

Synthesis, Self-assembly and Electrode Application of Mussel-inspired Alternating Copolymers

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Electronic Supplementary Information

Abstract We reported the first mussel-inspired alternating copolymer with a high amount of catechol groups (50% molar ratio) through a facile epoxy-amino click reaction between 9,9-bis(4-(2-glycidyloxyethyl)phenyl)fluorene (BGEPF) and dopamine (DA). The obtained copolymers were used to prepare carbon/nitrogen-doped α -Fe₂O₃ nanoparticles through self-assembly, coordination and calcination, which displayed excellent electrochemical performance as anode materials for Li-ion batteries.

Keywords Alternating copolymer; Catechol groups; Self-assembly; Li-ion batteries

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INTRODUCTION

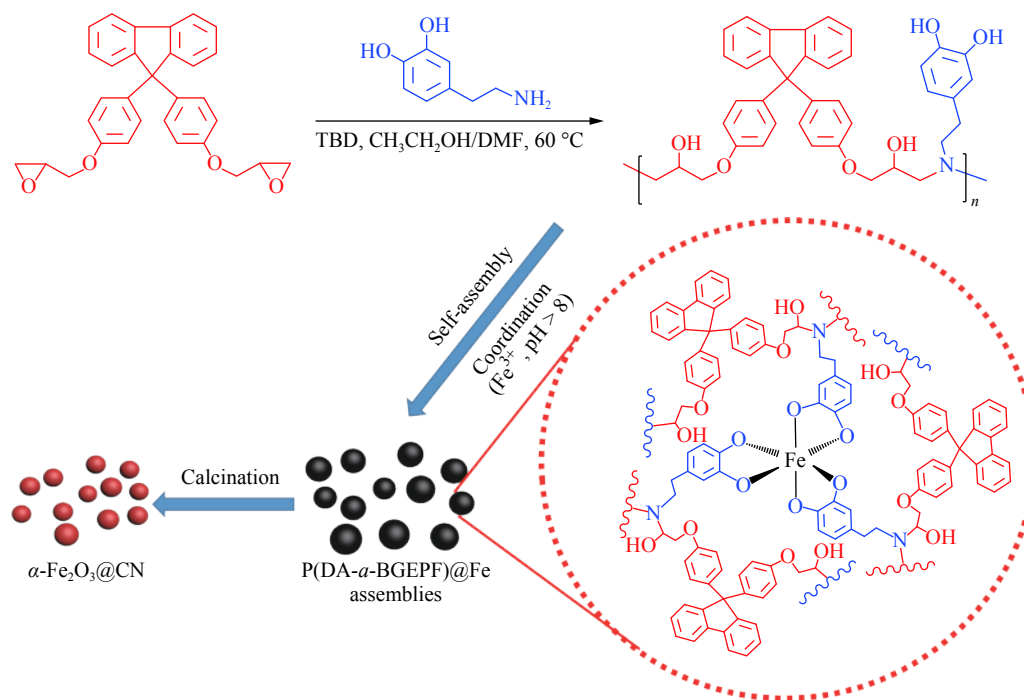
Mussel adhesion proteins, having a rich amount of catechol groups, can form robust adhesion to a wide variety of materials^[1–4]. Inspired by them, mussel-mimetic polymers containing catechol groups have received more and more attention in recent years, and they have shown great potentials in surface modification, stabilizers for nanoparticles, and adhesives^[2, 5–8]. Up to now, many kinds of catechol-functionalized polymers, including homo-polymers^[9], end-functionalized polymers, branched polymers^[10], random copolymers^[2, 11–15], graft copolymers^[16, 17] and block copolymers^[18–21], have already been reported. For instance, Westwood *et al.* synthesized random copolymers from 3,4-dimethoxystyrene and styrene using *n*-BuLi as initiator^[15]. Lee *et al.* reported grafted copolymers containing catecholic moiety by step-growth polymerization^[17]. Saito *et al.* reported block copolymers containing catechol moieties synthesized by reversible-addition fragmentation chain-transfer (RAFT) polymerization followed by deprotection of the methoxy groups^[19, 21]. Cho *et al.* synthesized diblock and triblock copolymers through the combination of atom transfer radical polymerization (ATRP) and catecholic oxidative chemistry^[22]. However, despite these progress, the catechol content of most synthetic catechol-functionalized polymers ranges from a few molar percent to 30 mol%^[23]. In

addition, for the polymer synthesis, catechol should be derived with polymerizable groups like double bonds first before polymerization, and both the monomer preparation and polymerization processes are time consuming. Thus, it is still a great challenge to synthesize mussel-inspired polymers containing a high amount of catechol groups but with a simple and low cost synthetic method.

Alternating copolymers are regular polymers with alternating repeating units. Recently, our group has reported a novel alternating copolymer obtained through facile diepoxide-dithiol click reactions, and the synthesized alternating copolymers can self-assemble into nanotubes, vesicles and other interesting structures^[24, 25]. Herein, we want to present the first catechol-functionalized alternating copolymer through epoxy-amino click reaction between 9,9-bis(4-(2-glycidyloxyethyl)phenyl)fluorene (BGEPF) and dopamine (DA) monomers (Scheme 1). The advantages of the present work lie in three aspect: (1) DA is directly used as the monomer, and no monomer functionalization process is needed here before polymerization; (2) The polymerization process is quite simple due to the natural advantage of epoxy-amino click reaction; (3) The obtained catechol-functionalized polymers P(BGEPF-*a*-DA)s have a regular alternating structure, and the molar ratio of catechol pendent groups reaches 50%. Interestingly, P(BGEPF-*a*-DA)s were successfully used to prepare α -Fe₂O₃ nanoparticles, which showed excellent electrochemical performance as anode materials for Li-ion batteries. Up to now, different methods have been used to fabricate various morphologies of Fe₂O₃^[26–28]. For example, Cao *et al.*

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Scheme 1 Schematic illustration of the click polymerization of P(DA-a-BGEPF)s and the preparation process of α -Fe₂O₃@CN nanoparticles

synthesized dendritic Fe₂O₃ microstructures by K₃Fe(CN)₆ deposition through the hydrothermal method^[26]. Lv *et al.* fabricated carbon-coated Fe₂O₃ *via* the pyrolysis of ferrocene^[27]. Wang *et al.* reported a method to obtain urchin-like α -Fe₂O₃ by hydrothermal treatment of α -FeOOH^[28]. To our knowledge, it is the first use of catechol-functionalized polymers in the preparation of α -Fe₂O₃ nanoparticles. Thus, the present work represents a new advance for catechol-functionalized polymer in synthesis method, molecular structure and applications.

EXPERIMENTAL

Materials

Dopamine hydrochloride (DA·HCl, 99%, Alfa), 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD, 98%, TCI), tris-(hydroxymethyl)aminomethane (Tris, 99%, Adamas) and BGEPF (98%, TCI) were used as received without further purification. Ferric chloride hexahydrate (FeCl₃·6H₂O), *N,N*-dimethylformamide (DMF) and ethanol (EA) were purchased from the domestic suppliers and used as received.

Measurements

¹H-nuclear magnetic resonance (¹H-NMR) measurement was carried out on a Varian Mercury Plus-400 nuclear magnetic resonance spectrometer using tetramethylsilane (TMS) as an internal standard and dimethylsulfoxide-d₆ (DMSO-d₆) was used as the solvent. The molecular weight of the alternating copolymer was measured by GPC on a HLC-8320 Gel Permeation Chromatography (TOSH, EcoSEC GPC System) system at 40 °C using polystyrene as the standard and LiBr-dissolved DMF solvent as mobile phase at a flow rate of 0.6 mL/min. Thermal gravimetric analysis (TGA) was

performed on Perkin Elmer TGA 7. About 5–10 mg of the sample was used and all the samples were heated from 25 °C to 800 °C at a heating rate of 20 °C/min under the oxygen atmosphere. DSC measurements were carried out on a DSC 204 F1 instrument. About 5–10 mg samples were used and heated from −50 °C to 200 °C at a rate of 10 °C/min. Dynamic light scattering (DLS) measurements were performed in aqueous solution under a Malvern Zetasizer 3000 HS (Malvern Instruments, Ltd.) equipped with a 125 mW laser light and operated at $\lambda = 633$ nm. All samples were measured at 20 °C and a scattering angle of 90°. Scanning electron microscopy (SEM) was performed on a JEOL-7401F scanning electron microscope with an acceleration voltage of 5 kV. The samples for SEM observation were prepared by dispersing the assembly solution onto single crystal silicon wafers. After natural drying, the samples were coated with a thin film of gold before measuring. Transmission electron microscopy (TEM) measurements were carried out on JEM-2010/INCAOXFORD, with an acceleration voltage of 200 kV. The sample was prepared by dropping the assembly solution onto a carbon-coated copper grid. The copper grid was then dried at room temperature for 48 h before characterization. High-resolution transmission electron microscopy (HRTEM) was conducted on TF30 JOEL 2100F at an accelerating voltage of 200 kV. The sample was prepared by adding the assembly solution onto an ultra-thin carbon film. The carbon film was dried at ambient temperature for 48 h. X-ray diffraction (XRD) measurements were performed on a X-ray diffractometer (D/MAX-2200/PC, Rigaku) equipped with Cu K α radiation (40 kV, 20 mA) at a rate of 1.0 °C/min over the range of 6 (2 θ). X-ray photoelectron spectroscopy (XPS) measurements

were carried out at a base pressure of about 5×10^{-8} Pa using an Mg X-ray (1253.6 eV) source. Inductively coupled plasma optical emission spectrometry (ICP-OES) analysis was performed on ThermoScientific iCAP6300 instrument.

Electrochemical Measurements

The active material ($\alpha\text{-Fe}_2\text{O}_3\text{@CN}$), acetylene black and CMC (carboxymethyl cellulose dissolved in water, a concentration of 18%) with a weight ratio of 7:2:1 were mixed homogeneously with water, and the obtained slurry was pasted on Cu foil and dried at 80 °C for 10 h in vacuum. CR2016-type coin cells were then assembled in an argon-filled glove box. The cells consisted of lithium foil (anode), Celgard 2400 (separator), and LiPF_6 (1 mol/L) in a mixed solvent of ethylene carbonate and dimethyl carbonate (1:1 volume ratio) (electrolyte). All batteries need allowing to stand still for 10 h after being put into the charge and discharge test. The galvanostatic charge and discharge were controlled between 0.1 and 3.0 V on a LAND-CT2001A instrument at room temperature. The cyclic voltammetry (CV) measurement was conducted with a CHI 600A electrochemical workstation at a scan rate of 0.1 mV/s.

Preparation of Alternating Copolymer P(DA-*a*-BGEPF)

The synthetic route to P(DA-*a*-BGEPF) is shown in Scheme S1 (in electronic supplementary information, ESI). Briefly, 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) (1.2 mmol), EA (5 mL) and DMF (5 mL) were added into a two-neck flask and stirred at 60 °C until getting a homogeneous solution. After 30 min of N_2 bubbling, dopamine hydrochloride ($\text{DA}\cdot\text{HCl}$) (1 mmol) was added. TBD was used to keep pH around 8.0. After 30 min of N_2 bubbling, BGEPF (1 mmol) was added into the solution. The reaction mixture was further stirred at room temperature for 48 h. The resulting mixture was poured into aqueous solution of HCl (pH 2), and the deposit was collected and dissolved in DMF and purified by dialysis against DMF and deionized water respectively. Finally, the purified product was obtained by freeze-drying.

Preparation of P(DA-*a*-BGEPF) Nanospheres

In brief, P(DA-*a*-BGEPF) (2 g) was dissolved in 100 mL of DMF and stirred at room temperature for 5 min. Then 300 mL of distilled water was added slowly into the mixture solution and stirred slightly for 30 min. Subsequently, the solution was dialyzed against deionized water for 24 h to remove DMF. Dry powder samples were obtained by freeze-drying under vacuum.

Preparation of P(DA-*a*-BGEPF)@Fe Nanospheres (Scheme S2 in ESI)

The P(DA-*a*-BGEPF)@Fe nanospheres were prepared by adding Fe^{3+} water solution dropwise into the DMF solution of P(DA-*a*-BGEPF). Typically, P(DA-*a*-BGEPF) (2 g) was dissolved in 100 mL of DMF and stirred at room temperature for 10 min. Then 300 mL of aqueous solution with $\text{FeCl}_3\cdot 6\text{H}_2\text{O}$ (2.84 g) was slowly added dropwise into the DMF solution and stirred for 30 min. And then Tris was added to the solution (pH > 8) and stirred at 60 °C in air for 24 h. DMF, Tris and the residual FeCl_3 were removed by dialysis method using deionized water. And the dry powder samples were got by freeze-drying under vacuum.

Preparation of $\alpha\text{-Fe}_2\text{O}_3\text{@CN}$ Nanoparticles

The P(DA-*a*-BGEPF)@Fe nanospheres were calcined in a tube furnace from 25 °C to 800 °C at a heating rate of 3 °C/min and kept in 800 °C for 3 h. The resulting particles were $\alpha\text{-Fe}_2\text{O}_3\text{@CN}$ nanoparticles.

RESULTS AND DISCUSSION

The click reaction between BGEPF and DA monomers was carried out at 60 °C with 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) as a catalyst (Scheme 1). The chemical structure of P(DA-*a*-BGEPF) was carefully characterized by using proton nuclear magnetic resonance ($^1\text{H-NMR}$), gel permeation chromatography (GPC), thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) measurements (Figs. S1 and S2, in ESI). Compared with the $^1\text{H-NMR}$ spectra of DA and BGEPF, both the proton signals from the benzene group of DA unit and phenyl fluorene groups of BGEPF unit appeared in the $^1\text{H-NMR}$ spectrum of P(DA-*a*-BGEPF) copolymers except for the broadening of the signals (Fig. S1, in ESI). In addition, the signal at $\delta = 8.08$ ppm belonging to the amino proton of DA (peak C, Fig. S1a in ESI) and the signals for epoxy groups in BGEPF (peaks a, b, c, Fig. S1b in ESI) disappeared completely, while some new signals (peaks a', b', c', Fig. S1c in ESI) appeared in the $^1\text{H-NMR}$ spectrum of P(DA-*a*-BGEPF) copolymer. All the information supported the formation of P(DA-*a*-BGEPF) copolymers. Moreover, the molar ratio between DA and BGEPF units in the copolymer was calculated by comparing the integral ratio of peak F with peak h (Fig. S1c, in ESI), and it is equal to 0.5:1, suggesting the 1:1 molar ratio between DA and BGEPF units. Thus, P(DA-*a*-BGEPF)s did have an alternating structure (Scheme 1).

The number-average molecular weight of P(DA-*a*-BGEPF) measured by GPC was 5000 with a polydispersity index (PDI) of 3.3 (Fig. S2a, in ESI). A small tailing peak was observed in the GPC trace, which might be attributed to the presence of low molecular weight fraction of regioisomers. According to the TGA curve, under the nitrogen atmosphere, the 5% weight loss temperature of P(DA-*a*-BGEPF) was around 230 °C and P(DA-*a*-BGEPF) completely decomposed at around 560 °C (Fig. S2b, in ESI). According to the DSC measurement, the glass transition temperature (T_g) of P(DA-*a*-BGEPF) was about 148 °C and no crystal melting peak was observed (Fig. S2c, in ESI), which revealed that P(DA-*a*-BGEPF) was amorphous.

In P(DA-*a*-BGEPF) alternating copolymers, the BGEPF units are hydrophobic, while the DA units are hydrophilic. Thus, the self-assembly ability of P(DA-*a*-BGEPF)s was well expected due to the amphiphilic nature. The self-assembly process was induced by dropwise adding deionized water into the P(DA-*a*-BGEPF)/*N,N*-dimethylformamide (DMF) solution, followed by dialysis against water to remove DMF. The morphology of P(DA-*a*-BGEPF) self-assemblies was observed by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) (Figs. 1a and 1b). Both of them indicated the formation of well-defined nanospheres with a narrow size distribution.

The statistical analyses of 400 particles from SEM image showed a size of (524 ± 68) nm (Fig. S3a, in ESI). The dynamic light scattering (DLS) measurement (Fig. S3b, in ESI) showed an average hydrodynamic diameter (D_h) of approximate 569 nm with a PDI of 0.25, which is in accordance with the results obtained from the SEM measurement.

It is known that the catechol groups in mussel adhesion proteins have a strong coordination ability to Fe^{3+} ions^[29–37]. Since P(DA-*a*-BGEPF) copolymers had a high amount of catechol groups (50 mol%), the coordination between P(DA-*a*-BGEPF) nanospheres and Fe^{3+} was well expected too. For the experiment, the FeCl_3 aqueous solution (0.035 mol/L) was added dropwise into the P(DA-*a*-BGEPF)/DMF solution (0.032 mol/L) (Scheme S2, in ESI). The solution was changed from transparent to black, indicating the occurrence of coordination. Then, the solution was heated in 60 °C with stirring for 10 h, which was finally dialyzed against water to remove DMF and the residual FeCl_3 . The obtained Fe^{3+} -coordinated self-assemblies were named as P(DA-*a*-BGEPF)@Fe (Scheme 1). Both the SEM and TEM images revealed that P(DA-*a*-BGEPF)@Fe assemblies were nanospheres but with a wider size distribution than that of P(DA-*a*-BGEPF) nanospheres (Fig. 1c and Fig. S4 in ESI). The DLS measurement also showed P(DA-*a*-BGEPF)@Fe nanospheres had a smaller D_h of approximate 527 nm and a wider PDI of 0.33 (Fig. S5a, in ESI). Evidently, the coordination of Fe^{3+} ions had some effect on the self-assembly process of P(DA-*a*-BGEPF).

The introduction of Fe^{3+} into P(DA-*a*-BGEPF)@Fe nanospheres was also carefully evaluated. Fig. 1(d) shows the scanning transmission electron microscopy (STEM) image of P(DA-*a*-BGEPF)@Fe nanospheres and Figs. 1(e)–1(i) present the corresponding composition maps of C, N, O and Fe elements, indicating the successful coordination of Fe^{3+} into nanospheres. The weight percentage of Fe element in P(DA-*a*-BGEPF)@Fe nanospheres was 13% as examined by the inductively coupled plasma (ICP). It is well known that in mussel adhesion proteins three catechol groups can coordinate with one Fe^{3+} ions^[6]. Thus, we believed the coordination between P(DA-*a*-BGEPF) and Fe^{3+} ions in P(DA-*a*-BGEPF)@Fe nanospheres might obey the same rule as shown in Scheme 1.

The TGA measurement of P(DA-*a*-BGEPF)@Fe nanospheres under the air atmosphere showed about 20.75% residual weight was kept after 600 °C during the heating of P(DA-*a*-BGEPF)@Fe samples (Fig. S5b, in ESI), which indicated the iron oxides might be obtained during the heating process. Thus, P(DA-*a*-BGEPF)@Fe nanospheres were calcined at 800 °C for 3 h in air with the heating rate of 3 °C/min from the room temperature and cooled in a tube furnace. The resultant products were nanoparticles with a diameter around 150 nm according to the SEM and TEM measurements (Fig. 2a and Fig. S6 in ESI). The STEM image and the corresponding elemental mapping images showed the homogeneous dispersion of C, N, O and Fe in the nanoparticles (see Figs. 2b–2g, in ESI). The sharp patterns in the X-ray diffraction (XRD) analysis indicated the highly

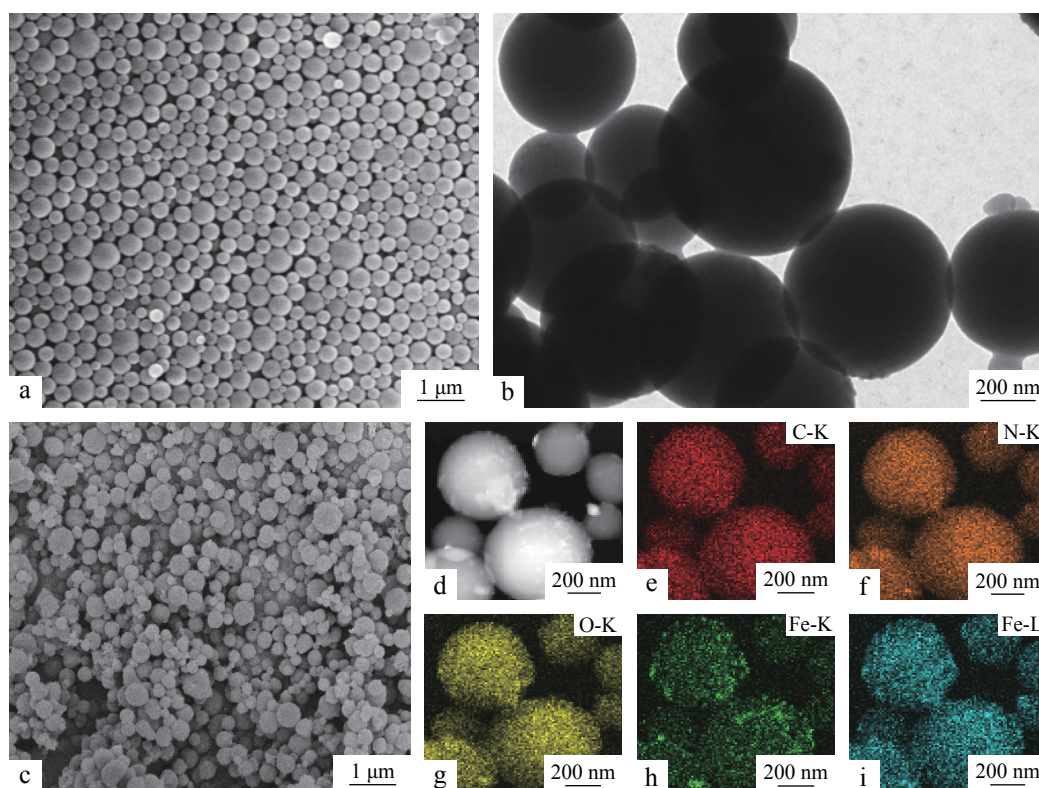


Fig. 1 SEM images of (a) P(DA-*a*-BGEPF) nanospheres, (b) P(DA-*a*-BGEPF) nanospheres, (c) P(DA-*a*-BGEPF)@Fe; (d) The STEM image of P(DA-*a*-BGEPF)@Fe and the corresponding elemental mapping images of (e) C (K-edge, red), (f) N (K-edge, orange), (g) O (K-edge, yellow), (h) Fe (K-edge, green) and (i) Fe (L-edge, blue).

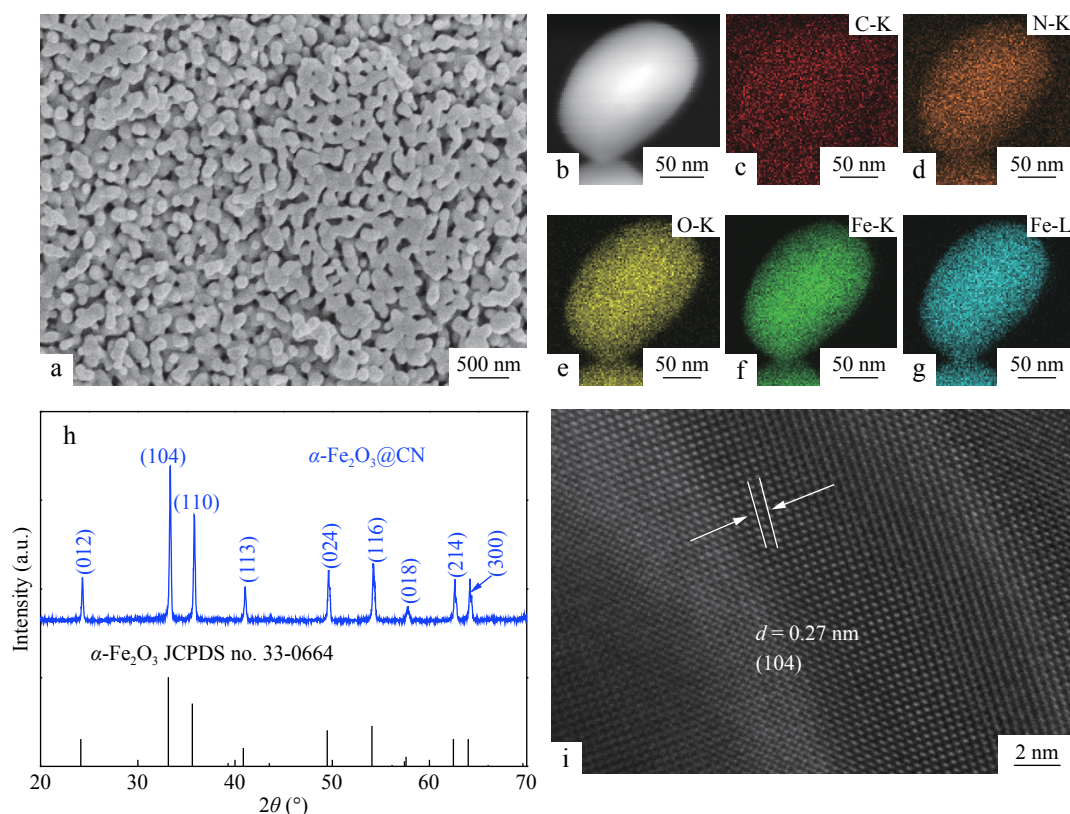


Fig. 2 Characterizations of α -Fe₂O₃@CN nanoparticles: (a) The SEM image; (b) The STEM image and the corresponding elemental mapping images of (c) C (K-edge, red), (d) N (K-edge, orange), (e) O (K-edge, yellow), (f) Fe (K-edge, green), (g) Fe (L-edge, blue), suggesting the homogeneous dispersion of C, N, O and Fe elements in the nanoparticles; (h) The XRD patterns; (i) The HRTEM image.

crystalline structure of nanoparticles, and all the identified peaks were assigned to α -Fe₂O₃ crystals (hematite, JCPDS No. 33-0664) (Fig. 2h). The high-resolution TEM (HRTEM) image also displayed that the nanoparticles had a *d*-spacing of 2.7 Å corresponding to the (104) plane of α -Fe₂O₃ (Fig. 2i)^[38]. The X-ray photoelectron spectroscopy (XPS) analysis showed the Fe 2p spectrum with the characteristic 2p_{1/2} (724.1 eV), 2p_{3/2} (710.9 eV) and satellite peaks (718.5 and 732.9 eV) assigned to the Fe³⁺ from Fe₂O₃ (Fig. S7a, in ESI)^[39]. In addition, the O 1s peak located at ~530 eV, indicating the existence of O²⁻ bonded with ferric iron (Fig. S7b, in ESI)^[40]. All these results proved the formation of α -Fe₂O₃ nanoparticles with dopant carbon and nitrogen elements after the calcination of P(DA-*a*-BGEPF)@Fe nanospheres. Thus, these nanoparticles were named as α -Fe₂O₃@CN (Scheme 1). The ICP measurement of α -Fe₂O₃@CN showed that the nanoparticles contained about 88.7% α -Fe₂O₃, and the left 11.3% should be attributed to the dopant carbon and nitrogen elements.

Up to now, α -Fe₂O₃ has attracted extensive attention as anode materials in Li-ion batteries due to its natural abundance, non-toxic properties and high theoretical capacity (α -Fe₂O₃: 1007 mA·h/g versus graphite: 372 mA·h/g)^[41–43]. Herein, the electrochemical performances of as-prepared α -Fe₂O₃@CN nanoparticles were also examined in an active material/Li half-cell configuration (Electrochemical measurement experiments are shown in ESI). The cyclic

voltammetry (CV) curves for the initial three cycles of α -Fe₂O₃@CN nanoparticle electrode at a scan rate of 0.1 mV/s between 0.01 and 3 V are shown in Fig. 3(a). In the first cathodic process, a large reduction peak was observed at 0.52 V, which is attributed to the reduction of Fe³⁺ to Fe⁰ together with the decomposition of the electrolyte and the formation of solid electrolyte interface (SEI) film^[44]. During the first anodic scan, the peaks at 1.64 and 1.75 V were related to the conversion from Fe⁰ to Fe²⁺ and from Fe²⁺ to Fe³⁺, respectively^[45]. The reversible conversion reaction can be described as follows: Fe₂O₃ + 6Li⁺ + 6e⁻ ⇌ 2Fe + 3Li₂O. In the following CV curves, the reduction peak shifted to higher voltage (0.95 V) with decreasing intensity, indicating the improved kinetics of the α -Fe₂O₃@CN electrode along with the lowered lithium insertion capacity^[46]. There is no obvious deviation peak during the following anodic scans. Fig. 3(b) shows one hundred cycles of galvanostatic charge-discharge curves of α -Fe₂O₃@CN electrode at the current density of 0.2 C. A distinct voltage plateau lying at 0.75 V was recorded during the initial discharge process, then the plateau moved to around 0.95 V during the following discharge process, which corresponded to the results from CV curves. As can be seen from the galvanostatic charge-discharge curves, the first cycle discharge capacity of α -Fe₂O₃@CN electrode reached 1430 mA·h/g at 0.2 C.

The cycling properties of α -Fe₂O₃@CN electrode were evaluated at a current density of 0.2 C for 100 cycles (see

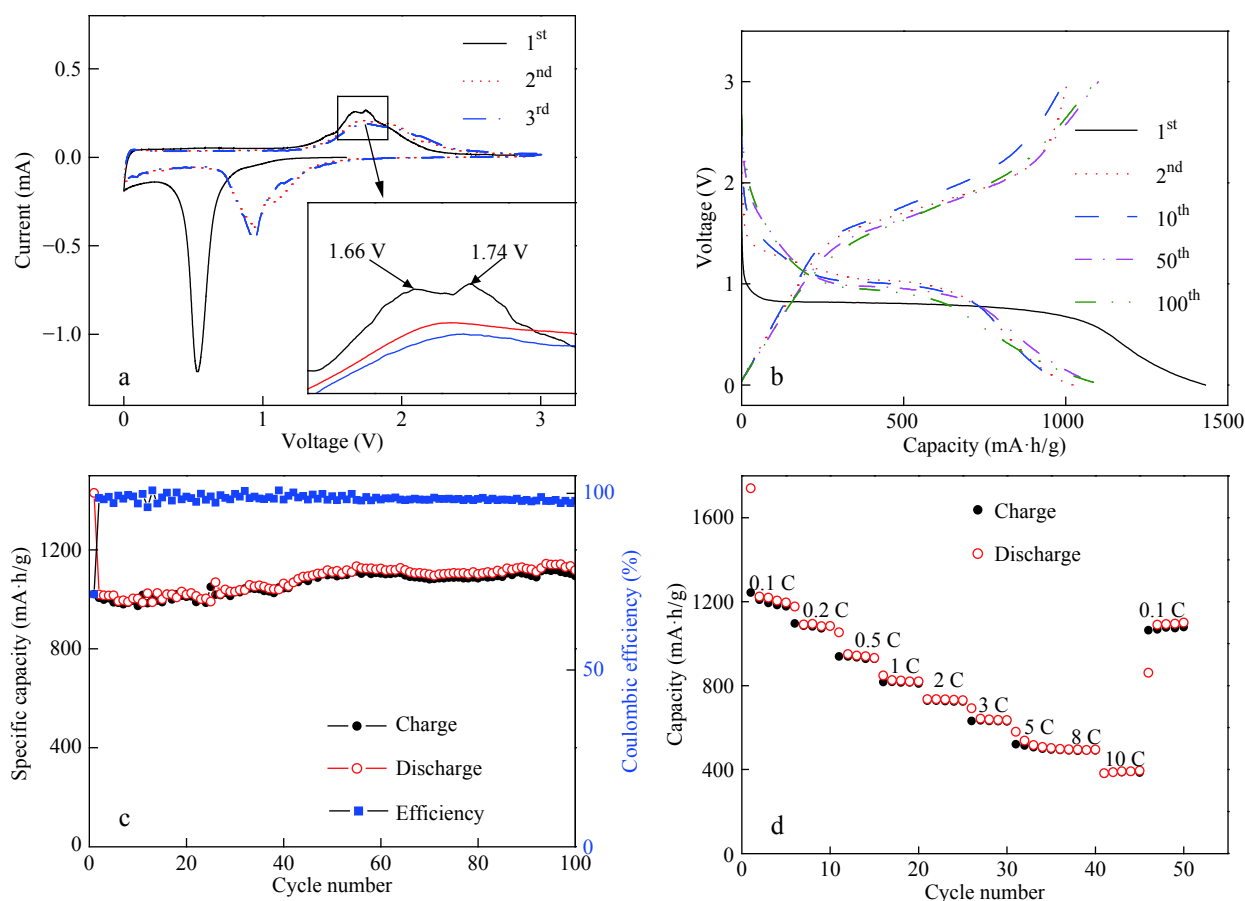


Fig. 3 Electrochemical performance characterizations of $\alpha\text{-Fe}_2\text{O}_3\text{@CN}$ electrode: (a) CV curves between 0.01 and 3 V at a scan rate of 0.1 mV/s; (b) Galvanostatic charge/discharge voltage curves between 0.01 and 3.0 V at 0.2 C; (c) Cycling performance at a rate of 0.2 C; (d) Rate capability at various current rates

Fig. 3c). The $\alpha\text{-Fe}_2\text{O}_3\text{@CN}$ electrode delivered an initial discharge capacity of 1430.5 mA·h/g and charge capacity of 1021.4 mA·h/g, leading to a limited initial coulombic efficiency of 71.4%. The coulombic efficiency is slightly low because of the formation of SEI film^[44]. However, in the 2nd cycle the coulombic efficiency surged to 98.7%, and leveled off at 97%–100% onwards. Meanwhile, the discharge capacity maintained at ~1100 mA·h/g during 100 cycles, confirming good stability of the $\alpha\text{-Fe}_2\text{O}_3\text{@CN}$ electrode.

The rate performance of the $\alpha\text{-Fe}_2\text{O}_3\text{@CN}$ electrode was further investigated at various current densities ranging from 0.1 C to 10 C (Fig. 3d). The capacity remained approximately 1200, 1080, 934, 815, 726, 631, 506, 489, and 387 mA·h/g under the rates of 0.1, 0.2, 0.5, 1, 2, 3, 5, 8, and 10 C, respectively. A high capacity of 1200 mA·h/g was achieved at 0.1 C. Even at a high current density of 10 C, a capacity of 387 mA·h/g was still remained. Remarkably, a stable capacity of 1100 mA·h/g can be resumed when the current reduced back to 0.1 C. The $\alpha\text{-Fe}_2\text{O}_3\text{@CN}$ anode reported here is among the best $\alpha\text{-Fe}_2\text{O}_3$ nanoparticle anodes in terms of cycling stabilities and rate capabilities for Li-ion batteries when compared to the literatures as listed in Table S1 (in ESI).

We assumed that the excellent electrochemical property of

$\alpha\text{-Fe}_2\text{O}_3\text{@CN}$ anode in Li-ion batteries was highly related with the particle structure. The small nanoparticle size can alleviate the mechanical strain generated from volume change during the insertion/extraction process of lithium ion^[38]. The carbon/nitrogen dopants can improve the structural stability and conductivity of $\alpha\text{-Fe}_2\text{O}_3\text{@CN}$ ^[47].

In addition, the good crystallinity of $\alpha\text{-Fe}_2\text{O}_3$ may also benefit cycling stabilities and rate capabilities. As a support, it was found the $\alpha\text{-Fe}_2\text{O}_3\text{@CN}$ showed small electrochemical impedance according to a very small diameter semicircle in the high-frequency region of the Nyquist plot (Fig. S8, in ESI). Nevertheless, the detailed mechanism for $\alpha\text{-Fe}_2\text{O}_3\text{@CN}$ anode in Li-ion batteries is still not clear and should be further studied in the future.

CONCLUSIONS

In conclusion, herein, we have reported the first catechol-functionalized alternating copolymer synthesized through click chemistry reaction between dopamine and BGEPPF. The obtained alternating copolymers P(DA-*a*-BGEPPF)s contained a high molar ratio of catechol groups (50 mol%) and could self-assemble into nanospheres with a diameter around 550 nm in DMF/water mixed solvent. The P(DA-*a*-BGEPPF) nanospheres could be crosslinked through the coordination between the catechol groups and Fe^{3+} ions to get the hybrid

P(DA-*a*-BGEPP)@Fe nanoparticles, which could be further changed into the carbon/nitrogen doped α -Fe₂O₃ nanoparticles α -Fe₂O₃@CN through calcination. The as-prepared α -Fe₂O₃@CN nanoparticles showed an ultrahigh capacity of 1134 mA·h/g at 0.2 C after 100 cycles and excellent rate capability when used as electrode materials in lithium half-cells. The P(DA-*a*-BGEPP) also had more potential properties like good adhesion ability and good interface modification ability. In addition, the compositions of the polymers can be easily adjusted by changing the copolymerized di-epoxy monomers or by adding the third copolymerized monomers. Thus, catechol-functionalized alternating copolymers with more polymer categories, functions and applications can be well expected in the future.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://dx.doi.org/10.1007/s10118-018-2151-6>.

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