PANI composite electrode with 25 wt% loading of PANI (CMK-PANI-1) has a higher electrochemical properties than both the m-CMK-3 electrode and the CMK-PANI composite electrode with 45 wt% loading of PANI. This high electrochemical properties is due to not only the relatively high specific surface area of 447 m²g⁻¹ and pore volume of 0.3 ml g⁻¹ and also nearly all the interior active sites are accessible for the electrolyte. Furthermore CMK-PANI-1 has also shown higher current values (I_p) in the cyclic voltammograms than the m-CMK-3 electrode. It is believed that the strategy may be used in fabricating other functional polymers inside mesoporous carbons with controlled pore channels for many applications, such as electrochemical sensors and biosensors with potential high performances.

Introduction

Porous carbons are useful in a wide range of applications, which include catalyst supports,¹ adsorbents,^{2,3} electrical double layer capacitors⁴ as well as electrode materials.⁵ Since the report of Ryoo *et al.* on the mesoporous carbon CMK-1 in 1999,^{6,7} ordered mesoporous carbons (OMCs) as electrode materials have been extensively studied,⁸ because of their ordered pore channels, high specific surface areas, narrow pore size distributions, high mechanical stability and electric conductivity. Despite their high potential in various applications, OMCs have found only a few electroanalytical usages. In 2007, Zhou *et al.* developed a polyoxometalate-OMC modified electrode, which shows high stability, fast response and good electrocatalytic activity for the determination of some biological molecules, including nitrite, bromate, ionate, and hydrogen peroxide and L-cysteine.^{9,10} Almost at the same time, OMC was adopted as a protein immobilization material to study the direct electrochemistry of hemoglobin (Hb).¹¹ Similarly, enzyme was immobilized in a Pt

nanoparticle/mesoporous carbon matrix to fabricate a glucose biosensor.¹²

As is well known, OMCs are excellent adsorbents for phenolic compounds owing to their abundant porous structure and high specific surface area, so they are promising candidates for the preconcentration and determination of phenolic compounds. An electrode made from mesoporous carbon CMK-3 has shown greater sensitivity to hydroquinone in comparison with electrodes made from multi-walled carbon nanotubes and Vulcan XC-72 carbon.¹³ Hou *et al.* investigated the electrocatalytic properties of OMCs with different pore characteristics for the oxidation of hydroquinone.¹⁴ Despite all of this progress, the hydrophobic nature of mesoporous carbons makes it difficult to explore the further applications of OMC in the biological field. Surface modification was thus investigated to change the surface characteristics of OMC in order to improve its properties. Generally, COOH groups can be introduced on the surface of carbon materials by using various oxidation agents.¹⁵ It has been shown that carboxy-mesoporous carbon obtained by a simple oxidation using ammonium persulfate solution (APS) presents a better adsorption capability for proteins than pristine mesoporous carbon.¹³

Polymeric materials having functional groups such as carboxylic acid, amine, hydroxyl, amidoxime, and sulfuric acid groups have attractive tunable properties. Observations of catalytic effects of pure polyaniline coatings on a host of redox reactions, include the quinone/hydroquinone couple, have been reported.^{16,17} PANI has been also considered as one of the most

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promising materials for electrode materials, not only owing to its high specific capacitance, but also because of ease of polymerization in aqueous media, high stability in air, simplicity in doping/dedoping. However, the main drawback for PANI as an electrode material is the poor cycling stability due to the large volumetric change in the doping/dedoping process. Therefore, the combination of porous carbon and PANI seems to be an effective method to fully utilize their respective advantages. However, it is not easy to control the growth of polymers inside ordered mesoporous carbon, owing to the poor wettability of the carbon surface for polar solvents. As a result, the polymerization process tends to complete on both the external and internal surface. Early in 2003, an impregnation then polymerization route was used to fabricate polymer-carbon composites and it was found that polystyrene was formed on both the inner and outer surfaces of the mesoporous carbon.¹⁸ In 2006, Wang *et al.* grew whisker-like PANI on the surfaces of mesoporous carbon. Unfortunately, the PANI was also formed on the external surface of the mesoporous carbon.¹⁹ In view of the fact that the mesopores of OMC were filled by PANI molecules, the specific surface area of the resultant composite was only $35 \text{ m}^2 \text{ g}^{-1}$ and thus the electric double-layer capacitance of OMC could not have been sufficiently utilized. In situ polymerization approach has been used for the polymerization of 3,4-ethylenedioxythiophene (PEDOT) with mesoporous carbon, but it turned the mesoporous structure into a nonporous structure, as the pores of mesoporous carbon CMK-3 were filled with PEDOT.²⁰ In sensor systems, materials with porous structures are preferred to nonporous structures, because the pores can provide channels for the interaction of active sites with guest molecules. Clearly, there is a great desire to develop a new strategy to incorporate functional polymers inside mesoporous carbons without altering their porous structures.

Here, we report for the first time the controlled synthesis of conducting polyaniline (PANI) inside OMC and the study of its application in biosensors. In this paper, PANI functionalized mesoporous carbon CMK-3 with porous channels was obtained by a combination of a simple surface modification and then in situ polymerization method. The morphology and pore structure of the resultant composites were investigated, and electrochemical characteristics were further studied. The electrochemical performance for electrocatalytic oxidation of hydroquinone (HQ) was investigated.

Experimental

Synthesis of mesoporous carbon

Triblock poly(ethylene oxide)-*b*-poly(propylene oxide)-*b*-poly(ethylene oxide) copolymer EO₂₀PO₇₀EO₂₀ (P123, Mw = 5800) was purchased from Aldrich. All chemicals used in this investigation were as received without further purification. The synthesis process of the self-ordered mesoporous silica SBA-15 is the same as described elsewhere under acidic conditions.²¹ The ordered mesoporous carbon was made from self-ordered mesoporous silica SBA-15 and the synthesis process is similar to that described by Jun *et al.* except the final carbonization.⁶ Generally, 1.25 g of sucrose was added into a solution of 0.14 g H₂SO₄ in 5 g of H₂O. After mixing fully, the solution was put into a drying

oven at 373 K for 6 h, then the temperature was increased to 433 K and held for 6 h. After adding further 0.8 g of sucrose, 0.09 g of H₂SO₄ and 5 g of H₂O, the mixture was heated again at 373 and 433 K successively for 6 h at each temperature. The carbonization was carried out by pyrolysis at 873 K under nitrogen gas environment. The silica template was removed using 5 wt% hydrofluoric acid (HF) at room temperature. The ordered mesoporous carbon CMK-3 was then obtained.

Synthesis of PANI inside CMK-3

The CMK-3 was surface modified by using sulfuric acid before the incorporation of PANI into it. In a typical synthesis: 0.28 g mesoporous carbon CMK-3 was treated with 2 M H₂SO₄ at 353 K for 3 h and then washed with deionized water, and dried at 353 K. The surface modified CMK-3 is denoted as m-CMK-3. The synthesis of PANI inside CMK-3 can be described as follows: the vapor of monomer aniline was absorbed inside the pores of m-CMK-3 at 313 K for 5 or 10 h. After this, 1 ml of ammonium persulfate aqueous (0.31 g APS in 25 ml of 0.2 M HCl solution) was added dropwise into the powder (0.5 g). Polymerizations were performed at ambient temperature for several hours and then dried under vacuum. The samples thus prepared were designated as CMK-PANI-1 and CMK-PANI-2, respectively.

Characterizations

The synthesized samples were characterized by X-ray diffraction (XRD) using a RigakuD/max2550VL/PC system operated at 1600 W power (40 kV, 40 mA) with Cu K α radiation ($\lambda = 0.15406 \text{ nm}$), at a scan rate of 5° min^{-1} and a step size of 0.050° in 2θ . Nitrogen adsorption measurements at 77 K were performed using an ASAP2020 volumetric adsorption analyzer, after the samples have been outgassed for 8 h in the degas port of the adsorption apparatus. The pore size distributions were determined by Barrett-Joyner-Halenda (BJH) analysis of the N₂ adsorption isotherm. Transmission electron microscopy (TEM) and energy-dispersive X-ray spectroscopy (EDX) were carried out on a JEOL 2010 microscope. Fourier transform-infrared (FT-IR) measurements were recorded with a PE Paragon 1000 spectrophotometer. Thermal gravimetric analysis (TGA) was conducted on a PE TGA-7 instrument with a heating rate of 20° C/min . Electrochemical measurements were carried out on a CHI-660C electrochemical workstation (Chenhua, Shanghai, China) with a three-electrode system: a glassy carbon (GC) electrode and a platinum wire as the working and auxiliary electrodes, respectively, and a saturated calomel electrode (SCE) as the reference electrode.

Preparation of modified electrode

The glassy carbon electrode (GC, 2 mm in diameter) surface was polished to a mirror finish with $0.02 \mu\text{m}$ alumina slurry and successively sonicated in 1 : 1 nitric acid, acetone and doubly distilled water. The functionalized ordered mesoporous carbon modified electrode was fabricated by the rubbing method as described here:²² the pretreated GC electrode was rubbed over the gel placed on a smooth glass slide, and the gel was mechanically attached to the surface. Then the gel on the electrode

surface was smoothed with a spatula to leave a thin gel film on the GC electrode surface.

Results and discussion

Synthesis of PANI inside m-CMK-3

CMK-PANI-1 and CMK-PANI-2 were made from m-CMK-3, with loading contents of PANI of 25 and 45 wt%, respectively from weight analysis. Fourier transform-infrared (FT-IR) spectra of CMK-PANI-1, CMK-PANI-2, m-CMK-3 and the original CMK-3 are shown in Fig. 1. As compared with the original CMK-3, the carboxyl functionalized CMK-3 surface has been confirmed by a new band at around 1665 cm^{-1} , typical of the stretching vibration of C=O present on the surface of m-CMK-3 (COOH). A characteristic stretching vibration of C–O groups at 1280 cm^{-1} appears in the FT-IR spectrum of m-CMK-3.²³ After the polymerization of aniline inside m-CMK-3, the increased intensities of the two adsorption peaks at around 2900 cm^{-1} ($\nu_{\text{C-H}}$) were observed. m-CMK-3 loaded with PANI (CMK-PANI) shows a shift of the carboxyl band from 1665 to 1735 cm^{-1} corresponding to $\nu_{\text{C=O}}$ of carboxylic groups. This distinct blue shift is owing to the hydrogen bonding of PANI with the carboxyl groups on the inner surface of m-CMK-3 in both composite CMK-PANI-1 and CMK-PANI-2. This observation is consistent with the results obtained by others, who reported a coulombic interaction between IBU and MCM-41.²⁴ In the spectra of CMK-PANI-1 and CMK-PANI-2, the characteristic peaks at 1562 and 1482 cm^{-1} correspond to the quinoid ring and the benzene ring, respectively. The bands in the range $1200\text{--}1400\text{ cm}^{-1}$ are the C–N stretching bands of an aromatic amine. From the literature, it can be deduced that HCl-doped PANI was obtained in our experiment.²⁵ The bands at 1027 cm^{-1} can be ascribed to --SO_3 . This result indicates that polyaniline was presented in the composites CMK-PANI-1 and CMK-PANI-2.

The structures of m-CMK-3 with different loading content of PANI (CMK-PANI) were characterized by X-ray diffraction (XRD) as shown in Fig. 2. The sample m-CMK-3 exhibits three well resolved reflections in the 2θ range between 2 and 5 , which can be indexed to an ordered hexagonal lattice typical of ordered mesoporous carbon with the unit length 8.5 nm . Distinct peaks were detected in CMK-PANI-1 in the small diffraction angle range ($2\theta < 2^\circ$), which illustrate the incorporation of PANI inside m-CMK-3 did not result in collapse of the ordered structure.

Fig. 1 FT-IR spectra of the resulting CMK-PANI-1, CMK-PANI-2, m-CMK-3 and the original CMK-3 as a comparison.

Fig. 2 Small-angle (a) and wide-angle (b) XRD patterns of m-CMK-3 and the composites CMK-PANI-1 and CMK-PANI-2.

In contrast, only a broad hump was observed for the sample CMK-PANI-2, possibly attributed to the destruction of the ordered structures, owing to too much PANI being loaded. This is further confirmed by transmission electron microscopy (TEM) observation. For CMK-PANI-1 and CMK-PANI-2, the shift of the diffraction peaks to lower angles would be attributed to the introduction of the polymers inside the pores. The XRD intensity of CMK-PANI-1 composite is significantly higher than that of the original m-CMK-3, due to the polymer filling of the micropores of the carbon frameworks for the same reason described by Choi *et al.*¹⁸ However, the (100) reflection with very weak peaks was detected for the sample CMK-PANI-2. The decrease of the intensity could be explained in terms of a loss of scattering contrast between the pore walls and pores of m-CMK-3 filled with PANI as described by Sauer *et al.*²⁶ or disappearance of the ordered pore structure to some extent. Thus the intensity increase of the diffraction peaks indicates the PANI coating on the surface of m-CMK-3 is thin so that homogeneous pore channels are still open. The d-spacing of CMK-PANI-1 was calculated to be about 9.2 nm which is 1.8 nm larger than that of m-CMK-3. The wide angle X-ray diffractions of the deposition products did not show distinct peaks, a result of the amorphous nature of the obtained products (Fig. 2b).

N_2 adsorption/desorption isotherms of the CMK-3, m-CMK-3, CMK-PANI-1 and CMK-PANI-2 are compared and shown in Fig. 3. The specific surface area of m-CMK-3 is reduced slightly to $717\text{ m}^2\text{g}^{-1}$ from $790\text{ m}^2\text{g}^{-1}$ of the original CMK-3 (Fig. 3a), whereas the average pore diameter of m-CMK-3 increases to around 3.5 nm from around 3.3 nm of the original CMK-3, determined by Barrett-Joyner-Halenda analysis (BJH method) (Fig. 3b). Thus the surface modification of CMK-3 using $2\text{ M H}_2\text{SO}_4$ can cause small changes in the pore diameter and surface area but would not result in collapse of the structures. After the polymerization of PANI inside the pores, the surface areas were

Fig. 3 N₂ adsorption/desorption isotherms of CMK-3, m-CMK-3, composites CMK-PANI-1 and CMK-PANI-2 (a) and the corresponding pore size distributions obtained by using the Barrett-Joyner-Halanda (BJH) model (b).

found to be 447 m²g⁻¹ and 120 m²g⁻¹, for CMK-PANI-1 and CMK-PANI-2, respectively. The average pore size of CMK-PANI-1 has decreased a little from 3.5 to 3.4 nm determined by the nitrogen adsorption. Combined with the XRD results, the wall thickness was increased around 0.85 nm after the formation of PANI inside the m-CMK-3 for CMK-PANI-1. Collectively, these data confirm that the pores are grafted with PANI. It's worth noting that the system (CMK-PANI-1) has an average pore diameter of 3.4 nm with pore volume of 0.3 cm³g⁻¹ even though 25 wt% of PANI formed inside the pores.

As for the sample CMK-PANI-2, much lower surface area of 120 m²g⁻¹ and pore volume of 0.1 cm³g⁻¹ were obtained. Theoretically, the BET surface area of CMK-PANI-2 should be around 400 m²g⁻¹ by the simple sum calculation from the weight content (55 : 45) of m-CMK-3 and PANI (the BET surface area of pure PANI measured by N₂ adsorption is 11 m²g⁻¹). The distinct decrease of the specific surface area compared with the original composite m-CMK-3 is mainly ascribed to the presence of dense polyaniline, implying that most mesopores of CMK-PANI-2 are blocked by PANI molecules.

Transmission electron microscopy was conducted to investigate the morphologies and microstructures of m-CMK-3 and the CMK-PANI composites. TEM images clearly revealed the presence of hexagonally ordered porous structures for both m-CMK-3 and the composites (Fig. 4a, c, e). TEM images of m-CMK-3 parallel to the pore direction are shown in Fig. 4b. The ordered porous structures were maintained in CMK-PANI-1 as demonstrated in Fig. 4d, illustrating that uniform polymerization was achieved throughout the porous network. No bulk aggregation of PANI was observed on the outer surface. That means the polymerization of PANI is confined in the pores of m-CMK-3. This is in good agreement with the results obtained from N₂ adsorption/desorption isotherms, and further proved by thermal gravimetric analysis (TGA) (Fig. 5). The largest weight

Fig. 4 TEM images of m-CMK-3 (a), composite CMK-PANI-1 (c), CMK-PANI-12 (e) and the high resolution images of m-CMK-3 (b), composite CMK-PANI-1 (d) and CMK-PANI-2 (f).

loss occurred at around 580 °C for m-CMK-3 and at around 450–460 °C for both CMK-PANI-1 and CMK-PANI-2. The reduction of the largest weight loss temperature for the CMK-PANI composites resulted from the polymerization of PANI inside the pores. Unlike the mixture of PANI with carbon (PANI + m-CMK-3), only one peak at 460 °C was observed for the largest weight loss of CMK-PANI-1. The data clearly demonstrate that the PANI coating is located inside the supporting pores and does not form separate material when the PANI loading is at 25 wt%.

Comparing with CMK-PANI-1, CMK-PANI-2 shows a salient morphology change of the internal surface of mesopores. A higher-magnification image shown in Fig. 4f illustrates

Fig. 5 TGA curves of composites CMK-PANI-1 and CMK-PANI-2, m-CMK-3 and the mixture of PANI and m-CMK-3 (PANI + m-CMK-3) as a comparison.

that the formation of PANI in the pore space results in a zigzag inner surface (indicated by the arrows), and some of the pores were blocked by filling PANI. This observation is consistent with the rapid decrease of the specific surface area and pore volume. Although the presence of PANI is difficult to observe directly from TEM due to the poor contrast between polymer and carbon, we can detect the existence of PANI thorns covering the external surface of the mesoporous carbon as indicated by the white circle shown in Fig. 4e. The existence of PANI on the external surface of CMK-3 was further proved by TGA analysis, as shown by the 6 wt% weight loss from 150 to 450 °C (Fig. 5).

Based on the analysis above, we conclude that the synthesis of PANI can be controlled into m-CMK-3, which can be attributed to the polymerization of aniline (ANI) inside m-CMK-3. The polymerization mechanism is schematically described in Scheme 1. Firstly, the surface modification of CMK-3 with $-\text{COOH}$ makes it easy for ANI to access the pore channels of CMK-3. At the same time, the surface modification changes the surface reactivity, increasing the interaction of the guest molecules with the inner carbon surface of m-CMK-3. Secondly, in situ polymerization of ANI results in PANI inside CMK-3. With a limited amount of PANI loading, PANI molecules in the composite CMK-PANI-1 are distributed on the inner surface of the pore channels of m-CMK-3, leaving the pore channels for the dispersion of guest molecules such as electrolyte. That means, the loading of PANI in the pore channels will enhance the electrochemical performance of the composite as an electrode for biosensors. However, if too much PANI is loaded (CMK-PANI-2), most of the pore channels are blocked by the excess PANI and the electrochemical performance of the composite will decrease. That is to say that there is an optimum loading of PANI in the composite in terms of the electrochemical performance.

Electrochemical reactivity

In order to evaluate the electrochemical characteristics of this new kind of composite material, cyclic voltammetry (CV) tests were performed to characterize the electrochemical capacitance performance of the samples and the results are given in Fig. 6. The typical rectangular-shaped curve suggests that the m-CMK-3 electrode exhibits an ideal double-layer capacitor behavior. The shape of the CV curves (within the potential window from -0.2 to 1.0 V vs. a saturated calomel electrode (SCE) at a scan rate of 100 mV s^{-1}) shown in Fig. 6a indicates that the

Scheme 1 A schematic illustration of the controlled synthesis of PANI inside CMK-3 via a surface modification then in situ polymerization method.

Fig. 6 A comparison of cyclic voltammograms for CMK-PANI-1, CMK-PANI-2 and m-CMK-3 within the potential window -0.2 to 1.0 V vs. SCE in $0.05 \text{ M H}_2\text{SO}_4$ at the scan rate of 100 mV s^{-1} (a) and cyclic voltammograms of 1 mM hydroquinone recorded at CMK-PANI-1, CMK-PANI-2 and m-CMK-3 electrodes in 0.20 M phosphate buffer ($\text{pH } 7.40$) (b).

capacitance characteristic of the composite CMK-PANI-1 is distinct from that of an electric double layer capacitor. The observed two pairs of cathodic and anodic peaks (C1/A1 and C2/A2) resulted from the redox capacitance with the peak currents of C1 and C2 at 0.24 and 0.48 V , respectively. The C1/A1 peaks are attributed to the redox transition of the PANI between a semiconducting state (leucoemeraldine form) and a conducting state (polaronic emeraldine form). The C2/A2 peaks are due to the emeraldine–pernigraniline transformation.²⁷ This is because the pore channel structure of CMK-PANI-1 with the mesopores of 3.4 nm in size enables the electrochemical accessibility of electrolyte to the PANI phase, which is fundamental for materials showing the character of supercapacitors. However, the further increase of PANI in the composite did not significantly increase the contribution of PANI as shown in Fig. 6a for the sample CMK-PANI-2. The voltammogram of CMK-PANI-2 is almost the same as that of m-CMK-3, resulting just from the double layer capacitance of m-CMK-3, no signs of the faradiac capacitance of PANI were observed. This result demonstrates that the capacitance of the PANI was not realized if the composite is overloaded with the PANI, due to the poor accessibility for electrolyte ions to the PANI phase (Scheme 1). Consequently, CMK-PANI-1 displays a large specific charge and discharge capacity which is more than three times those of m-CMK-3 and CMK-PANI-2.

In the presence of hydroquinone, the cyclic voltammograms are given in Fig. 6b. The bare m-CMK-3 and CMK-PANI-1 show a similar large potential gap about $\Delta E_p = 180 \text{ mV}$ between the redox peaks. The peak separation value drops to $\Delta E_p = 80 \text{ mV}$ for CMK-PANI-2 with the cathodic potential at 0.155 V and anodic potential at 0.235 V . This suggests CMK-PANI-2 exhibits a faster electron transfer rate than both the PANI-CMK-1 and m-CMK-3, attributed to the dense

polyaniline inside the CMK-3 and a small amount of PANI outside the pores. However, the peak current of CMK-PANI-2 decreased greatly as compared with that of m-CMK-3. It can be explained in term of the inaccessibility of PANI in the pores by the electrolyte, because the pore channels were largely blocked by excess PANI as discussed above. It is worth mentioning the average peak current (i_{av} , defined as the average of cathodic and anodic peak currents) at CMK-PANI-1 for HQ is 1.5 times larger than that of CMK-PANI-2, attributed to the homogeneous dispersion of PANI inside the pores thus great accessibility for the electrolyte. It was reported that mesoporous carbon itself exhibited high electrocatalytic properties toward the oxidation of HQ.¹⁴ In view of the fact that the average peak current i_{av} of CMK-PANI-1 is 25% higher than that of m-CMK-3, the CMK-PANI composite is clearly a promising candidate for effective electrochemical sensors.

Conclusions

A novel electroanalytical system was synthesized based on polyaniline (PANI) functionalized ordered mesoporous carbon (CMK-3). The conducting PANI forms in situ inside CMK-3 pores after the surface modification treatment of CMK-3, resulting in a PANI/mesoporous carbon composite. The polymer layers coated on the internal surface of CMK-3 have been proved by the TEM, N₂ adsorption measurement and further the resulting electrochemical properties. CMK-3 with 25 wt% loading of PANI possesses a high specific surface area of 447 m²g⁻¹, making PANI molecules available for faradaic reaction and mesoporous carbon a stronger support for the maintenance of electrical conductivity and mechanical strength of PANI. The composite with 45 wt% of PANI results in a great decrease of the specific surface area to 120 m²g⁻¹, attributed to the blockage of the pores by the excess PANI as well as the existence of PANI on the outer surface of CMK-3. The composite electrode with 25 wt% PANI shows excellent electrocatalytic performance for the oxidation of HQ and is a potential advanced carbon electrode material for electrochemical sensing applications. It would be expected that the strategy used in this investigation may be used in fabricating other functional polymers inside mesoporous carbons with controlled pore channels for other applications.

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