



Cite this: *Chem. Commun.*, 2017, 53, 881

Received 24th October 2016,
Accepted 2nd December 2016

DOI: 10.1039/c6cc08515f

www.rsc.org/chemcomm

Highly porous N-doped graphene nanosheets for rapid removal of heavy metals from water by capacitive deionization†

Lianjun Liu,^a Xiaoru Guo,^a Rebecca Tallon,^b Xingkang Huang^a and Junhong Chen^{*a}

This work reports on a highly porous N-doped graphene-based capacitive deionization device, which exhibits a high removal efficiency (90–100%), fast removal (<30 min), and good regeneration performance (10 cycles, 99% retention) for multiple heavy metals (Pb²⁺, Cd²⁺, Cu²⁺, Fe²⁺, etc.) in water with a wide range of concentrations (0.05–200 ppm).

A number of methods have been developed to remove heavy metal ions from water, including chemical precipitation, ion-exchange by resin or zeolite, adsorption by carbon, membrane filtration (e.g., reverse osmosis or RO), and electrodialysis (ED).^{1–3} However, these conventional methods often suffer from problems of limited efficiency at low metal concentrations, fouling by organic matters, high cost and pressure drop, or low regeneration rates. Alternatively, capacitive deionization (CDI) has emerged as a robust, energy-efficient, and cost-effective competitor to RO and ED, with applications ranging from metal ions removal, water softening, to desalination at a low total dissolved solids (TDS) concentration (<5000 ppm).^{3–8} The major market advantages of CDI are (1) low life-cycle cost, (2) ability to remove a wide range of ionic contaminants, (3) high recovery rate (>90%), and (4) low energy consumption.

The CDI technology has been extensively studied for applications of water softening and desalination, including materials innovation (e.g., graphene, carbon nanotube or CNT, mesoporous carbon, metal oxide/carbon),⁹ theoretical modeling, architectural optimization,⁸ kinetics and mechanism studies,¹⁰ and energy recovery;^{10–14} however, CDI for the removal of heavy metals is still in its infancy. So far only a few studies have been reported on the removal of Cu²⁺, Pb²⁺, As³⁺, Cd²⁺, and Cr³⁺ ions using activated carbon cloth (ACC),^{15,16} plasma-treated CNTs,¹⁷ carbon aerogel,^{18,19} and TiO₂/carbon fibers.²⁰ For example, Huang *et al.* attempted to concurrently remove Pb²⁺, Cd²⁺ and

Cr³⁺ using ACC-based CDI, but the removal efficiency can only reach 40–80% even after 2 h (0.05–0.5 mM, 1.2 V).¹⁵ Obviously, it still requires considerable efforts to enhance the metal adsorption capacity, accelerate the removal, and improve the cycling stability. To this end, it is highly desirable to develop new adsorbent materials with the combination of high surface area, porous structure, high conductivity, and good stability.

Graphene, a 2D carbon nanosheet, is of particular interest for CDI because of its outstanding electrical conductivity, superior mechanical flexibility, large surface area, and high thermal-chemical stability. Graphene-based materials, such as hydrogels, sponges, and 3D macroporous structures, have been widely studied for water desalination,^{21–25} but seldom for heavy metal removal. On the other hand, the aforementioned graphene materials are prepared by hydrothermal plus freeze drying and microwave or template-assistant methods, which are time-consuming and thus costly. Furthermore, the resulting graphene has a relatively small pore volume. It is hence very necessary to develop a facile and cost-effective method to construct porous graphene with a high pore volume.

Here we report on novel crumpled N-doped graphene (CNG) nanosheets by a facile one-pot method, *i.e.*, thermally treating a mixture of graphene oxide and cyanamide at 900 °C (see experimental in the ESI†). As expected, the as-prepared CNG had a mesoporous structure with a high surface area (695 m² g⁻¹), a large pore volume (2.27 cm³ g⁻¹), and abundant defective sites (Fig. S1, ESI†). This unique CNG was used as electrode material for membrane-CDI to remove multiple heavy metals (e.g., Pb²⁺, Cd²⁺, Cu²⁺, Ni²⁺, Zn²⁺, Co²⁺, Fe²⁺) simultaneously (see the schematic/device in Fig. S2, ESI†). We expect to achieve a high adsorption capacity, high removal efficiency, fast removal, and good cycling performance. To the best of our knowledge, this is the first report on simultaneous removal of multiple heavy metals from water using CNG-based MCDI technology.

Transmission electron microscopy (TEM) and SEM/energy dispersive X-ray spectroscopy (EDS) were conducted to identify the morphology and surface composition of CNG sheets. The TEM image in Fig. 1a clearly shows that CNG has a crumpled

^a University of Wisconsin-Milwaukee, Mechanical Engineering Department, Milwaukee, WI, 53211, USA. E-mail: jhchen@uwm.edu

^b A.O. Smith Corporation, Corporate Technology Center, Milwaukee, WI, 53224, USA

† Electronic supplementary information (ESI) available. See DOI: 10.1039/c6cc08515f



concentrations (0.05–200 ppm). For solutions with low initial concentrations (50–500 ppb), Pb^{2+} and Cd^{2+} can be quickly removed within 5 min (Fig. S6a, ESI†). The efficiency can reach almost 100% (Fig. 2d), and the residual Pb^{2+} is below the EPA recommended action level of 15 ppb. This low initial concentration range can mimic the real environmental systems, where large volumes of dilute solution could be treated. For solutions with high concentrations (1–200 ppm), CNG-based MCDI also demonstrated a superior efficiency (100%) to deionize Pb^{2+} and Cd^{2+} from water, while it took a longer duration (at least 30 min) at 200 ppm. This result indicates that our material and device have great potential to treat wastewater containing high concentrations of heavy metals. More importantly, at 200 ppm the adsorption capacity of NG for Pb^{2+} and Cd^{2+} can reach 521 mg g^{-1} and 498 mg g^{-1} , respectively. The removal capacity of Pb^{2+} delivered by CNG was at least twice higher than that of graphene-based aerogel, ACC, and CNTs reported previously.^{4,15,17} This superior performance is primarily because CNG could provide a large ion-accessible surface area, porous structure for fast ion transport, and highly conductive networks, while N-doping plays a critical role in creating such a unique crumpled structure. N dopants could also change spin density and charge distribution of carbon atoms in the graphene, thereby inducing the formation of surface “activated sites”. Such activated sites could participate in the electro-sorption of ions.²⁸ Noticeably, different from the conventional adsorption process that is usually a time-consuming process (a few hours or longer), the present MCDI not only offers a high removal efficiency and a high capacity, but also achieves a high removal rate.

Besides Pb^{2+} and Cd^{2+} , the real water system may contain other interfering cations and anions, such as Ni^{2+} , Co^{2+} , Fe^{2+} , Cu^{2+} , Zn^{2+} , Mg^{2+} , Ca^{2+} , Cl^- , NO_3^- , and SO_4^{2-} . To determine the selectivity of CNG-based MCDI, we conducted competitive adsorption of multiple metal ions using MCDI. Among the various cations (Fig. 3a), Fe^{2+} was most easily removed with a high efficiency and a high rate ($\sim 96\%$ at 15 min), while the elimination of Cd^{2+} was the slowest ($\sim 80\%$ at 30 min). Cu^{2+} and Pb^{2+} showed a similar removal trend, but their removal efficiency was slightly higher than that of others (Co^{2+} , Ni^{2+} , Zn^{2+} , Mg^{2+} and Ca^{2+}). Eventually, the removal efficiency of all the nine cations could reach 90–100% at 45 min. This is an important finding that demonstrates the strong capability of

CNG-based MCDI to remove multiple metals efficiently ($>90\%$), quickly (<45 min), and simultaneously. Theoretically, the anions (Cl^- , NO_3^- , SO_4^{2-}) from metal precursors will also be attracted by the positively charged electrode. In this work, however, the removal of anions was not measured. Our future work will focus on the study of removal of both anions and cations after optimizing the operation conditions.

We also simulated the kinetics of heavy metal sorption using a pseudo first-order kinetic model, following the Langmuir adsorption model. The equation can be expressed as follows:

$$q_t = q_e(1 - e^{-kt})$$

where q_t and q_e are the adsorption amount (mg g^{-1}) at time t and at equilibrium, and k is the rate constant (min^{-1}). As shown in Fig. 3b, Fe^{2+} shows the highest rate constant (0.232 min^{-1}), over 100% and six times higher than that of Pb^{2+} (0.077 min^{-1}), Cu^{2+} (0.089 min^{-1}) and Cd^{2+} (0.031 min^{-1}), respectively. During the MCDI process, the electrostatic attraction should dominate the adsorption of metals. However, from Fig. 3 one can find that the removal efficiency and rate constant are different for the different types of ions at the initial 25 min. This difference may be caused by the surface functional groups of CNG ($-\text{OH}$, $-\text{COOH}$) and metal ion properties (radius, ionic potential, hydrated radius and charge size).^{15,29} The high efficiency and rate for Fe^{2+} is because Fe^{2+} could be easily oxidized to Fe^{3+} , which has a higher charge size and stronger affinity to surface OH groups than other ions. In this case, Fe ions have a preference to occupy the adsorption sites even in the presence of other competitive ions. The least favorable adsorption for Cd^{2+} is mainly due to its larger hydrated radius and expulsion effect by competitors,²⁹ consistent with the literature reports that Cd^{2+} showed a lower efficiency than Pb^{2+} and Cr^{3+} .¹⁵ Among the mixed ions, Pb^{2+} has the largest ionic radius (1.32 \AA) and atomic weight (207) and larger electronegativity (2.33), which can contribute to its favorable adsorption, while Cu^{2+} has a stronger affinity to complex with hydroxyl groups. Obviously, there is a trade-off among the above-mentioned factors, which may have a combined effect on the adsorption process, thereby leading to a comparable efficiency and rate constant between Cu^{2+} and Pb^{2+} but higher than those of others like Zn^{2+} , Co^{2+} , Ni^{2+} and Cd^{2+} .

A good regeneration performance of CNG is quite important for heavy metal removal. Fig. 4a shows the removal efficiency of Pb^{2+} and Cd^{2+} during the first 10 cycles, which were conducted by repeating adsorption (charging at 1.2 V) and desorption (discharging at 0 V) processes in a Pb^{2+} + Cd^{2+} solution. It is clearly seen that at each cycle, the efficiency for Pb^{2+} and Cd^{2+} remained at $\sim 100\%$, suggesting that the CNG electrodes can be completely regenerated and reused over 10 cycles without any significant degradation. More importantly, the regeneration process is facile and eco-friendly without any acid washing or post treatment process. The $I-t$ curves during the charge-discharge process further demonstrate that CNG-based MCDI has an outstanding recovery rate and reversibility (Fig. 4b). The charge-discharge process in one cycle only takes ~ 30 min. This good performance (high retention efficiency (99%) and

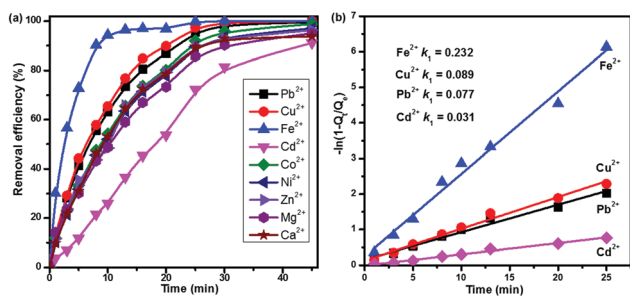


Fig. 3 MCDI performance for multiple ions removal: (a) time-dependent efficiency and (b) kinetics for Fe^{2+} , Cu^{2+} , Pb^{2+} , and Cd^{2+} (~ 10 ppm for each metal ion, flow rate: 50 ml min^{-1} , 25 mg materials, 100 ml solution, 1.2 V).



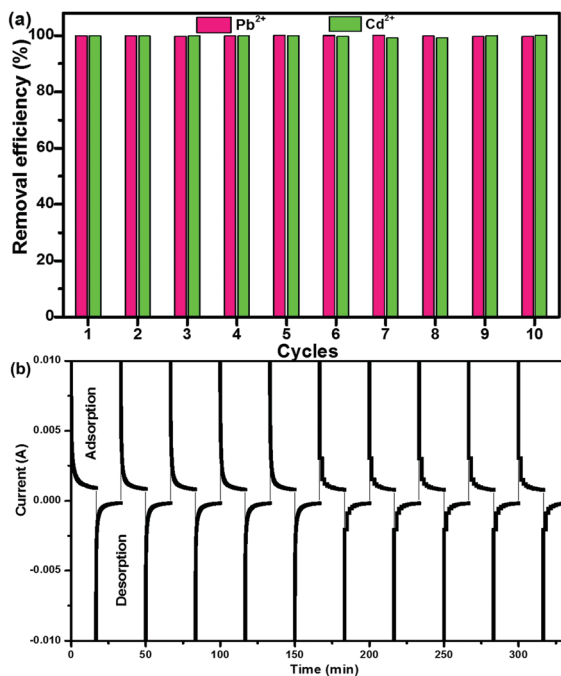


Fig. 4 (a) The removal efficiency of Pb^{2+} (pink bar) and Cd^{2+} (green bar) during 10 cycles. The efficiency is calculated on the basis of concentration after 15 min adsorption; at the end of each cycle, the electrode materials were regenerated by discharging at 0 V. Fresh feeding water (50 ml, ~ 20 ppm $\text{Pb}^{2+} + \text{Cd}^{2+}$) was then introduced to replace the original solution; and (b) the $I-t$ curves of adsorption (charge at 1.2 V) and desorption (discharge at 0 V) over 10 cycles.

high regeneration rate) may result from the unique porous structure of crumpled NG networks and application of ion-exchange membranes that facilitate ion transport, minimize the co-ion expulsion effect, and enhance the charge efficiency. The superior recycling performance and stability indicate the promise of CNG MCDI for water purification.

In summary, we have developed a facile one-pot method to construct a highly porous N-doped graphene with a high surface area and a large pore volume. The resulting CNG was used as the electrode material for MCDI to remove multiple heavy metals from water. The CNG-based MCDI demonstrated a high removal efficiency (90–100%), a high removal rate (<30 min), a high capacity (~ 500 mg g^{-1}) and a good recycling performance (10 cycles, 99% retention) to remove Pb^{2+} and Cd^{2+} simultaneously from water with a wide range of concentrations (0.05–200 ppm). More importantly, the CNG-based MCDI also has a strong capability to remove multiple metals efficiently, concurrently and quickly (>90% within 45 min). The findings reported in this work shed light on the application of CNG-based MCDI for water

purification and softening, which can potentially compensate the current technologies for heavy metal removal.

The ion exchange membrane used to assemble the CDI device was provided by Pentair.

Notes and references

- 1 F. L. Fu and Q. Wang, *J. Environ. Manage.*, 2011, **92**, 407–418.
- 2 M. Hua, S. J. Zhang, B. C. Pan, W. M. Zhang, L. Lv and Q. X. Zhang, *J. Hazard. Mater.*, 2012, **211**, 317–331.
- 3 I. Duru, D. Ege and A. R. Kamali, *J. Mater. Sci.*, 2016, **51**, 6097–6116.
- 4 X. Gu, Y. Yang, Y. Hu, M. Hu and C. Wang, *ACS Sustainable Chem. Eng.*, 2015, **3**, 1056–1065.
- 5 T. Humpalik, J. Lee, S. C. O'Hern, B. A. Fellman, M. A. Baig, S. F. Hassan, M. A. Atieh, F. Rahman, T. Laoui, R. Karnik and E. N. Wang, *Nanotechnology*, 2011, **22**, 292001.
- 6 S. Porada, R. Zhao, A. van der Wal, V. Presser and P. M. Biesheuvel, *Prog. Mater. Sci.*, 2013, **58**, 1388–1442.
- 7 F. A. AlMarzooqi, A. A. Al Ghaferi, I. Saadat and N. Hilal, *Desalination*, 2014, **342**, 3–15.
- 8 M. E. Suss, S. Porada, X. Sun, P. M. Biesheuvel, J. Yoon and V. Presser, *Energy Environ. Sci.*, 2015, **8**, 2296–2319.
- 9 S. Daer, J. Kharraz, A. Giwa and S. W. Hasan, *Desalination*, 2015, **367**, 37–48.
- 10 F. Duan, Y. Li, H. Cao, Y. Xie and Y. Zhang, *Desalin. Water Treat.*, 2014, **52**, 1388–1395.
- 11 Y. Zhao, Y. Wang, R. Wang, Y. Wu, S. Xu and J. Wang, *Desalination*, 2013, **324**, 127–133.
- 12 M. A. Anderson, A. L. Cudero and J. Palma, *Electrochim. Acta*, 2010, **55**, 3845–3856.
- 13 R. Zhao, P. M. Biesheuvel and A. van der Wal, *Energy Environ. Sci.*, 2012, **5**, 9520–9527.
- 14 P. Dlugolecki and A. van der Wal, *Environ. Sci. Technol.*, 2013, **47**, 4904–4910.
- 15 Z. Huang, L. Lu, Z. X. Cai and Z. J. Ren, *J. Hazard. Mater.*, 2016, **302**, 323–331.
- 16 C. S. Fan, S. C. Tseng, K. C. Li and C. H. Hou, *J. Hazard. Mater.*, 2016, **312**, 208–215.
- 17 L. F. Yang, Z. Shi and W. H. Yang, *Surf. Coat. Technol.*, 2014, **251**, 122–127.
- 18 X. Y. Gu, Y. Yang, Y. Hu, M. Hu and C. Y. Wang, *ACS Sustainable Chem. Eng.*, 2015, **3**, 1056–1065.
- 19 Z. Wang, L. Yue, Z. T. Liu, Z. H. Liu and Z. P. Hao, *J. Mater. Chem.*, 2012, **22**, 14101–14107.
- 20 L. Peng, Y. P. Chen, H. Dong, Q. R. Zeng, H. J. Song, L. Y. Chai and J. D. Gu, *Water, Air, Soil Pollut.*, 2015, **226**, 203.
- 21 Y. Liu, T. Chen, T. Lu, Z. Sun, D. H. C. Chua and L. Pan, *Electrochim. Acta*, 2015, **158**, 403–409.
- 22 Y. Liu, X. Xu, M. Wang, T. Lu, Z. Sun and L. Pan, *J. Mater. Chem. A*, 2015, **3**, 17304–17311.
- 23 S. S. Zhao, T. T. Yan, H. Wang, G. R. Chen, L. Huang, J. P. Zhang, L. Y. Shi and D. S. Zhang, *Appl. Surf. Sci.*, 2016, **369**, 460–469.
- 24 Z.-Y. Yang, L.-J. Jin, G.-Q. Lu, Q.-Q. Xiao, Y.-X. Zhang, L. Jing, X.-X. Zhang, Y.-M. Yan and K.-N. Sun, *Adv. Funct. Mater.*, 2014, **24**, 3917–3925.
- 25 X. Xu, Y. Liu, T. Lu, Z. Sun, D. H. C. Chua and L. Pan, *J. Mater. Chem. A*, 2015, **3**, 13418–13425.
- 26 L. Liu, X. Huang, X. Guo, S. Mao and J. Chen, *J. Power Sources*, 2016, **328**, 482–491.
- 27 I. R. Pala and S. L. Brock, *ACS Appl. Mater. Interfaces*, 2012, **4**, 2160–2167.
- 28 G. A. Ahmad Amiri, M. Shanbedi, M. Savari, S. N. Kazi and B. T. Chew, *Sci. Rep.*, 2015, 17503.
- 29 Y. Ding, Y. G. Liu, S. B. Liu, Z. W. Li, X. F. Tan, X. X. Huang, G. M. Zeng, Y. Y. Zhou, B. H. Zheng and X. X. Cai, *RSC Adv.*, 2016, **6**, 5223–5232.

