Supporting information

Highly Porous N-doped Graphene Nanosheets for Rapid Removal of Heavy Metals from Water by Capacitive Deionization

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Experimental section

1. Materials synthesis

GO was prepared from natural graphite by a modified Hummers' method, as reported in our previous work.¹ Crumpled N-doped graphene (CNG) was synthesized by a facile one-pot method. Briefly, 0.2 g GO and 6 g cyanamide were dissolved in 100 ml deionized water by stirring for 1 h. Then, the solution was evaporated at 80 °C to obtain the complex, which was ground in a mortar. The obtained powder was calcined at 900 °C for 0.5 h in an Ar atmosphere.

2. Materials characterization

The crystal structures of the electrode materials were identified by X-ray diffraction (XRD, Bruker D8-Advance X-ray powder diffractometer). Raman spectroscopy was conducted with a Renishaw Raman spectrometer (Renishaw Inc., Wotton-under-Edge, UK; Inc., 1000B) with an HeNe laser. The specific surface area and pore volume were analyzed by nitrogen adsorption-desorption at 77 K using the Brunauer-Emmett-Teller (BET) method (Micromeritics, ASAP 2020). Scanning electron microscopy (SEM) (Hitachi S4800) was used to obtain the surface morphology. The surface dispersion of C, O, and N elements was analyzed by X-ray elemental mapping. The morphology of CNG was visualized by Amplitude contrast transmission electron microscopy (TEM) carried out with 300 keV electrons in a Hitachi H9000NAR instrument with 0.18 nm point and 0.11 nm lattice resolution.

3. Batch mode CDI performance

The electrodes were fabricated by using 85% of CNG as working electrode and 15% of butyl sodium rubber (BSR, 50% water suspension) as a binder. The amount of CNG was about 25 mg. During the fabrication process, DI water and a few drops of ethanol were added to ensure it could easily form homogeneous slurries. The mixture was then coated onto graphite foil paper (the active area is 8 cm × 8 cm). The thickness of the coating layer is about 150 µm. The obtained electrodes were dried in a vacuum oven at 90 °C overnight. The CDI treatment unit was assembled with a pair of parallel electrode plates, ion exchange membranes, insulating spacers, and rubber gasket. Cation and anion membranes were placed on the top of electrode materials. Between them, a woven spacer with a 150-200 µm thickness, a mesh opening of 250-300 µm and a 50-60% open surface was used to guide the water flow in the CDI unit.

The MCDI performance of the CNG electrodes was measured in a batch mode, which was conducted in a continuous circulating system. The flow rate (10 mL/min – 100 mL/min) was controlled by a

peristaltic pump. The volume of Pb²⁺+Cd²⁺ solution was 50 mL. The initial ion concentrations were 0.05 ppm, 0.1 ppm, 0.5 ppm, 1 ppm, 10 ppm, 20 ppm, 50 ppm, and 200 ppm. The cell voltages were 1.2 V for adsorption and 0 V for desorption, controlled by a CHI660D electrochemical workstation. At a given time, 5 mL solution was collected for analysis. The concentration changes of Pb²⁺+Cd²⁺ solution were measured by an Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES). The removal efficiency for heavy metals was calculated by the following equation:

$$E\% = \frac{C_o - C_t}{C_o} \times 100$$

where C_o and C_t are the concentrations of metal ions at the beginning and at t time, respectively.

The adsorption capacities of Pb²⁺ and Cd²⁺ were calculated from the following equation:

$$q = (C_o - C_t) \times v/m$$

where Co and Ct are the initial and final concentrations of ions, respectively, V is the total volume of solution, and m is the mass of electrode materials.

4. Electrochemical measurement

To explore the electro-sorption ability of the CNG-based electrodes, the potential sweep cyclic voltammetry (CV) was carried out in the 1.0 M KCI solution by a CHI 660D in a three-electrode setup, including a CNG glassy electrode as a working electrode, 1M Ag/AgCl as a reference electrode, and a graphite rod as a counter electrode, respectively. The scan rates were ranging from 25 mV/s to 500 mV/s. The scan voltage window was -0.4 – 0.8 V (vs. Ag/AgCl).



Figure S1. (a) Schematic for heavy metal ions removal from water using membrane-CDI (MCDI), (b) scanning electron microscopy (SEM) image of crumpled N-doped graphene sheets, and (c) digital photo of a prototype CDI device.



Figure S2. (a) XRD pattern and (b) Raman spectrum for CNG



Figure S3. (a) N₂-adsorption/desorption isotherms and (b) pore size distribution for CNG.

CNG displayed typical type-IV isotherms with a type H₃ hysteresis loop (Figure S3a), suggesting the existence of slit-shaped mesopores caused by the spacing between thin graphene sheets. The pore size distribution shows that CNG has a combination of small (3.5 nm) and large (28.9 nm) mesopores (Figure S3b).







Figure S5. CDI performance (without ion-exchange membrane) for Pb²⁺ and Cd²⁺ removal (~20 ppm, flow rate: 50 ml/min, 25 mg materials, 50 ml solution, 1.2 V, batch mode).



Figure S6. The removal efficiency of Pb²⁺ and Cd²⁺ at different concentrations.

Table S1. Comparison of metal removal efficiency using different electrode materials

Materials	Metal ions	Voltage	Efficiency (time)	Reference
TiO ₂ /active carbon fiber	As ⁴⁺	1.5 V	0.5 h (70%), 2.5 h (97%)	2
Air-plasma treated CNTs	Pb ²⁺	0.45 V	1 - 2 h (<30%)	3
Activated carbon cloth	Pb ²⁺ , Cd ²⁺ , Cr ³⁺	0.6-1.2 V	2 h (22%-42%)	4
Carbon aerogel	Cr ³⁺	1.3 A h	pH =2, 97.5%, pH =4.5, 72% pH =7, 78%	5
Graphene-resol	Fe ³⁺	2.0 V	~60% (80 min – 100 min)	6
N-doped graphene	Pb ²⁺ , Cd ²⁺ (Fe ²⁺ , Cu ²⁺ , Ni ²⁺ , Zn ²⁺ , Co ²⁺ , Mg ²⁺ , Ca ²⁺)	1.2 V	5 min (95-96%), 15 min (>99%) <45 min (> 90%)	This work

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