Electronic Supplementary Material (ESI) for RSC Advances.

Supplementary Information

Nitrogen-Doped Graphene-TiO_xN_y Nanocomposite Electrode for Highly Efficient Capacitive Deionization

Yuchen Wu[a,b], Gaopeng Jiang[b], Qian Li[b], Zisheng Zhang*[a] and Zhongwei Chen*[b]

a. Department of Chemical and Biological Engineering. University of Ottawa. 161 Louis Pasteur Private, Ottawa, Ontario K1N 6N5, Canada. Email: Jason.zhang@uottawa.ca

b. Department of Chemical Engineering, University of Waterloo, 200 University Ave W, Waterloo, Ontario N2L 3G1, Canada. E-mail: zhwchen@uwaterloo.ca,

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Calibration of SCE electrode

The SCE electrode was calibrated in NaCl solution using SCE to Reversible Hydrogen Electrode (RHE) in an open circuit as shown in **Fig. S2**. The result was adding +0.5V to the potential of SCE in NaCl solution, which means the -1V to 0V was -0.5V to 0.5V in actual.

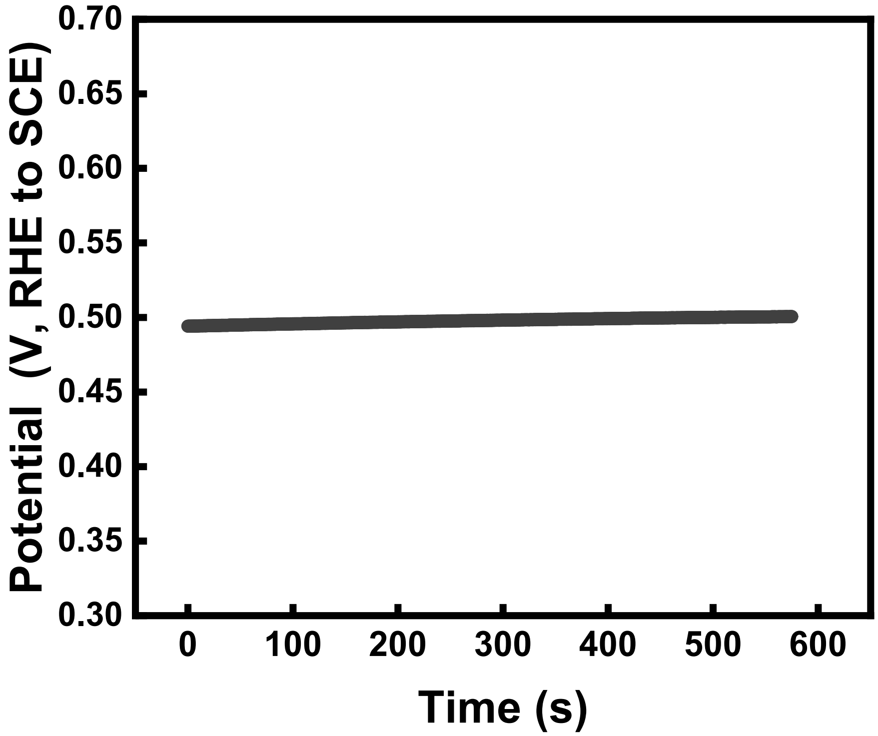

Fig. S1 Open circuit plot of SCE to RHE vs time.

Calibration of conductivity-salinity

The salinity of the water is based on a series calibration with a series of standard NaCl solution.

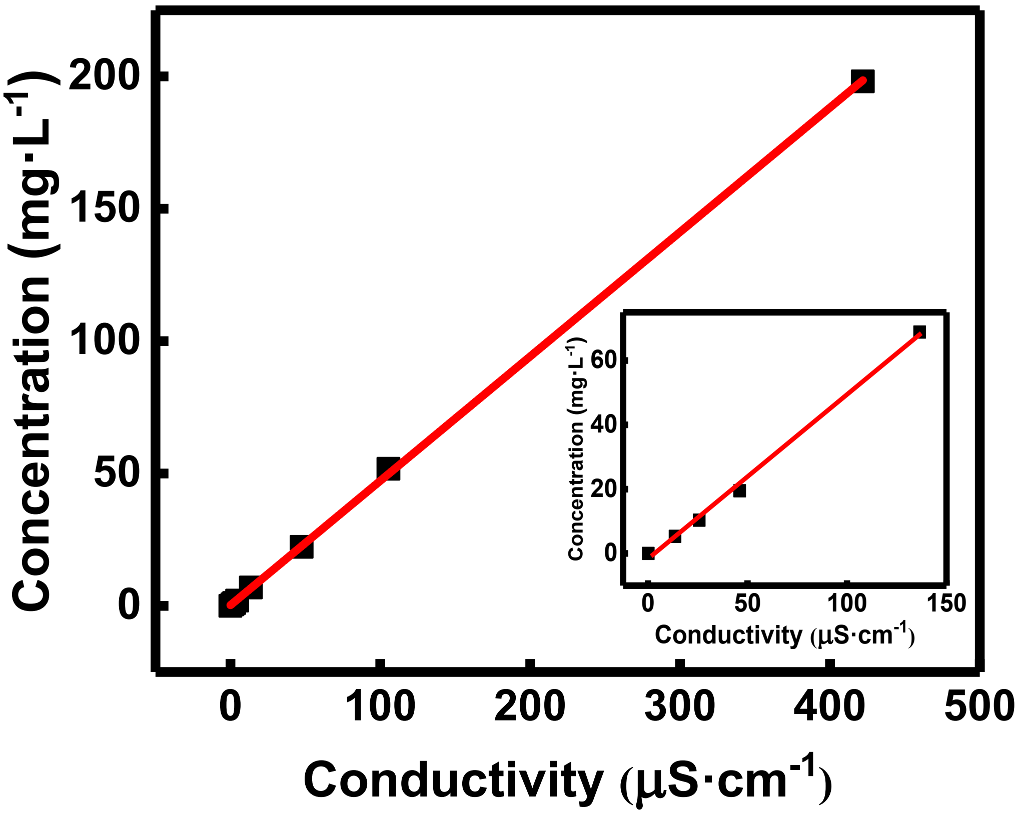

Fig. S2 calibration of the Conductivity to NaCl Concentration. The inserted graph is the enlarged part from 0-300 μS/cm^2.

The calibrated **Equation 1** of Conductivity-Concentration is:

$$C = 2.33873 * Conductivity(\mu S) + 3.60607\#(1)$$

Where the R^2=0.99993, indicating that the salinity of the solution can be considered as a linear dependent to the conductivity.

Supporting XRD information

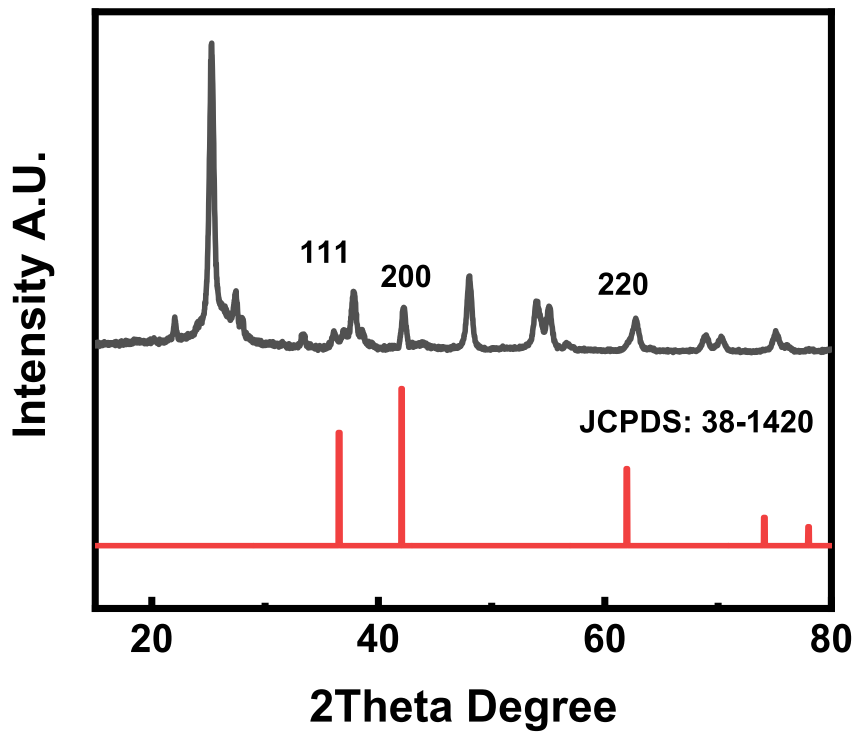

Fig. S3 XRD Patterns of NG-TiO_xN_y and JCPDS card of TiN

Supplemental SEM information

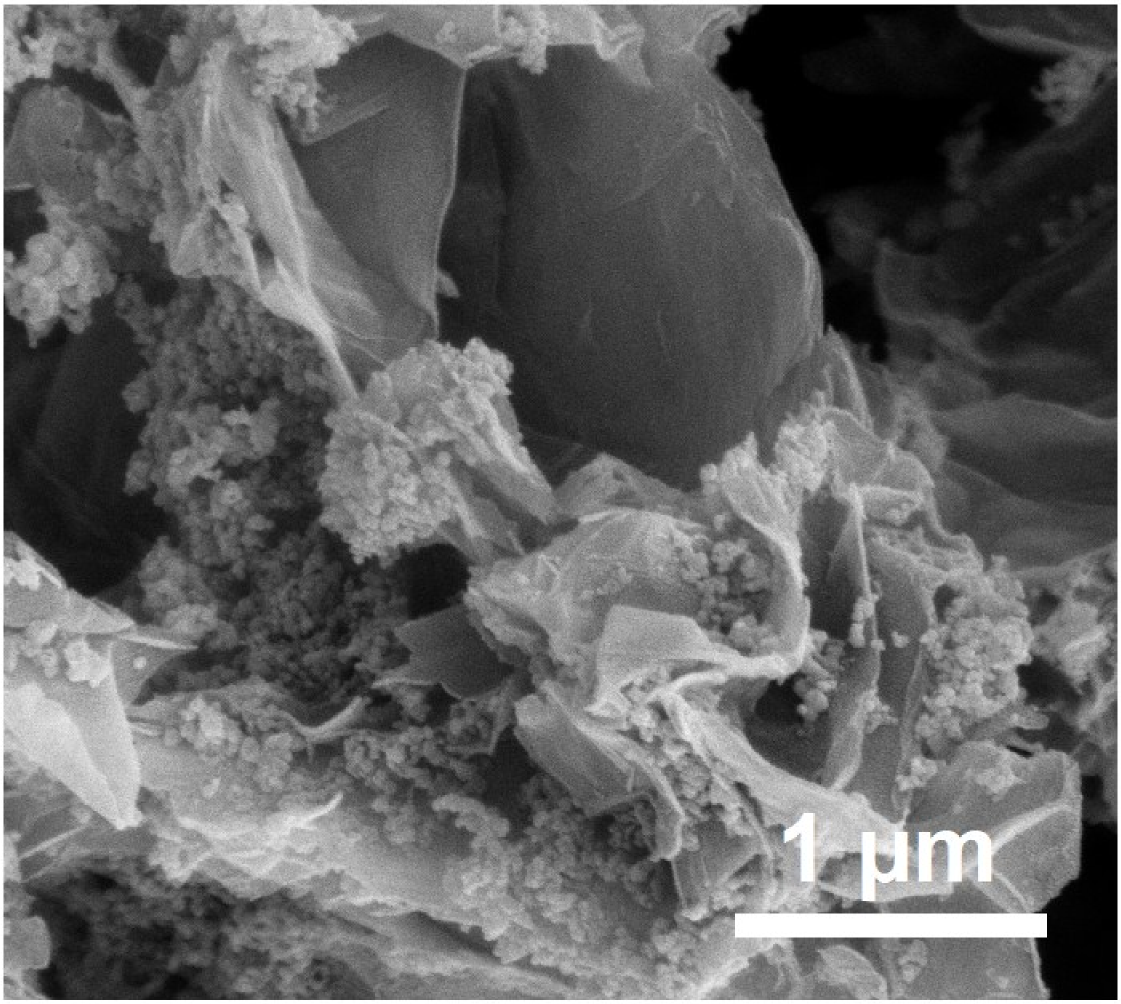

Fig. S4 Low magnification SEM image of the NG-TiO_xN_y .

Supplemental XPS wide survey

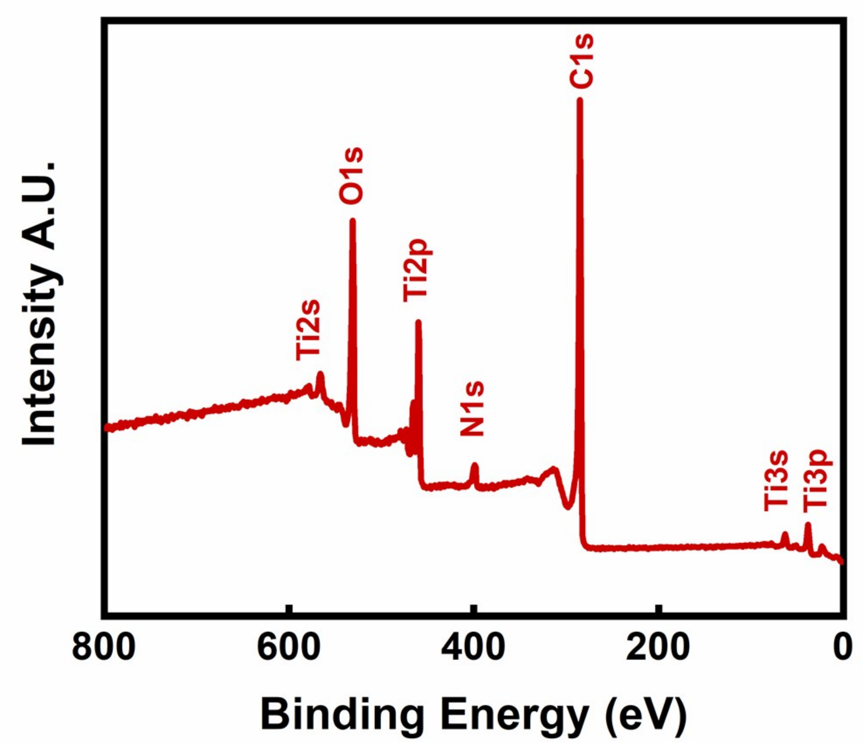

Fig. S5 XPS survey of the NG-TiO_xN_y.

Supplemental Ti 2p scan information

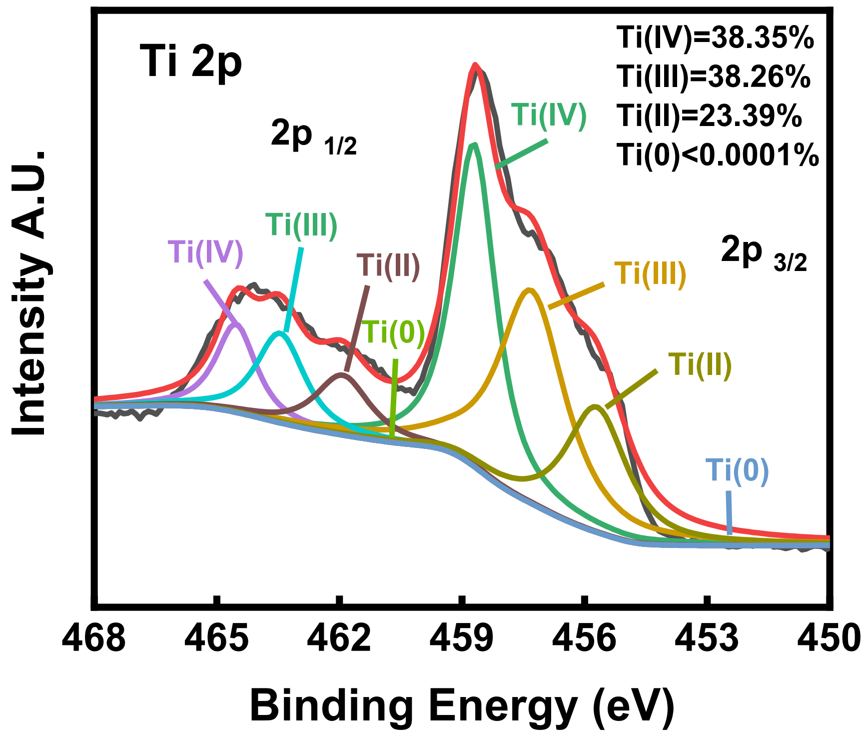

Fig. S6 Ti 2p XPS analysis of various Ti states.

Schematic of a flow-by CDI process

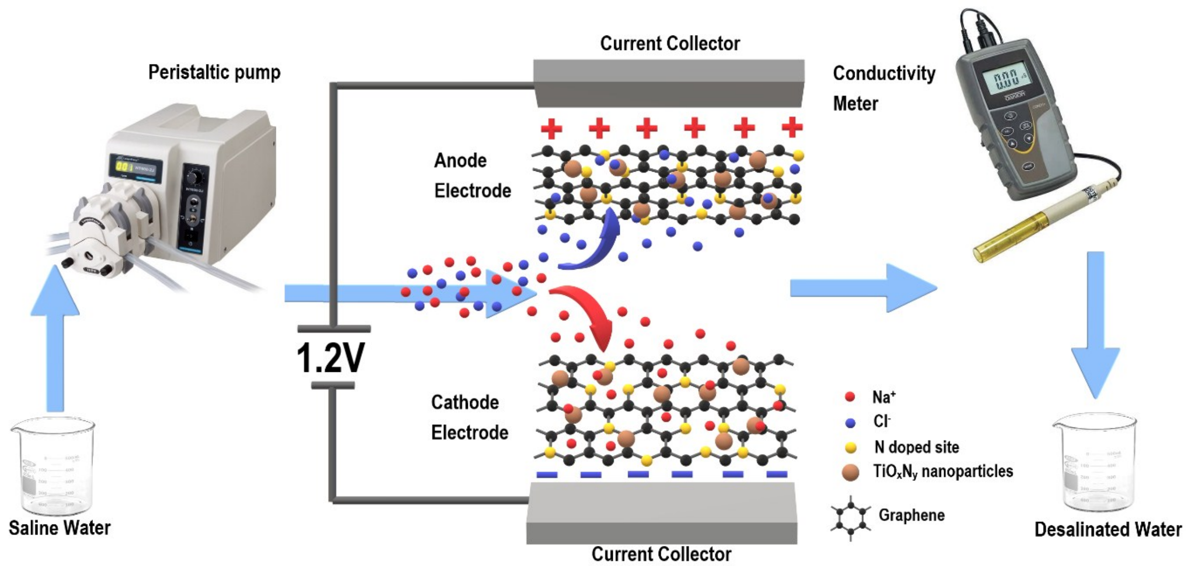

Fig. S7 Schematic of a flow-by CDI process

Supplemental Tables

Table S1 Lattice constants and N/Ti ratio of NG-TiO_xN_y.

	2θ/°	d $_{(220)}$ / Å	a/ Å	y
NG-TiO_xN_y	62.371	1.490	4.2211	0.6122

In this study, we conducted the nitridation process by the ammonia treatment of solid rGO-TiO_2 rather than the gaseous titanium precursor such as titanium tetrachloride. Thus, the nitridation is insufficient and the degree of nitridation is relatively low. Here, we made an attempt to calculate N/Ti ratio (y) using the reported method and XRD data listed in **Table S1**.[1]

The d_{220} is determined according to Bragg's law:

$$d_{220} = \frac{n\lambda}{2sin\theta}$$

TiN lattice parameter is then calculated:

$$a_{TiN_y} = d_{220}\sqrt{h^2 + k^2 + l^2}$$

From the obtained values of lattice parameters, the N/Ti ratio of TiO_xN_y in NG-TiO_xN_y is calculated:

$$a_{TiN_y} = 4.1925 + 0.0467y$$

Thus, the value of y is roughly 0.61 in the NG-TiO_xN_y nanocomposite. However, there is no fixed stoichiometry between nitrogen and titanium in titanium nitride. The N/Ti ratio varies from 0.6 to 1.2 and depends on the degree of nitridation.[2] In our design, the mass ratio of GO to TiO_2, the mass of rGO-TiO_2 charged in the ceramic boat, the porosity and morphology of rGO-TiO_2 as well as other experimental factors may affect the degree of nitridation. Thus, the value of y varies from sample to sample and from batch to batch.

Table S2 Oxidization states and atom percentage of Ti species in NG-TiO_xN_y.

i	Ti (IV)	Ti (III)	Ti (II)	Ti (0)
$O_{Ti(i)}$	+4	+3	+2	0
$P_{Ti(i)}$ /%	38.35	38.26	23.39	~0

According to Fig. R1, four different oxidation states were observed for Ti in NG-TiO_xN_y, namely Ti(IV), Ti(III), Ti(II) and Ti(0).[3, 4] The average oxidation state of titanium is calculated via the following equation:

$$Ti_{average} = \sum (O_{Ti(i)} \times P_{Ti(i)})$$

Where the $O_{Ti(i)}$ and $P_{Ti(i)}$ are the oxidation state and corresponding atom percentage of each Ti species. The values are listed in the above **Table S2**.

Thus, the calculated average oxidation state of Ti is +3.1497.

It is assumed that the oxidation states of all the nitrogen (O_N) and oxygen (O_O) that were bonded with Ti in the NG-TiO_xN_y composite are -3 and -2, respectively. Then, with the N/Ti ratio (y) calculated as 0.6122, the value of x can be calculated as follows:

$$x = -\frac{Ti_{average} + y * O_N}{O_O}$$

Then, we obtained the value of x as 0.6565，roughly 0.66.

References

1. V. Valvoda, R. Černý, R. Kužel, J. Musil and V. Poulek, *Thin Solid Films*, 1988, **158**, 225-232.
2. L. Toth, *Transition metal carbides and nitrides*, Elsevier, 2014.
3. M. C. Biesinger, B. P. Payne, B. R. Hart, A. P. Grosvenor, N. S. McIntryre, L. W. Lau and R. S. Smart, 2008.
4. M. C. Biesinger, B. P. Payne, A. P. Grosvenor, L. W. Lau, A. R. Gerson and R. S. C. Smart, *Applied Surface Science*, 2011, **257**, 2717-2730.