Three-Dimensional Graphene/Metal Oxide Nanoparticle Hybrids for High-Performance Capacitive Deionization of Saline Water

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The shortage of clean freshwater poses one of the greatest threats to the humanity due to the increasing demand for drinking water caused by the growing population as well as worsening water quality from pollution.1,2 Currently, desalination of saline water is the most effective means to large-scale increase the fresh water supply beyond what is available from the hydrological cycle.3,4 Unfortunately, most of the well-developed desalination technologies such as distillation, electrodialysis and reverse osmosis, are high demand and need specialized and expensive infrastructures, which have dramatically limited their application in the developing world where energy and capital supply are very limited.5-7 Therefore, it is highly desirable to develop the innovative desalination technology with cheap materials, simple equipments, easy operation, and ready miniaturization.8,9 Among the emerging desalination approaches, capacitive deionization (CDI) technology is believed to be one of the most promising techniques that meet all of the above requirements.10-13 CDI is an electrochemical method for removal of salt from aqueous solutions by taking advantage of adsorption of the excessive ions in the electrical double layer region of the porous electrodes.12 The greatest advantage of CDI is its high theoretical energy efficiency for desalination. For instance, the intrinsic energy required by CDI for brackish waters is ≈ 0.1 kWh m\(^{-3}\), which is superior to that of reverse osmosis (≈ 0.2 kWh m\(^{-3}\)), the most efficient technique presently available.11-15 Another noteworthy advantage is its low equipment and operational costs because CDI is a low-pressure, non-membrane based desalination process that is controlled by a low applied voltage (0.8-1.2 V).

Though the concept of CDI was conceived in 1960s,16 CDI-based desalination techniques are still far from practical use due mainly to the lack of suitable electrode materials with high electroadsorption capacity and rate. Generally, a desirable CDI electrode material should possess the following features:12 (i) large capacitance and specific surface area available for electroosorption of salts; (ii) high electronic conductivity; (iii) fast response to ion adsorption-desorption; (iv) robust chemical and electrochemical stability; (v) easy to process and assemble; (vi) high resistance to biofouling and organic fouling. Till now, the mostly used electrode materials are carbon-based materials including activated carbon (AC),17 carbon aerogel,18 mesoporous carbon,19 carbon nanotubes20 and graphene.21 Nevertheless, the NaCl adsorption capacity of all the above mentioned carbon-based materials is in the range of 0.1-10 mg/g, which is much lower than the theoretical estimations.14 To obtain the high performance electrode materials, we need to overcome two big challenges: fully understanding the relationship between electrode structures and charge/mass (salt ions) transfer processes,22,23 and developing a controllable method to construct CDI electrode materials with desired surface compositions and structures.

In this work, we present a novel, simple and versatile method to fabricate three dimensional (3D) graphene/metal oxide (including TiO\(_2\), CeO\(_2\), Fe\(_2\)O\(_3\), and Mn\(_3\)O\(_4\)) nanoparticle (NP) hybrids, denoted as graphene aerogel/metal oxide (GA/MO) hybrids. Design and fabrication of 3D GA/MO hybrids as the high performance CDI electrode materials are mainly based on the following considerations. Graphene, as a robust two dimensional (2D) sheet of sp\(^2\)-hybridized carbon, perfectly meets the requirement of high specific surface area, excellent electronic conductivity, and good chemical and electrochemical stability.24 Furthermore, differing from other amorphous or one-dimensional (1D) carbon materials, graphene sheets can easily self-assemble into 3D networks,25 not only offering a large number of accessible open pores to NaCl in solution but also allowing for the growth and anchoring of functional inorganic nanomaterials with high loading amount.24,26 The incorporation of metal oxide will remarkably improve the capacitance of graphene-based materials.27 Especially for TiO\(_2\), its characteristics of low toxicity, good stability, and high dielectric constant to hold more electric charges endow itself with a desirable candidate for the graphene/metal oxide nanocomposites.28,29 As an example, the high-quality graphene/TiO\(_2\) composites have been synthesized by using TiCl\(_4\), and graphene oxide as the precursors in the presence of polyvinylpyrrolidone (PVP) stabilizers, and they exhibit good photochemical and electrochemical properties.29

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In a typical synthesis of graphene aerogel/TiO$_2$ (GA/TiO$_2$) hybrids with 60.4 wt% TiO$_2$ loading amount, TiCl$_3$ (60 mg) was mixed with 30 mL of graphene oxide aqueous solution (GO, 2 mg mL$^{-1}$). Subsequently, 100 $\mu$L NH$_3$·H$_2$O (28 wt%) were added to the mixture to form a homogenous suspension under ultrasonication. After that, the suspension was subjected to hydrothermal treatment in a Teflon-lined autoclave at 180 °C for 12 hours to generate GA/TiO$_2$ hydrogel. Finally, the monolithic GA/TiO$_2$ hybrids were obtained by freeze-drying of as-prepared hydrogel (Figure 1). Scanning electron microscopy (SEM) images clearly reveal the well-defined 3D open pore nature of the GA/TiO$_2$ product (Figure 1A,B). The pores are 5–25 $\mu$m in size, and the walls are consisted of thin hybrid graphene–TiO$_2$ layers. The Brunauer–Emmett–Teller (BET) specific surface area of GA/TiO$_2$ is measured to be 187.60 m$^2$/g (Figure S1A, Supporting Information), which is much higher than that of commercial TiO$_2$ NP (about 10 m$^2$/g) and some reported graphene-metal oxide hybrids. [26b] The detailed nanostructures of the hybrid GA/TiO$_2$ layers can be further discerned by transmission electron microscopy (TEM), high-angle annular dark field (HAADF) microscopy and high-resolution TEM (HRTEM) imaging. As shown in Figure 1C–E, a large amount of TiO$_2$ NPs with diameters of 4–9 nm are uniformly distributed on the graphene sheets. Both XRD pattern (Figure 1F) and HRTEM image show that the attached TiO$_2$ NPs are anatase phase (JCPDS no: 21–1272). The loading amount of TiO$_2$ NPs in the hybrids could be easily tailored by changing the added amount of TiCl$_3$ precursor (Figure S2). Interestingly, even when the content of TiO$_2$ is increased to more than 70 wt%, the 3D open-pore structure of GA/TiO$_2$ hybrids is preserved, and the TiO$_2$ NPs on graphene layers keep the same sizes of 4–9 nm with the increased density (Figure S2J and S2K). We also notice from Raman spectrum (Figure 1G) that the peaks at 1348.2 cm$^{-1}$ and 1595.3 cm$^{-1}$, corresponding to the characteristic D and G bands of graphene, respectively, are of similar intensity, indicating the reduction of graphene oxide to graphene after hydrothermal treatment.[24,26b] The specific Raman vibrational modes located at 156.0 cm$^{-1}$ ($E_g$), 393.7 cm$^{-1}$ ($B_{1g}$) and 636.1 cm$^{-1}$ ($E_g$) also confirm that the attached TiO$_2$ NPs are anatase phase.[30]

A series of control experiments is performed to better understand the formation mechanism of GA/TiO$_2$ hybrids. First, pH value of the suspension adjusted by ammonia is found to be one of the key factors that significantly affect the structure of final products (Figure S3 and the corresponding discussion).[31d] In brief, the bar-like TiO$_2$ NPs of obviously larger sizes are found to grow on the graphene layers if the excess amount of ammonia is added and the hydrothermal reaction solution is basic after hydrothermal reaction. This is because the alkaline solution can promote hydrolysis of TiCl$_3$ precursors, resulting in the formation of large sized TiO$_2$ NPs. Secondly, the presence of graphene has great impact on the morphology and size distribution of TiO$_2$ NPs. If there is no graphene in the solution, TiO$_2$ NPs grow much bigger to about 8–20 nm and connect with each other (Figure S4). This result demonstrates that 2D graphene not only acts as the heterogeneous nucleation sites for TiO$_2$ NPs, but also confines their growth. Thirdly, 3D open-pore structure is remarkably collapsed for pure graphene samples treated by the same hydrothermal and freeze-drying process (Figure S5). It is clear that the introduction of TiO$_2$ NPs effectively reduces the $\pi$–$\pi$ stacking interactions among the graphene sheets, and is thus beneficial for the formation of 3D open-pore structure.[26b]

Armed with the above experimental evidences as well as the observations on the intermediate products (Figure 2), one can deduce the formation mechanism of GA/TiO$_2$ hybrids (Scheme 1). First of all, after adding TiCl$_3$, graphene oxide

![Figure 1](image-url)
Finally, GA/TiO$_2$ hybrids are achieved after 12 hours hydrothermal treatment. The end of reaction might be monitored by XPS survey, in which the intensity of as-formed O-Ti bond is much higher than that of O–C bond (Figure 2 E) and there is no absorbed Cl$^-$ ion to be detected (Figure 2 D).

It is worth mentioning that so far the successfully synthesized 3D GA/MO hybrids are only GA/Fe$_3$O$_4$ composites, which are prepared via self-assembly of graphene sheets into aerogel either in the presence of ready-made Fe$_3$O$_4$ NPs or with hydrolysis of Fe$^{3+}$ precursors. The difficulty in extension of the above techniques to other metal oxides lies in the fact that the interactions between GO sheets and metal ion precursors are insufficient to guarantee the exclusive growth of NPs (Figure S6). Finally, GA/TiO$_2$ hybrids are achieved after 12 hours hydrothermal treatment. The end of reaction might be monitored by XPS survey, in which the intensity of as-formed O-Ti bond is much higher than that of O–C bond (Figure 2 E) and there is no absorbed Cl$^-$ ion to be detected (Figure 2 D).

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metal oxide NPs on the surface of GO sheets. Herein, we propose this new and general preparation strategy, which utilizes low valence metal ions (e.g., Ti$^{3+}$) as the precursors to synthesize the corresponding high valence metal oxide (e.g., TiO$_2$)-graphene hybrids. The oxidation of low valence metal ions by GO would result in chemical adsorption of these ions on GO sheets, providing more powerful anchored sites for the growth of metal oxide NPs compared with the high valence metal ions only based on physical adsorption.$^{[26b, c, 32]}$ To verify this assumption, we also select TiCl$_4$ as the precursor, and after the same hydrothermal process, the obvious phase separation rather than uniform composite structure is found for the generated TiO$_2$ NPs and graphene sheets (Figure S7).

This fabrication method offers several unique advantages. Many hybrid systems including GA/CeO$_2$, GA/Fe$_2$O$_3$ and GA/Mn$_3$O$_4$ have been successfully produced using the corresponding precursors of CeCl$_3$, FeCl$_3$ and MnCl$_2$, respectively (Figure 3 and Figure S8). Moreover, one readily obtains the GA/MO hybrids with high loading amount of metal oxide NPs. For instance, the content of TiO$_2$ NPs in hybrids can reach more than 70 wt% compared to the previously-reported 30 wt% of Fe$_3$O$_4$ NPs in hybrid nanocomposites. Lastly, this synthesis system is simple and environmental-friendly, which only includes graphene oxide, metal chloride, ammonia and water. As comparison, current methods for preparation of graphene/metal oxide hybrids mostly involve organic stabilizers or surfactants (e.g., PVP)${}^{[29]}$ and expensive organic metal compounds (e.g., tetrabutyl titanate (IV)) and organic solvent (e.g., dimethyl formamide).${}^{[26, 31b, 31c, 32]}$ Therefore, our method may open the door toward facile synthesis of varying types of graphene-based composite materials.

The CDI performance of GA/TiO$_2$ hybrids is investigated and compared with other popular materials including pure graphene aerogel (GA) and commercial AC. Firstly, the cyclic voltammetry (CV) measurements of electrode materials in 0.1 M NaCl are carried out to evaluate their electrochemical properties for CDI (Figure 4A, 4B and S9), because specific capacitance of the electrode materials in NaCl solution is an important factor for evaluating ions adsorption capacity.$^{[22]}$ The capacitance examination on all the samples was performed in a conventional three-electrode system at room temperature, where the Ag/AgCl electrode and Pt plate (1 × 1 cm) were...
Figure 4. (A) CV curves of AC, GA, GA/TiO$_2$ in 0.1 M NaCl solution at a scan rate of 100 mV s$^{-1}$; (B) The specific capacitance of AC, GA, GA/TiO$_2$ at different scan rates; (C) Cycling performance of GA/TiO$_2$ at a scan rate of 100 mV s$^{-1}$, inset presents the CV curves before and after the 1000 cycles. (D) Desalination capacity of AC, GA and GA/TiO$_2$ with different equilibrium concentrations and the corresponding Langmuir isotherm fitted curves; (E) Desalination efficiency of AC, GA and GA/TiO$_2$ in 500 mg/L NaCl solution at different times; (F) Electrosorption and regeneration cycles of GA/TiO$_2$ in 500 mg/L NaCl.

Served as reference and counter electrodes, respectively. Figure 4A displays the representative CV curves of GA/TiO$_2$ (the loading amount of TiO$_2$ NPs is 16.0 wt%) and GA and AC at high scan rate of 100 mV s$^{-1}$. The rectangular CV curves of graphene-based materials (GA/TiO$_2$ and GA) demonstrate the ideal double layer capacitor behavior without Faradaic reactions. The calculation of specific capacitance based on the integrated area of CV curve shows that GA/TiO$_2$ hybrids have a high specific capacitance of 119.7 F/g, considerably larger than that of GA (53.1 F/g) and AC (only 11.3 F/g). Figure 4B further reveals that, at the scan rates ranging from 5 mV s$^{-1}$ to 1000 mV s$^{-1}$, GA/TiO$_2$ hybrids possess substantially higher specific capacitances than that of GA and AC. The specific capacitance of GA/TiO$_2$ is up to 142.6 F/g at 5 mV s$^{-1}$, and this value largely surpasses that of other reported CDI electrode materials (Table S1). Furthermore, the decrease tendency of the specific capacitance of GA/TiO$_2$ hybrids slows down with the increase of scan rates (cyan curve in Figure 4B), disclosing the low ion diffusion resistance of the electrode materials.

The superior electrochemical properties of GA/TiO$_2$ hybrids are also highlighted by their excellent cyclic stability. There is no change in the specific capacitance of GA/TiO$_2$ hybrids after 1000 cycles, and their CV curves keep the original shapes (Figure 4C). The impressive electrochemical stability should be attributed to the stable 3D structures of GA/TiO$_2$ hybrids. We also notice that the specific capacitance of GA/TiO$_2$ hybrids in 6 M KOH can reach about 245.4 F/g at a scan rate of 5 mV s$^{-1}$ and 152.5 F/g at a scan rate of 1000 mV s$^{-1}$ (Figure S10), suggesting that they might become the promising candidates for supercapacitors electrode materials.

The actual CDI performance of GA/TiO$_2$ hybrids is evaluated in NaCl solution at room temperature by using a single CDI cell with an applied voltage of 1.2 V (Scheme S1). Figure 4D summarizes NaCl electrosorption capacity (milligram of the adsorbed NaCl per gram of electrode materials, see Supporting Information for detailed calculation on NaCl electrosorption capacity) of GA/TiO$_2$ hybrids, GA and AC at different concentrations of the feeding salts. It is clear that GA/TiO$_2$ hybrids have the best electrosorption capacity among the three electrode materials. Since water is deemed not suitable for drinking if the Total Dissolved Solids (TDS, measured in mg/L) is higher than 500 mg/L, we choose two specific NaCl concentrations (500 mg/L and 6000 mg/L) to compare the performance of these electrode materials. At the feeding concentration of 500 mg/L, the electrosorption capacity of GA/TiO$_2$ is 15.1 mg/g, which is 1.5 and 12.6 times of that of GA (9.9 mg/g) and AC (1.2 mg/g), respectively; While, at 6000 mg/L, the corresponding capacity is 24.2 mg/g for GA/TiO$_2$, which is 1.6 and 7.3 times of that of GA (15.4 mg/g) and AC (3.3 mg/g). In addition, the electrosorption data could be fitted according to the Langmuir equation (Equation 1).

$$Q = Q_m K_L C / (1 + K_L C)$$

where $C$ (mg/L) is the equilibrium concentration of NaCl, $Q_m$ (mg/g) is the maximum electrosorption capacity, and $K_L$ (mg/L) is the Langmuir constant. As shown in Figure 4D, the Langmuir isotherm fitted curves fit well with the experiment data (correlates coefficient, $R^2 \geq 0.99$), and the maximum electrosorption capacity ($Q_m$) of GA/TiO$_2$, GA and AC is calculated to be 25.0 mg/g, 15.8 mg/g and 3.6 mg/g, respectively. Notably, the electrosorption capacity of the GA/TiO$_2$ hybrids outperforms all the other CDI electrode materials reported recently (Table S1). One can also use the charge efficiency (A) to explore the electrosorption behaviors of electrode materials. The charge efficiency refers to the number of salt molecules removed from solution per electron transferred as function of cell voltage. As Table S2 shown, the charge efficiency of...
GA/TiO$_2$, GA and AC is 0.68, 0.73 and 0.40 at 1.2 V, respectively. The charge efficiencies of GA-based electrode materials are considerably higher than that of AC. This result further discloses the advantages of the GA-based materials as the CDI electrode materials.

Besides the electrodosorption capacity, electrodosorption rate is another important criterion for the actual application of CDI electrode materials. The previously reported materials usually needed tens of minutes and even several hours to reach their electrodosorption equilibrium.$^{[17-21]}$ Figure 4E presents the time-evolved desalination behaviors of three electrode materials in 500 mg/L NaCl solution. Evidently, the electrodosorption of NaCl for GA/TiO$_2$ hybrids can quickly reach equilibrium within 200 s, which is much shorter than AC (more than 800 s) and other reported materials.$^{[17-21]}$ Finally, the desalination cycling is performed to investigate the reversibility of GA/TiO$_2$ hybrids during the desalination and regeneration process. GA/TiO$_2$ hybrids electrode can be completely regenerated and reused for over 10 cycles by an imposed voltage (Figure 4F). It further reveals both the fast response and high reversibility of electrodosorption-desorption behavior of GA/TiO$_2$ hybrids.

The excellent CDI performance of GA/TiO$_2$ hybrids including high NaCl electrodosorption capacity, fast electrodosorption rate and good reversibility are directly related to their 3D porous hybrid structures. Typically, the CDI process in the porous electrodes may be divided into four steps: (i) mass transfer of salt ions inside the electrode pores; (ii) ion electrodosorption and energy storage in the electrical double layer of the electrode; (iii) mass transfer of salt ions between electrode and saline water, and (iv) salt ion diffusion within the saline water. So CDI electrode materials must benefit both the ion electrodosorption in the electrical double layer and the mass (ions) transfer processes.$^{[22]}$ In other words, high capacitance in saline water should be one of the key characteristics for high-performance CDI electrode materials, and the other one is the proper structures facilitating the ion transfer processes. For our system, the high specific capacitance of GA/TiO$_2$ hybrids (119.7 F/g at 100 mV s$^{-1}$ and 142.6 F/g at 5 mV s$^{-1}$)$^{[27,37]}$ which is considerably larger than that of GA and AC (Figure 4B), ensuring the ion electrodosorption capability in the electrical double layer.$^{[22,37]}$ The fact that hybridization with TiO$_2$ NPs can improve the electrodosorption capacity of carbon materials is confirmed by comparison of AC ($Q_m$ = 3.6 mg/g) and AC/TiO$_2$ hybrids ($Q_m$ = 5.0 mg/g) (Figure S11). Furthermore, 3D open-pore structure of GA/TiO$_2$ hybrids will reduce the mass transport resistance of salt ions inside the electrode as well as between the electrode and the saline water.$^{[25g]}$ This structural feature gives rise to the high electrodosorption rate of GA/TiO$_2$ hybrids. As comparison, the conventional AC needs much more time to reach the adsorption equilibrium because it does not have such open-pore structures (Figure S12).

In conclusion, a novel and general approach is proposed to synthesize the well-defined 3D GQ/MO hybrids using low valence metal ions as the precursors. For the first time, we demonstrate that these GA/MO hybrids of open pore structures can be used as the high performance CDI electrode materials. Impressively, with respect to three important parameters of the CDI process, electrodosorption capacity, rate and reversibility, the GA/TiO$_2$ hybrids outperform the currently reported materials (Table S1). It is expected that this work will not only offer a promising way to develop high effective CDI electrode materials, but also holds the potential to be applied in other areas such as supercapacitors, catalysis (e.g., oxygen reduction reaction) and newly-emerged “capacitive mixing” technique.$^{[38]}$

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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