Synthetic Biopigment Supercapacitors

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ABSTRACT: Biomass-based energy storage devices have drawn increasing attention owing to their renewability and sustainability, particularly that the heteroatom-doped carbons derived from natural polymers are regarded as the promising candidates in discovering advanced electrode materials for supercapacitors. This work has developed a facile one-pot fabrication strategy toward synthetic pheomelanin nanoparticles with controllable size and chemical composition (i.e., sulfur content) via the copolymerization of dopamine and cysteine. The resulting synthetic pigment materials possess outstanding thermal stability and are able to directly transform into monodispersed S,N-codoped carbon spheres with unaltered morphology. Compared with conventional polydopamine-based carbon spheres, the present carbonized pheomelanin nanoparticles with electroactive sulfur atoms could possess lower charge-transfer resistance and consequently higher specific capacitance (e.g., 243 F g\(^{-1}\) at 1 A g\(^{-1}\)). This research continues to inspire researchers to develop new kinds of energy storage materials based on synthetic biopigment materials.

KEYWORDS: synthetic pheomelanin, biopigment, N,S-codoping, supercapacitors

INTRODUCTION

Highly efficient energy storage devices play important roles in meeting the requirements of both excellent energy density and higher power output for numerous applications, including plug-in electric vehicles, electrical starter systems, and backup power sources.\(^1\) Among them, supercapacitors have been widely employed on account of their unique features, including superior power density, extended cycle life, and rapid charge/discharge rate.\(^3\)−\(^6\) It has been regarded as the most appropriate energy storage system to fill the vacancy amid the conventional low energy density capacitors and low power density batteries.\(^3\) The sophisticated use of various functional materials, which include carbon materials, metal oxides, and conducting polymers, may hold the key to developing advanced supercapacitors.\(^7\) Very recently, one new possible way for this quest is to search in nature as a source of materials or inspiration\(^8\)−\(^11\) and the journey can lead to the use of naturally occurring macromolecules or bioinspired materials for promoting the discovery of new supercapacitors.

Melanin is a kind of unique biopolymer pigments that is widely existing in most living organisms with lots of important functions, including UV protection, antibiotic function, thermoregulation, and free radical scavenging.\(^11\)−\(^15\) Generally, there are three main classes of melanin biopigments with distinct chemical compositions and physical properties: eumelanin, pheomelanin, and neuromelanin.\(^16\) Among them, the most common type is eumelanin, a kind of black-to-brown biopigment usually prepared from a scheme that 5,6-dihydroxyindole and 5,6-dihydroxyindolecarboxylic acid intermediates are copolymerized under oxidizing conditions.\(^17\) As their synthetic analogues, polydopamine (PDA)-based materials are also under active investigations as mussel-inspired surface chemistry for multifunctional coatings,\(^18,19\) nontoxic bioimaging agents,\(^20−22\) skin pigmentation-inspired polydopamine sunscreens,\(^23\) photocatalytic materials,\(^24\) and photothermal therapeutic agents.\(^25−27\) Interestingly, melanin and melanin-inspired materials usually demonstrate unique structural and functional features compared with many established polymerized aggregate materials. In particular, PDA-based eumelanin-like nanomaterials exhibit excellent electrical properties and the carbonized ones could possess high-level electroactive N and sp\(^2\) C, leading to reduced charge-transfer resistance.\(^15,28\) To further improve their electrochemical performance for practical applications as supercapacitors,
researchers have developed several methods to introduce sulfur element into the PDA system to generate N,S-codoped carbon materials, which fully benefit from the synergistic effect between nitrogen and sulfur atoms within the carbon materials. While many efforts have been well documented, concerns have arisen that the facile fabrication of robust N,S-codoped carbon supercapacitors is still largely limited by complex operations and involves toxic chemicals. Therefore, it remains a critical challenge to seek for novel synthetic and biofriendly materials toward the simple fabrication of N,S-codoped carbon materials and electrode materials.

Pheomelanin is another type of melanin pigments containing benzothiazine portions that are mainly responsible for the color of red hair. Its chemical (i.e., naturally contains sulfur and nitrogen atoms) and structural (i.e., similar conjugate structures existing after carbonation, like PDA-based synthetic eumelanins) features greatly inspired us to prepare the corresponding synthetic pheomelanin and related functional materials. Note that the carbonized synthetic pheomelanins could be well utilized as the activated N,S-codoped carbon materials, which probably enhance the capacitance and conductivity of resulting supercapacitors. In this work, we report our first effort toward this goal through the preparation of synthetic pheomelanin as N,S-codoped carbon precursors for further supercapacitor fabrication.

**EXPERIMENTAL SECTION**

**Materials and Methods.** 

**Chemicals.** Dopamine hydrochloride (95%) was purchased from Saan Chemical Technology (Shanghai) Co. Ltd. Cysteine (96%) was obtained from J&K (Beijing) Co. Ltd. Ammonia and ethanol were purchased from Titan Technology (Shanghai) Co. Ltd. All chemicals were used without further purification. Deionized (DI) water was prepared by a laboratory water purifier (UPH-I-10T) (Chengdu, Sichuan).

**Preparation of Synthetic Pheomelanin Nanoparticles.** Dopamine hydrochloride (400 mg) and different quantities of cysteine and ammonia were completely dissolved in 90 mL of DI water and 30 mL of ethanol and mixed with the help of agitation at room temperature for 48 h (Tables S1 and S2). The solution was pale yellow after stirring for about 3–24 h. The passage of yellowing time depended on the increase of the quantity of cysteine added; then, the solution turned dark brown. With the delay of the reaction time, the color gradually deepened and black turbid solution was acquired after 48 h. The resulting synthetic pheomelanin nanoparticles (SPNPs) were separated from the solution by centrifugation (15 000 r min\(^{-1}\)) as a brown-black powder and washed with DI water three times.

**Preparation of Polydopamine (PDA) Nanoparticles.** Dopamine hydrochloride (400 mg) and 1.5 mL of ammonia were completely dissolved in 90 mL of DI water and 30 mL of ethanol and mixed with the help of agitation at room temperature for 48 h. The resulting PDA was separated from the solution by centrifugation (15 000 r min\(^{-1}\), 10 min) as a brown-black powder and washed with DI water three times.

**Preparation of Carbonized Nanoparticles.** Carbonized nanoparticles were obtained by carbonizing the SPNPs and PDA at 800 °C for 2 h in N\(_2\) at a rate of 5 °C min\(^{-1}\). Then, the PDA-800 °C or SPNP-2-800 °C residue was mixed with KOH under the weight ratio of 1:4, ground for 40 min, and activated at 700 °C for 1 h in N\(_2\) at a rate of 5 °C min\(^{-1}\). Ultimately, the obtained carbon samples with hierarchical porous structures were washed with 0.1 M HCl solution and DI water and then dried at 80 °C overnight.

**Characterization.** Scanning electron microscope (SEM) images were obtained using a Nova Nano SEM 450 microscope with a mica plate. Several drops of sample suspension were dropped on the mica plate; the plate was used in the spin-coating method to sweep away the excess water. Samples were completely dried overnight under vacuum before testing.
able features. The solution was pale yellow at the very beginning and then turned to dark brown after stirring for a while. Finally, the solution became a black turbid system after 48 h of reaction. The targeted SPNPs then could be simply collected after several centrifugation/redispersion processes in deionized water. Note that such fabrication processes for SPNPs can be easily scaled up without any serious limitations. The particle sizes and sulfur contents of the formed SPNPs were measured by a scanning electron microscope (SEM) and the elemental analysis (EA) technique, respectively. The detailed information was summarized in Table S1 and Figure S1. It was observed that the sulfur contents doped in SPNPs could increase correspondingly with the increase in addition of cysteine during the reaction (Figure 1b, red line). The particle size of formed SPNPs was greatly influenced by the used ammonia volume (Figure 1b, black line, Figure S2, and Table S2), which agreed well with the observations from the conventional synthetic method toward PDA nanoparticles. We then used X-ray photoelectron spectroscopy (XPS) examination to understand the exact chemical structures of the carbonized SPNPs. As represented in Figure 3a, the survey spectrum of SPNP-2-800 °C from XPS established the existence and element contents of C, N, O, and S within the particles. Furthermore, deconvolution of C 1s high-resolution spectra disclosed the existence of graphite structure (284.5 eV), C−N (285.5 eV), C=O (286.7 eV), and O−C=O (288.6 eV) (Figure 3b C 1s) and we also observed the presence of large population of sp² C structure after carbonization (see Figure 3c, C 1s curve, sp³ C 12.63% < sp² C 77.63%). Note that the sp³ C structure confirmed the existence of a graphite structure in the nanoparticle, consequently possessing low charge-transfer resistance. Also, the deconvolution of N 1s high-resolution spectra can be attributed to pyridinic N (398.2 eV), pyrrolic N (399.8 eV), graphitic N (400.5 eV, 53.76%), and pyridinic-N oxides (−NOx−) (403.3 eV) (Figure 3c, N 1s). On the basis of references, graphitic N and pyrrolic N are advantageous for the creation of electroactive sites. In view of the S 2p high-resolution spectra, two peaks located at 163.6 and 164.8 eV

resulting samples carbonized at 800 °C as SPNP-1-800 °C, SPNP-2-800 °C, and PDA-800 °C. Electron energy-loss spectroscopy (EELS) mapping was used to study the morphology and chemical composition of the resulting SPNPs after carbonization operation. As shown in Figure 1f, it was clearly observed that the carbonization process did not result in an obvious change of the morphology of SPNP-2-800 °C and the existence of N and S elements in the carbonized SPNP was also confirmed by EELS results. Further combined with the EA analysis data shown in Figure 1f, we could conclude that the carbonization process may cause the slight loss of N, S heteroatoms in the SPNP-2 system and the N heteroatom in the PDA system since the C=S bond and C=N bond are little bit weaker than the C−C bond, which agreed well with many previous reported results. Above all, we were able to successfully employ the one-pot copolymerization fabrication strategy to prepare a family of synthetic pheomelanin nanoparticles with tunable size (80−313 nm) and composition (3.88−8.70 wt % sulfur content), which can be further used in supercapacitor applications after carbonization and activation.

We then used electrospray ionization mass (ESI-MS) spectrometry to explore the polymerization mechanism for the formation of nanoparticles (Figure 2). For instance, several m/z peaks were detected for newly produced oligomeric intermediates at representative experimental conditions for SPNP-2 at 10 min of reaction time point. Notably, the covalent conjugation between cysteine and oligomers during the polymerization was also confirmed by the ESI-MS data (Figure 2). We then used X-ray photoelectron spectroscopy (XPS) examination to understand the exact chemical structures of the carbonized SPNPs. As represented in Figure 3a, the survey spectrum of SPNP-2-800 °C from XPS established the existence and element contents of C, N, O, and S within the particles. Furthermore, deconvolution of C 1s high-resolution spectra disclosed the existence of graphite structure (284.5 eV), C−N (285.5 eV), C=O (286.7 eV), and O−C=O (288.6 eV) (Figure 3b C 1s) and we also observed the presence of large population of sp² C structure after carbonization (see Figure 3c, C 1s curve, sp³ C 12.63% < sp² C 77.63%). Note that the sp³ C structure confirmed the existence of a graphite structure in the nanoparticle, consequently possessing low charge-transfer resistance. Also, the deconvolution of N 1s high-resolution spectra can be attributed to pyridinic N (398.2 eV), pyrrolic N (399.8 eV), graphitic N (400.5 eV, 53.76%), and pyridinic-N oxides (−NOx−) (403.3 eV) (Figure 3c, N 1s). On the basis of references, graphitic N and pyrrolic N are advantageous for the creation of electroactive sites. In view of the S 2p high-resolution spectra, two peaks located at 163.6 and 164.8 eV

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Figure 1. (a) Fabrication of synthetic pheomelanin nanoparticles (SPNPs). (b) Sulfur content (wt %) of SPNPs and different nanoparticle sizes of SPNPs. (c) SEM image of SPNP-2 (313 ± 23 nm) and DLS data of SPNP-2 (inset). (d) UV−vis spectra of SPNP-2 (blue line) and PDA (red line). (e) Electron energy-loss spectroscopy (EELS) mapping analysis of SPNP-2-800 °C. (f) Table of sulfur content before and after carbonization of PDA and SPNPs.

Figure 2. ESI-MS spectrum of raw product solution of SPNP-2 after 10 min of reaction and possible intermediates structures during the reaction.
corresponded to S 2p3/2 (37.36%) and S 2p1/2 (41.69%), and another inconspicuous peak at 167.8 eV could be attributed to the sulfur oxidation state (e.g., $\text{SO}_x^-$) (Figure 3d, S 2p). Therefore, as a result of the above, the N and S elements have been effectively imported to the electrode materials and graphite structure was also formed in the carbonized SPNPs.

To further expand the property as electrode materials for supercapacitors, SPNP-2-800 and PDA-800 °C were activated by KOH and then pyrolyzed for 1 h at 700 °C (the resulting samples were named SPNP-2-KOH and PDA-KOH, respectively). The purpose of this operation was to introduce the mesoporous structures into the materials, as usually performed in many other carbon-based material systems. Notably, such activation could increase the specific surface area and pore volume of the electrode material, which further improved its total supercapacitor performance significantly. First, it was also found that the KOH activation process did not induce the morphological change of the samples, as evident by the SEM results shown in Figure S4. We then conducted $\text{N}_2$ adsorption–desorption characterizations at 77 K of SPNP-2-KOH and PDA-KOH to evaluate these critical parameters mentioned above. For example, upon observation of typical $\text{N}_2$ adsorption–desorption isotherms of SPNP-2-KOH and PDA-KOH (Figure 4a,b), we found that both isotherms primarily exhibited typical type IV isotherm behaviors with hysteresis loops that were characteristically related to the capillary condensation of $\text{N}_2$ into the mesopores. A clear condensation stage in the relative pressure ($P/P_0$) between 0.2 and 0.8 was observed, indicating a uniform mesoporous structure, typically derived from etching by KOH. The pore size distributions of these samples are also shown in Figure 4 (the insets in Figure 4a,b), and we can see that the pore sizes have a significant increase to around 4 nm, again demonstrating the introduction of mesopores within the carbonized nanoparticles. The BET surface area ($S_{\text{BET}}$) was measured to be as high as 693.9 m$^2$ g$^{-1}$ (for SPNP-2-KOH) and 761.2 m$^2$ g$^{-1}$ (for PDA-KOH). For comparison, we also conducted the $\text{N}_2$ adsorption–desorption experiments on SPNP-1-800 °C, SPNP-2-800 °C, and PDA-800 °C. From the $\text{N}_2$ adsorption–desorption isotherms and pore size distributions of these samples, it was found that these testing samples took micropores as the main pore structure and the $S_{\text{BET}}$ was measured to be 315.7 m$^2$ g$^{-1}$ (SPNP-2-800 °C), 324.2 m$^2$ g$^{-1}$ (SPNP-1-800 °C), and 345.7 m$^2$ g$^{-1}$ (PDA-800 °C) (Figure S5). Moreover, Raman spectra were obtained to further measure the microstructures of the products SPNP-2-KOH (Figure S6, red line) and SPNP-2 (Figure S6, blue line). The peaks situated at 1320 and 1590 cm$^{-1}$ were attributed to the typical D band and G band of carbon materials, which were consistent with the disordered and graphitic structures, respectively. Note that the D/G ratio of band intensities ($I_D/I_G$) was normally applied to mirror the graphitization degree of carbon materials. SPNP-2-KOH with the calculated $I_D/I_G$ of 0.98 at 1320 and 1590 cm$^{-1}$ was higher than that of SPNP-2 (0.88) since the activation procedure commonly degraded the carbon framework, leading to more defects and increased $I_D/I_G$. Therefore, we could clearly see
that the hierarchical porous structures of the samples were successfully generated and their BET specific surface areas were greatly improved. The proportion of graphite structure was also increased by carbonization and the KOH activation process.

To explore the electrochemical performances of similar-sized SPNP-2-KOH and PDA-KOH samples as the supercapacitor electrodes, cyclic voltammetry (CV) tests were first carried out using a three-electrode system in a 6 M KOH aqueous electrolyte at room temperature. Note that the 6 M KOH aqueous electrolyte was popularly used for supercapacitor parameter measurement in the previous work, probably benefiting from the fast mobilities of K⁺ and OH⁻ ions. The CV curves of SPNP-2-KOH and PDA-KOH at changed scan rates in the voltage range of −1.0 to 0 V are shown in Figure 4c,d. According to the results, all electrode materials exhibited analogous rectangular shapes at the low scan rates, indicating a typical double-layer capacitor peculiarity of the charge/discharge process; however, these electrode materials all presented the peculiar quasi-rectangular shape of CV curves at the high scan rate, demonstrating the hierarchical porosity and large specific surface area of SPNP-2-KOH and PDA-KOH. The shape of the CV curves seemed to be quite stable without any noticeable redox peaks and nearly maintained the status for the entire scan, demonstrating that notable electrochemical capacitor performance exists in the SPNP-2-KOH electrode in a fast charge/discharge process. Additionally, galvanostatic charge–discharge (GCD) characterizations of SPNP-2-KOH and PDA-KOH were also performed at changed current densities, as demonstrated in Figure 4e,f. SPNP-2-KOH and PDA-KOH electrodes display conventional triangular shapes at a current density of 1.0 A g⁻¹, demonstrating good electrochemical capacitive property. Computing from the GCD curves, it was observed that the specific capacitances and rate capability of SPNP-2-KOH electrodes outperformed PDA-KOH obtained at the same carbonization temperature, which might be due to the synergistic effect between N and S and the specific hierarchical microporous and mesoporous structures. Compared with the mono-heteroatom doping, codoping usually showed better enhancement owing to the synergistic interactions among the doping atoms. Specifically, in N,S-codoped mesoporous carbon materials, sulfur elements could provide a more polarized surface and reversible pseudosites for improved electrochemical performance. Note that such effect has been reported in both theoretical and experimental studies on the synergistic improvement between N and S elements during the recent years. The codoping of S and N could introduce asymmetrical spin and charge density, which leads to numerous carbon atom active sites within the system. 

Figure 5a compares the CV curves of SPNP-2-KOH and PDA-KOH, both measured at a scan rate of 500 mV s⁻¹. It can be concluded that the area surrounded by the CV curves of SPNP-2-KOH is obviously larger than that in the PDA-KOH electrode, implying the large capacity of the SPNP-2-KOH electrode. The specific capacitances of SPNP-2-KOH and PDA-KOH at a current density of 1 A g⁻¹ could be calculated as 243 and 178 F g⁻¹, respectively. SPNP-2-KOH possessed a 37% improvement over the specific capacitance of typical PDA after carbonization and KOH activation (Figure 5b). We also investigated the specific capacitance of the carbonized samples before KOH activation and found that the capacitance of SPNP-2-800 °C was higher than that of SPNP-1-800 °C and PDA-800 °C (Figures 5b and S7). The results confirmed that SPNPs with rich doped heteroatoms should exhibit a larger specific capacitance on account of pseudocapacitance contribution and the synergistic enhancement between N and S elements. Moreover, cycling stability typically is a chief aspect in defining the supercapacitors for further applications. Also, the cycling stability of the SPNP-2-KOH electrode materials was estimated by reduplicative charge/discharge measurements at a steady current density of 10 A g⁻¹ for 10 000 cycles, as revealed in Figure 5c. Note that 94.8% capacitance of the original value was detected to be maintained, demonstrating its outstanding cycling stability as electrode materials. The high durability could be attributed to the hierarchical porous structure of SPNP-2-KOH, smoothing both electrons and electrolyte ions. The Nyquist plots of the PDA-800 °C, SPNP-1-800 °C, SPNP-2-800 °C, PDA-KOH, and SPNP-2-KOH are shown in Figure 5d. All of the products presented the very characteristic quasi-vertical line at low frequencies, signifying perfect capacitance behaviors. The 45° line in the middle-frequency section is defined as the Warburg impedance and refers to the characteristic of ion spread over poriferous electrode materials. Notably, all SPNP products presented shorter Warburg impedance regions compared to those of the corresponding PDA materials (Figure 5d), suggesting the lower ion transportations impedance of SPNPs than that of PDA. It is likely because that electrolyte ion was preferable for these micropores than mesoporous routes. In the amplified high-frequency section, the diameter of semicircles indicated the electron transfer procedure (inset of Figure 5d). SPNP-2-KOH with the minimum diameter displayed the least charge-transfer resistance, whereas PDA-800 °C displayed the maximum charge-transfer resistance. It may because of the existence of synergistic enhancement amid N and S elements within SPNPs, leading to lower charge-transfer resistance compared to that of the PDA system. Therefore, all of the discussions above strongly supported the low charge-
transfer resistance and high specific capacitance of SPNPs after suitable treatments, which allows us to develop a new generation of biomacromolecular pigment-based energy storage devices.

CONCLUSIONS

In summary, we have established a facile one-pot fabrication strategy toward synthetic pheomelanin nanoparticles with controllable size and composition (sulfur content) via the copolymerization of dopamine and cysteine in alkaline solutions. The resulting synthetic pheomelansins possess outstanding thermal stability and can directly convert to monodispersed S,N-rich carbon spheres without morphological change. Compared with conventional polydopamine-based carbon spheres and traditional biomass-based porous carbon materials (i.e., natural cotton, 198 F g\(^{-1}\), flower petals, 154 F g\(^{-1}\)), the present pheomelanin nanoparticles with extra electroactive sulfur could possess lower charge-transfer resistance, more electroactive sites, and accordingly higher specific capacitance. This work will continue to inspire us to rationally develop a series of energy storage materials based on synthetic biomacromolecular pigment materials.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.9b10956. SEM images of SPNPs; TGA curve of SPNP-2; SEM images of SPNP-2-800 °C, PDA-800 °C, PDA-KOH, and SPNP-2-KOH; nitrogen adsorption–desorption isotherms and pore size distributions of SPNP-2-800 °C, SPNP-1-800 °C, and PDA-800 °C; Raman curves of SPNP-2 and SPNP-2-KOH; CV and GCD curves of carbonized SPNP-2-800 °C, SPNP-1-800 °C, and PDA-800 °C; and formulation of all synthetic pheomelanin nanoparticles (PDF)

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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