Graphene

One Versatile Route to Three-Dimensional Graphene Wrapped Metal Cyanide Aerogels for Enhanced Sodium Ion Storage

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Abstract: Facile and controllable integration of metal cyanides (MCs) into three-dimensional graphene (3DG) with advantageous structures is of fundamental importance for the development of superior MC-based electrode materials for electrochemical energy storage and catalysis. Here a facile and versatile spatially-confined Ostwald ripening strategy was developed to synthesize a series of 3DG wrapped MC aerogels with different compositions, size, and structure based on the chemical instability of MC in the reaction system. Remarkably, the integration of Prussian blue (PB) into 3DG, with such unique architecture, largely improves the rate performance and long-term cycling stability of PB as a cathode material for sodium ion batteries.

Metal cyanides (MCs) are one kind of classical microporous coordination polymer (MCP), consisting of metal ions coordinated by CN bridges, which have gained renewed interest in recent years as potential electrode materials for electrochemical energy storage[1] and catalysis,[2] especially in sodium ion storage,[1] water oxidation,[2a] and CO₂ reduction,[2b] due to their tailorability and porous structures that are suitable for the transport of guest ions, and adjustable metal ions with redox activity. However, the intrinsic poor electronic conductivity of most MCs and inefficient electron and ion transport in the whole electrodes have largely compromised their electrochemical properties, especially in terms of rapid response and long-term cycling stability. In this context, integrating MCs into free-standing porous conductive frameworks, such as three-dimensional graphene (3DG) aerogel, is one promising route to alleviate these problems when considering the huge successes of 3DG in improving the electrochemical properties of various electrochemical active components (ECACs).[3] Moreover, the electrochemical properties of MCs might be further optimized by deliberately wrapping MCs within graphene to modify their interactions, just as previously reported.[4] Thus it is of great interest to design a novel class of free-standing 3DG/MC aerogels, with MCs wrapped within graphene, for fundamental investigations and potential applications in electrochemistry.

To fabricate 3DG wrapped ECACs aerogels, pre-encapsulation of ECACs with graphene oxide (GO) before the formation of 3DG/ECACs frameworks or post-modification of 3DG/ECACs with GO were often necessary. These extra steps usually need further modifications of ECACs with surfactants to create effective interactions between ECACs and GO, which are tedious and undesirable. Thus, novel and simple synthetic strategies based on new mechanisms are highly pursued. Most of the previously reported 3DG/ECACs composites possess multilayered ECACs-graphene-ECACs sandwich-like structures.[3] It could be speculated that 3DG wrapped ECACs aerogels may be designed by removing the ECACs deposited on the surface of 3DG frameworks while maintaining the ECACs wrapped by graphene. To realize this, appropriate ECACs that are not stable in the self-assembly reaction systems should be employed. Recently, other groups and ourselves have carried out extensive research on nano-/micro-structured MCs.[5] It was revealed that MCs are often not stable in acidic and basic environments and they could be dissolved or transformed into larger and more stable structures by Ostwald ripening. In addition, acidic and basic reaction environments could be created during the fabrication processes of 3DG/ECACs by chemical reduction methods.[5] Therefore, self-assembly of graphene/MC composites by chemical reduction might be one promising route to build 3DG wrapped MCs aerogels.

However, the fabrication of 3DG/MC aerogels is impeded by a lack of advances in the development of graphene/MC composites, with well-defined structure, in recent years.[5c,d] Even though graphene/Prussian Blue (PB) composites have been widely studied, the synthetic methods based on the unique nature of PB[5c,d] (that is not possessed by most MCs) could not be extended to other graphene/MC composites. We therefore developed a versatile method to synthesize a series of dispersible GO/MC composites through in situ combination induced by excess metal ions. We subsequently integrated them into one class of novel 3DG/MC aerogels with most MCs wrapped within graphene in a strategy based on spatially-confined Ostwald ripening. This represents one significant step for the controllable synthesis of new GO/MC and 3DG/MC composites with featured structures, which will pave the way for the develop-
opment of novel MC-based high-performance electrode materials. As schematically shown in Figure 1a, the GO/MC composites are fabricated by adding an excess of metal ions into GO/ligand solutions. In this case, excess metal ions act as modifiers, covering the MC particles and inducing the deposition of MC particles on GO by the coordination interaction and electrostatic attraction. Then the obtained dispersible GO/MC composites were self-assembled into 3DG/MC aerogels by a chemical reduction method (Figure 1b). Owing to poor stability of MCs in basic environments, most MC particles deposited on the surface of graphene were dissolved while those MC particles sandwiched by graphene were transformed into larger particles by spatially-confined Ostwald ripening (Figure 1c), and 3DG/MC aerogels with MCs sandwiched between reduced GO (RGO) were obtained. As a proof of concept application, the obtained 3DG/PB aerogel was directly utilized as a free-standing cathode material for a sodium-ion battery without current collector, extra conductive agent, or binder. Due to highly efficient electron and ion transport in the whole electrode and the unique contact style of PB with 3DG, the 3DG/PB aerogel possesses outstanding rate performance and long-term cycling stability, which is among the best results reported to date.

To demonstrate the concept and disclose the underlying mechanism, GO/PB composite and 3DG/PB aerogel were firstly synthesized and characterized. The GO/PB composite was simply obtained by adding an excess of Fe$^{2+}$ into a GO/[Fe(CN)$_6$]$_4^{3-}$ dispersion. Oxygen dissolved in water may partly oxidize Fe$^{2+}$ and [Fe(CN)$_6$]$_4^{3-}$ to Fe$^{3+}$ and [Fe(CN)$_6$]$_3^{3-}$, leading to the formation of PB. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images in Figure 2a and b show that the obtained GO/PB composite inherits the well-defined two-dimensional morphology of GO, and irregular PB nanoparticles with size around 20 nm disperse on both sides of GO with only slight aggregation. An excess of metal ions is necessary for the successful loading of PB on GO. Decreasing the content of Fe$^{2+}$ would lead to the unsuccessful combination of PB on GO (Figure S1 in Supporting Information). It is possible that the excess of metal ions causes the PB nanoparticles to be covered with Fe$^{3+}$ and promotes the adsorption of PB nanoparticles on GO by coordination interactions and electrostatic attraction. This could be validated by a negative zeta potential ($-42.4$ mV) of PB nanoparticles prepared by employing an equal equimolar quantity of [Fe(CN)$_6$]$_4^{3-}$ and Fe$^{2+}$ and a positive zeta potential ($+1.12$ mV) of PB nanoparticles fabricated by using a ten times higher molar ratio of Fe$^{2+}$ compared to [Fe(CN)$_6$]$_4^{3-}$. The obtained GO/PB composite is dispersible in water (inset in Figure 2a), which provides a good foundation for their further treatment, such asfiltrating them into films and integrating them into hydrogels.

After being reduced by sodium ascorbate, the GO/PB composite was self-assembled into 3DG/PB aerogel (Figure 2c and d and Figure S2) with an interpenetrating porous structure. It

![Figure 1. Schematic illustration of the synthetic strategy of 3DG wrapped MC aerogels. (a) Excess metal ions induce the combination of GO and MCs, (b) Self-assembly of GO/MC composites by chemical reduction, (c) Spatially-confined Ostwald ripening.](image)

![Figure 2. (a) SEM and (b) TEM pictures of GO/PB composite (inset in a: Photograph of stable GO/PB composite dispersion). (c, d) SEM images of 3DG/PB aerogel (inset in c: Photograph of 3DG/PB aerogel). (e) Raman spectra, (f) XRD patterns, and (g) FTIR spectra of GO/PB and 3DG/PB aerogel.](image)
can be observed that PB nanoparticles with sizes ranging from 40–80 nm uniformly deposit on the surface of RGO (Figure S2). Moreover, the higher-magnification SEM image in Figure 2d shows that most of PB nanoparticles are well-encapsulated into the adjacent RGO by face-to-face conformal contact. This is not the case in GO/PB and most previously reported 3DG/ECAC composites, 2,6,8 where ECACs often deposit on the both sides of graphene. It is possible that GO/PB was firstly self-assembled into 3DG/PB with a common structure (Figure 1b), and then most of the PB particles deposited on the surface of the graphene were dissolved, whereas those PB particles sandwiched by graphene were protected and transformed into larger particles by spatially-confined Ostwald ripening (Figure 1c). 3 This could be verified by serious ripening which took place in the control sample, which was fabricated during continuous stirring (Figure S3).

The transformation process of 3DG/PB aerogel from GO/PB was further characterized by XRD, Raman spectroscopy, and Fourier transform infrared (FTIR) spectroscopy. The largely improved Raman intensity ratio of the D band to G band (I_D/I_G) of 3DG/PB (1.76) compared to that of GO/PB (1.09) demonstrated that GO was reduced to RGO (Figure 2e). 3 The size change of PB was confirmed by stronger and sharper peaks in the XRD that correspond to the (002), (220), and (400) planes of PB (JPCDS 73–0087) in 3DG/PB (Figure 2f). The average sizes of PB calculated based on Scherrer formula are about 19 and 60 nm for GO/PB and 3DG/PB, respectively, which is in consistent with the SEM and TEM results. Additionally, those peaks in the XRD pattern are slightly shifted to lower angle for 3DG/PB (Figure 2f). This might be caused by sodium uptake and reduction of Fe⁴⁺ and [Fe(CN)₆]³⁻ in PB, 10 as further verified by the slight blue-shift of characteristic peaks of PB in Raman and FTIR spectra (Figure 2e and g). 11,14,19 The XRD peak of 3DG at 23.8° also appeared in the 3DG/PB pattern, yet not in the GO/PB pattern, indicating the conformal coating of RGO on PB promoted the stacking of RGO. The above results show that the chemical instability of PB in the basic reaction environment and the unique stacking structure of graphene in 3DG leads to the formation of one kind of novel 3DG/PB composite with most PB sandwiched between graphene.

To examine the generality of this strategy, the fabrication of other GO/MC composites and 3DG/MC aerogels were carried out. As shown in Figure 3, a series of GO/MC composites and 3DG wrapped MC aerogels were successfully designed. Firstly, Fe⁴⁺ was replaced by Ni²⁺ ions, the GO/Ni-Fe Prussian blue analogue (PBA) composite (Figure 3a and 3b) in Supporting Information) was obtained. The obtained face-centered-cubic structured Ni-Fe PBA (JCPDS, 75-0037) in GO/Ni-Fe PBA consisted of irregular nanoparticles with size about 15 nm and they uniformly dispersed on the whole surface of GO. After being treated by sodium acrose, 3DG wrapped Ni-Fe PBA aerogel was obtained (Figure 3a, and 3c, Figure S4 and S5). The average size of Ni-Fe PBA nanoparticles increased to 30 nm. In a second reaction, [Fe(CN)₆]⁴⁻ was substituted by [Co(CN)₆]³⁻, and a GO/Fe-Co PBA composite (Figure 3b, and 3d, and Figure S6) and 3DG wrapped Fe-Co PBA aerogel (Figure 3b, and 3e, Figure S6 and S7) were successfully fabricated.

The face-centered-cubic structured Fe-Co PBA 9 (JPCDS, 89–3732) in the GO/Fe-Co PBA composite were spherical particles with an average size of about 270 nm. Despite of its large size, a similar Ostwald ripening process took place in the 3DG/Fe-Co PBA. Those Fe-Co PBA particles transformed into truncated cubes with an average size of around 380 nm. Hoffman-type MCs (HMCs) are another kind of important MCs, thus the construction of graphene/HMC composites is also highly attractive. By a similar synthetic procedure, a GO/Ni-Ni HMC composite 10 (Figure 3c, and 3g, and Figure S8) and 3DG wrapped Ni-Ni HMC aerogel (Figure 3c, and 3h, Figure S8 and S9) were successfully constructed. It can be observed that a large amount of Ni-Ni HMC nanosheets with a lateral dimension of around 40 nm covered the whole surface of GO. After transforming into 3DG/ Ni-Ni HMC aerogel, larger Ni-Ni HMC nanosheets with an average lateral dimension of about 200 nm were wrapped within the RGO. The different size and morphology of these MCs originates from their different crystal structures, solubility products, and chemical stability. The above results clearly demonstrate that this method is so versatile that MCs with different compositions, size, and morphology could be loaded on the surface of GO and then integrated into 3DG/MC aerogels with most MCs sandwiched between graphene. This method might be extended to synthesize MCPs composed of various metal ions and other ligands.

In consideration of the advantageous architecture, the obtained free-standing 3DG/PB aerogel could be a promising cathode material for sodium ion batteries. Pioneering studies have demonstrated the importance of high Na content and good crystallinity for PB as the cathode material of sodium ion batteries 3,6,11,15 thus we fabricated a novel kind of 3DG/PB (Figure S10 and S11) aerogel with larger cubic PB nanoparticles wrapped within graphene in the presence of NaCl and sodium acrose. Thermogravimetric analysis (TGA) (Figure S12) demonstrates that the loading mass of PB in 3DG/PB aerogel is about 53 wt.%. 16 For comparison, bare irregular PB particles
with a wide size distribution (Figure S13) were prepared in the absence of GO and used as a control sample. N₂ adsorption analysis was conducted to examine the porous structure and specific surface area of the 3DG/PB aerogel. As shown in Figure 4a, the 3DG/PB aerogel exhibits a IUPAC Type IV curve with steep N₂ uptake in the relatively low P/P₀ region. This suggests that there are many mesopores in the 3DG/PB aerogel, which could be confirmed by a narrow Barrett–Joyner–Halenda (BJH) pore size distribution centered at 2.8 nm (inset in Figure 4a). The unique porous structure gives the 3DG/PB aerogel a high Brunauer–Emmett–Teller (BET) surface area of about 214 m² g⁻¹, much higher than that of pure PB (24 m² g⁻¹). In addition, the 3DG/PB aerogel could be mechanically pressed into a free-standing flexible film with a good electrical conductivity of 2.5 S cm⁻¹ (Figure 4b). The film could be folded many times with negligible structural degradation and electrical conductivity loss. Thus the 3DG/PB aerogel was directly used as the cathode for a sodium ion battery without any binder, conductive agent, or current collector. It is to be noted that the current rate and capacity of 3DG/PB were calculated based on the whole electrode while that of bare PB was based on pure PB in the following electrochemical characterizations.

Despite the similar discharge–charge voltage profiles of 3DG/PB and bare PB at 0.25 C (1 C = 100 mA g⁻¹) (Figure 4c and Figure S14 in Supporting Information), in which two typical voltage plateaus corresponding to the redox reactions of low-spin Fe bonded to C and high-spin Fe bonded to N, the 3DG/PB aerogel demonstrates highly enhanced electrochemical properties (Figure 4c–e and Figure S15), especially in rate performance and long cycle life. As shown in Figure 4d, when the discharge–charge rate increases from 0.25 to 2.5, 10, and 25 C, the capacity of 3DG/PB slightly decreases to 97, 94, 89,
and 84 mAh g\(^{-1}\), respectively. When the discharge–charge rate returns to 10 C, its capacity returns to 89 mAh g\(^{-1}\), which fully demonstrates the structural stability of PB during the cycling process. In contrast, a large deterioration in the electrochemical properties of bare PB is observed. When the discharge–charge rate increases from 0.25 to 1, 2.5, 10, and 25 C, the specific capacity of bare PB hugely decreases to 70, 63, 47, and 7 mAh g\(^{-1}\), respectively. In addition, after the rate performance test, a long-term cycle test at 10 C was carried out (Figure 4e). Exceptionally, the 3DG/PB aerogel still demonstrates excellent long-term cycling performance with high capacity (80 mAh g\(^{-1}\)) and high Columbic efficiency (almost 100 %) up to 1000 cycles, corresponding to 0.01 % degradation per cycle. By contrast, the capacity of bare PB decreased to 42 mAh g\(^{-1}\) after 340 cycles.

As shown in Table S1, the superior electrochemical performance of 3DG/PB is among the best previously reported results when the current rate and capacity of PB in previous reports were normalized to the whole electrode. To reveal the underlying reasons, the electrode reaction kinetics of 3DG/PB and bare PB after long-term cycle tests were examined by electrochemical impedance spectroscopy (EIS). As displayed by the Nyquist plots in Figure 4f, the 3DG/PB aerogel exhibits smaller charge-transfer resistance (153.5 \(\Omega\), Figure S16 and Table S2) than bare PB (902.6 \(\Omega\)). This result demonstrated that the robust and complete conductive networks offered by 3DG largely enhanced the charge transfer process during discharge–charge processes, which is consistent with other reports. Moreover, well-defined cubic PB, without obvious structural degradation, was still wrapped within graphene after the long-term test for the 3DG/PB aerogel electrode (Figure S17). According to the above results, the excellent electrochemical performances of 3DG/PB could be attributed to the following several points: (1) the continuous conductive network in the whole free-standing electrode and the intact contact of PB with RGO ensure effective electron transport;\(^{[7,8,11]}\) (2) the open 3D porous structure provide more efficient contact between the electrolyte and PB, and guaranteed rapid ion transport;\(^{[3,4]}\) (3) the unique RGO/PB/RGO sandwich-like structure and face-to-face contact style may stabilize the PB by preventing structural destruction during Na\(^{+}\) intercalation/de-intercalation.\(^{[46]}\) The featured 3D porous structure leads to superior electrochemical properties of 3DG wrapped PB aerogel as the cathode material for sodium ion batteries, which provides some helpful insights for further development of high-performance 3DG-based composites electrode materials.

In conclusion, an excess metal ion induced combination strategy was developed to ensure the successful loading of MCs on GO. Then based on the chemical instability of MCs in the reaction system, a facile and versatile spatially-confined Ostwald ripening strategy was established for the effective synthesis of 3DG wrapped MC aerogels. This method is so versatile that MCs with different compositions, size, and morphology could be wrapped into 3DG. Due to the 3D porous conductive network and unique contact style of PB with RGO, the obtained free-standing 3DG wrapped PB aerogel was directly used as the cathode for a sodium ion battery and delivered an extraordinary rate performance of 84 mAh g\(^{-1}\) at 25 C and unprecedented cycling stability with 90 % capacity retention after 1000 cycles at 1 C, which is among the best results reported so far. We believe that the current synthetic strategy could be extended to the synthesis of other 3DG wrapped MCP aerogels as high-performance electrode materials for wide range of applications.

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### Conflict of interest

The authors declare no conflict of interest.

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