Electronic Supplementary Information

Effective charge-discriminated group separation of metal ions under highly acidic condition using nanodiamond-pillared graphene oxide membrane

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Experiment Sections:

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2. **Section S2. (Fig. S2)** The species distribution of the metal ions tested.

Captions:

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Section S1. Effect of different ND:GO ratio on the separation ability of NPG membranes.

As a preliminary experiment, the separation performance of NPG membranes with different ND:GO ratio were investigated. Three kinds of NPG membranes were prepared, the mass ratio were ND:GO=1:1 (marked as NPG-11), ND:GO=1:3 (marked as NPG-13), and ND:GO=1:6 (marked as NPG-16), respectively. Then, the selectively permeation ability of the membranes were investigated in 4M HNO_3 solution, and the results were shown in Fig. S1. All the as-prepared NPG membranes exhibited the ability of charge-discriminated group separation to different extents in the permeation rate and the ion-selectivity. It is clear that the NPG membrane with ratio of ND:GO=1:3 could be a better option. It is worth mentioning that NPG-11 membrane had crumbled naturally after 48 h exposure to the atmosphere, while NPG-13 and NPG-16 membranes remained visually unchanged.

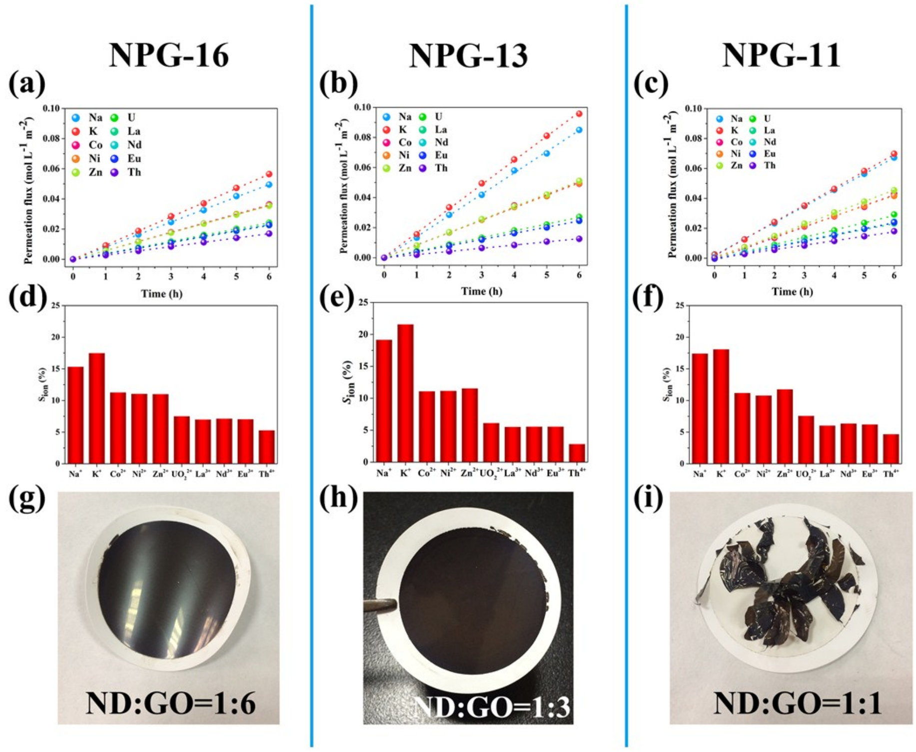

Fig. S1 The permeation flux, cation selectivity and the digital photograph (exposure to the atmosphere for 48 h) of NPG-16 (a, d, g), NPG-13 (b, e, h), and NPG-11(c, f, i) membranes.

Section S2. The species distribution of the metal ions tested.

Using the chemical speciation program CHEMSPEC (C++)[1], the species distribution of the metal ions used in the experiments was calculated to the best of our ability. The species distribution of Na^+, K^+, Co^{2+}, Ni^{2+}, Eu^{3+}, UO_2^{2+} and Th^{4+} were shown in Fig S6 respectively. The lack of the species distribution data of Zn^{2+}, La^{3+}, Nd^{3+} is due to the shortage of relative data in the original program.

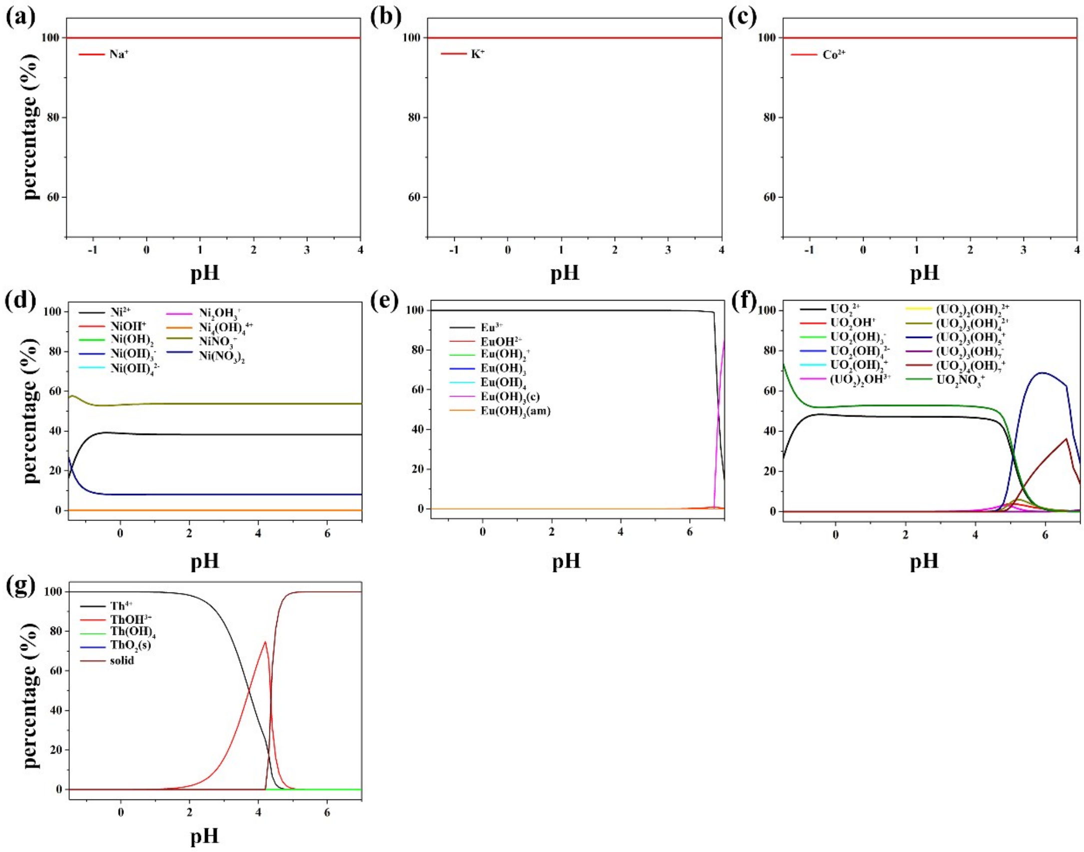

Fig. S2 The species distribution of Na^+, K^+, Co^{2+}, Ni^{2+}, Eu^{3+}, UO_2^{2+} and Th^{4+} in different concentrated nitric acid solution.

6. J. Zhu, X. Wang, T. Chen and C. Liu, *Scientia Sinica Chimica*, 2012, **42**, 856-864.

Table S1. Hydrated diameters (r_H) of the cations involved in the experiments.[2-5]

ion	Na^+	K^+	Co^{2+}	Ni^{2+}	Zn^{2+}	La^{3+}	Nd^{3+}	Eu^{3+}	UO_2^{2+}	Th^{4+}
r_H (Å)	7.16[1]	6.62[1]	8.46[1]	8.08[1]	8.60[1]	9.22[2]	9.22[2]	9.30[2]	11.6[3]	8.4[4]

1. E. R. Nightingale, *The Journal of Physical Chemistry*, 1959, **63**, 1381-1387.
2. F. David, V. Vokhmin and G. Ionova, *J. Mol. Liq.*, 2001, **90**, 45-62.
3. T. Yamaguchi, Y. Sakamoto, S. Nakayama and T. T. Vandergraaf, *J. Contam. Hydrol.*, 1997, **26**, 109-117.
4. G. Johansson, M. Magini and H. Ohtaki, *J. Solution Chem.*, 1991, **20**, 775-792.

Table S2. S_{ion}* and Relative Standard Deviation (RSD) of bivalent transition cations and trivalent lanthanide cations after permeating through the as-prepared nanofiltration membrane for 6 hours.

	Co^{2+}	Ni^{2+}	Zn^{2+}	average S_{ion}	RSD
S_{ion} (GO) %	12.04	11.99	12.66	12.23	±2.48
S_{ion} (NPG) %	11.08	11.15	11.52	11.25	±1.72

	La^{3+}	Nd^{3+}	Eu^{3+}	average S_{ion}	RSD
S_{ion} (GO) %	4.00	4.60	5.04；	4.55	±9.32
S_{ion} (NPG) %	5.50	5.55	5.55	5.54	±0.39

S_{ion}*: ion-selectivity

$$S_{ion} = \frac{c_{ion}}{c_{total}} \times 100\%$$

c_{ion} is the concentration of the particular cation and c_{total} is the sum of the concentration of all cations in the permeate part.

Table S3. The permeation flux and the S_{ion} data of NPG nanofiltration membrane in reusability experiments.

First round of recycling experiments.

	Na^+	K^+	Co^{2+}	Ni^{2+}	Zn^{2+}	La^{3+}	Nd^{3+}	Eu^{3+}	UO_2^{2+}	Th^{4+}
permeation flux at 6 h (mol L^{-1} m^{-2})	0.085	0.096	0.050	0.050	0.051	0.024	0.025	0.026	0.037	0.012
S_{ion} (%)	19.1	21.4	11.1	11.1	11.5	5.5	5.5	5.8	6.1	2.8

Third round of recycling experiments.

	Na^+	K^+	Co^{2+}	Ni^{2+}	Zn^{2+}	La^{3+}	Nd^{3+}	Eu^{3+}	UO_2^{2+}	Th^{4+}
permeation flux at 6 h (mol L^{-1} m^{-2})	0.079	0.087	0.045	0.048	0.049	0.024	0.023	0.023	0.026	0.012
S_{ion} (%)	19.1	21.0	10.8	11.4	11.8	5.7	5.6	5.5	6.2	2.9

Fifth round of recycling experiments.

	Na^+	K^+	Co^{2+}	Ni^{2+}	Zn^{2+}	La^{3+}	Nd^{3+}	Eu^{3+}	UO_2^{2+}	Th^{4+}
permeation flux at 6 h (mol L^{-1} m^{-2})	0.073	0.081	0.045	0.046	0.047	0.024	0.021	0.022	0.024	0.010
S_{ion} (%)	18.5	20.6	11.4	11.6	11.9	6.2	5.3	5.7	6.1	2.7

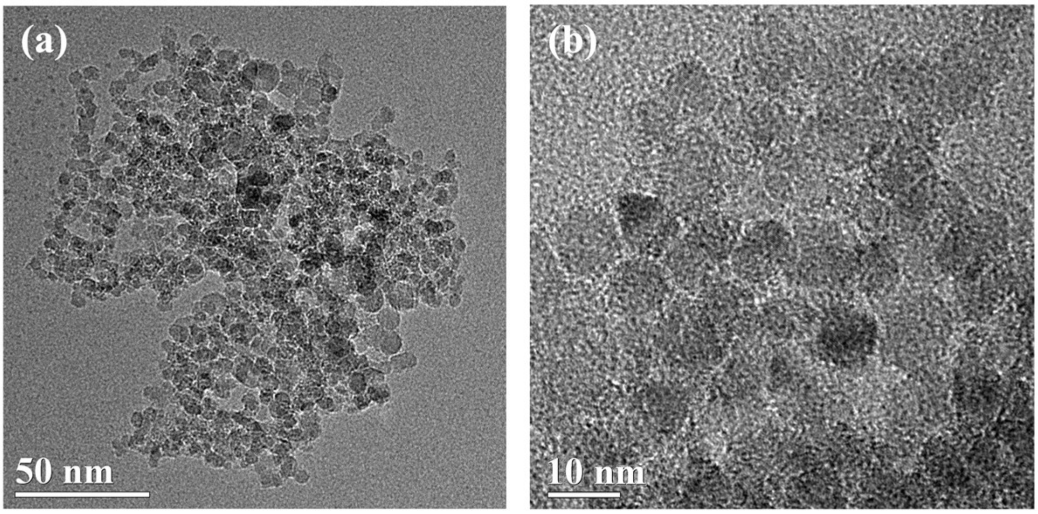

Fig. S3 The TEM image of pristine ND nanoparticles.

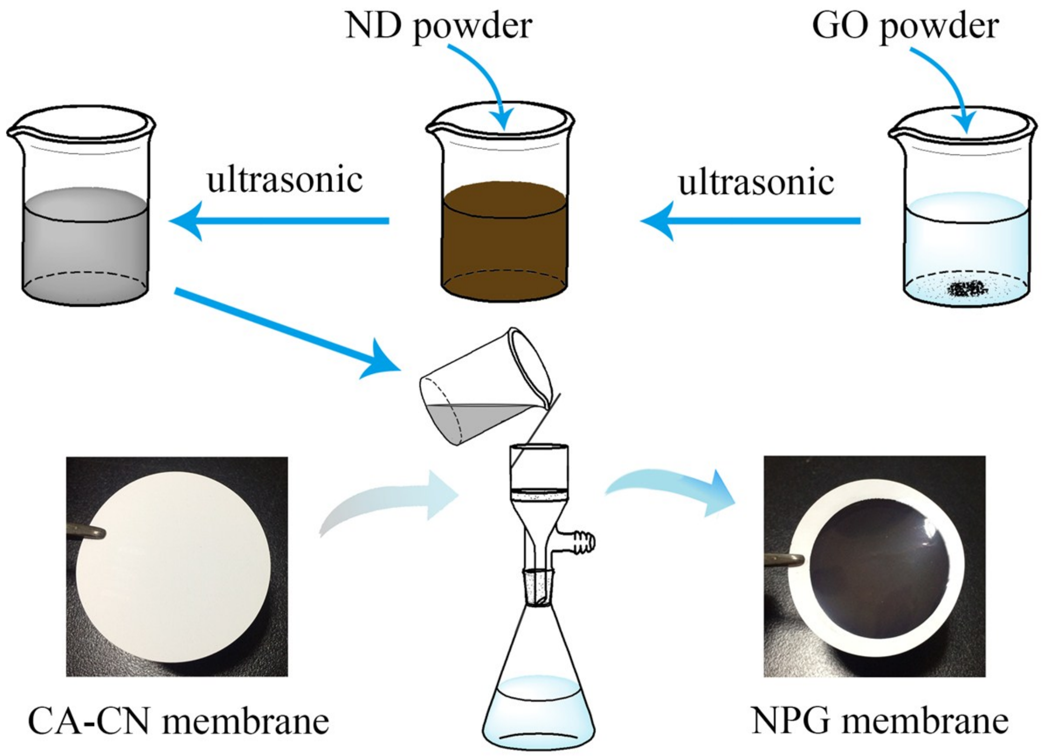

Fig. S4 The schematic diagram of the preparation procedure of NPG nanofiltration membrane.

The O1s high-resolution XPS of three kinds of nanomaterials is shown in Fig. S5. The peaks located at around 533.0 and 532.0 eV can be ascribed to C-O (epoxy and hydroxyl) and C=O (carbonyl and carboxyl) respectively.[6]

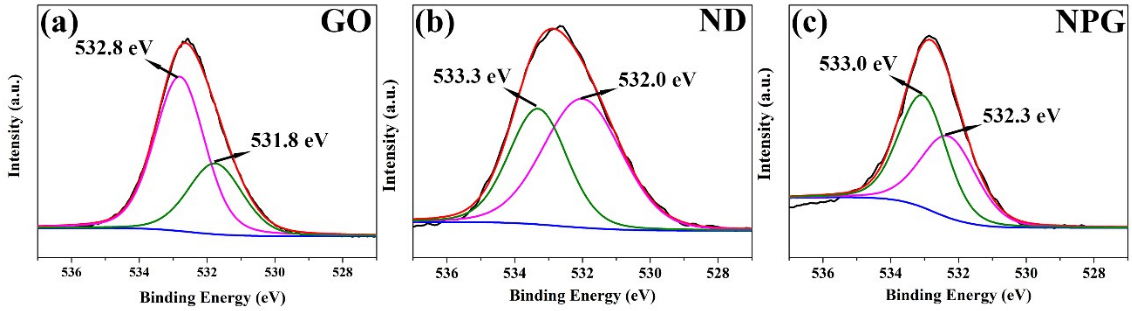

Fig. S5 XPS O1s high-resolution spectra of GO, ND and NPG.

5. C. M. Chen, J. Q. Huang, Q. Zhang, W. Z. Gong, Q. H. Yang, M. Z. Wang and Y. G. Yang, *Carbon*, 2012, **50**, 659-667.

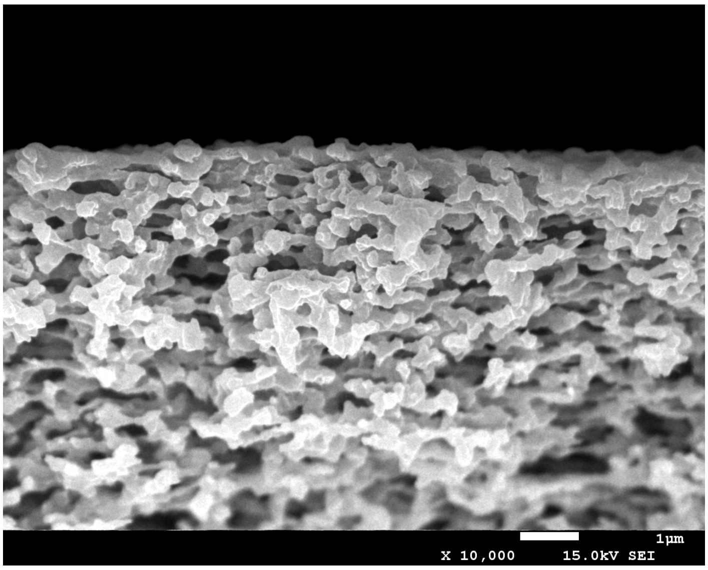

Fig. S6 The cross-section SEM image of CA-CN base membrane.