1 *Supporting Information*

2 **Capacitive Removal of Heavy Metal Ions from Wastewater *via* an**

3 **Electro-Adsorption and Electro-Reaction Coupling Process**

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14 The Supporting Information includes 73 pages, 39 Figures, and 14 Tables.

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EXPERIMENTAL SECTION

Chemicals.

NaCl (AR, 99%), Pb(NO$_3$)$_2$ (AR, 99%), Fe(NO$_3$)$_3$ (AR, 99%), Ni(NO$_3$)$_2$ (AR, 99%), Co(NO$_3$)$_2$ (AR, 99%), Cu(NO$_3$)$_2$ (AR, 99%), Cr(NO$_3$)$_3$ (AR, 99%), Cd(NO$_3$)$_2$ (AR, 99%), (NH$_4$)$_{10}$W$_{12}$O$_{41}$~xH$_2$O (AR, 99%), aniline (AR, 99%), methyl blue (AR, 99%), Graphene and CH$_3$CH$_2$OH (AR, 99%) were purchased from Sinopharm Chemical Reagent Co. Ltd. Dopamine hydrochloride (AR, 99%) and NH$_3$·H$_2$O (28-30%) were obtained from Aladdin Chemistry Co. (Shanghai, China).

Preparation of W$_{18}$O$_{49}$/C. W$_{18}$O$_{49}$/C samples were synthesized by a simple and reasonable synthesis scheme. 1.2 g of (NH$_4$)$_{10}$W$_{12}$O$_{41}$~xH$_2$O was added to 100 mL of tris-buffer solution (pH = 8.5) with a 5-min ultrasonic treatment. The mixed solution was heated and stirred for 30 min at 80°C. 0.4 g of dopamine hydrochloride was added to the above solution and stirred for 120 min. Then 160 mL of CH$_3$CH$_2$OH was added to the suspension and stirred for 1 h. Finally, 1.2 mL of NH$_3$ ·H$_2$O was added to the solution, stirred for 120 min, then centrifuged with CH$_3$CH$_2$OH, washed, and dried in vacuum for 12 h. The obtained mixtures were carbonized in a nitrogen atmosphere at 750 °C for 4 h (5 °C/min) to obtain W$_{18}$O$_{49}$/C.

The tris-buffer solutions preparation: 2 g of trimethylol aminomethane was dissolved in 2 L deionized water, and the pH value of the solution was adjusted to 8.5 by adding 0.1 mol/L hydrochloric acid.

Characterization.

The morphology and structure of the materials were observed by SEM (Sigma-300),

TEM (JEOL JEM-200CX), and HRTEM (FEI Tecnai G2 F20). The structure composition of the materials was explored by X-ray diffractometer (XRD) (X-ray diffractometer, Cu-K-α, 40kV mA). The composition of the sample was analyzed by PHI-5300 X-ray photoelectron spectroscopy (XPS). The Raman spectra were measured with 633 nm laser on HORIBA Science Raman spectrometer. The in-situ Raman measurements were carried out in the voltage range of −0.6 to 0.6 V at a CV scanning rate of 0.2 mV/s using the 633 nm Ar+ laser Raman spectrometer (HORIBA Science). The concentration of ions was tested by ICP-OES. The isothermal adsorption-desorption curve of nitrogen was studied via Autosorb-IQ$_2$. The specific surface area and pore size distribution of the samples were calculated by Brunauer-Emmett-Tell (BET) method and density functional theory (DFT) model, respectively. The wettability of the sample to water was tested by Kruss and DSA100 droplet shape analyzer. The electrochemical performance of the samples was evaluated by an electrochemical workstation (CHI 660E Chenhua, Shanghai). The concentrations of the aniline and methyl blue organic pollutants were detected by UV–vis spectrophotometer

Electrochemical Experiments.

The polytetrafluoroethylene (PTFE), conductive carbon black and the prepared material (5 mg) were fully mixed at a 1:1:8 mass ratio to make the square film, which was cast on graphite film (GF) collector to make asymmetric capacitive deionization experimental working electrode. The CV and galvanostatic charge−discharge (GCD) curves and electrochemical impedance spectroscopy (EIS) were measured in the 1000 mg/L NaCl solutions with a three-electrode system. The calomel electrode and GF serve

as reference electrode and counter electrode, respectively. The capacitance is

theoretically calculated by formula (Eq. S1):

$$C = \frac{\int I dV}{2mv\Delta V} \tag{S1}$$

C is the capacitance (F/g), I is the response current density (A), m is the mass of active

material (g), v is the scanning rate (V/s), and ΔV is the applied voltage window during

the CV test (V).

The thickness of electrodes is measured by a Micrometer. T_1 is thickness of electrodes
(μm), T_2 is average total thickness (882 μm), T_3 is average current collector (GF)
thickness (866 μm). Both the T_2 and T_3 are measured by a micrometer. The thickness of
electrodes is calculated by formula (Eq. S2) in theory:

$$T_1 = T_2 - T_3 \tag{S2}$$

The thickness of electrodes for electrochemical test of CV, GCD and EIS is closed to

16 μm.

Batch-Mode Capacitive Removal Experiments.

PTFE, conductive carbon black and the prepared material (40 mg) were fully mixed at

a 1:1:8 mass ratio to make the square film, which was cast on graphite film (GF)

collector to make asymmetric capacitive removal experimental working electrode.

Meanwhile, the symmetric electrode was made by fully mixing polytetrafluoroethylene

(PTFE), conductive carbon black and activated carbon (40 mg) according to the mass

ratio of 1:1:8. In the comparative experiment, the working electrode and counter

electrode of AC electrode were prepared in the same way. The spacer is placed between

two electrodes to separate them. 65 mL of NaCl solution circulates through the

electrode through the peristaltic pump at 40 mL/min. The conductivity meter (Seven

214   Multi of Mettler Toledo) is used to monitor the electrical conductivity of NaCl solution.

215   The pH value of the solution is adjusted by using 0.1 mol L^{-1} NaOH or HNO_3 solutions

216   to make the range between 4 and 8.

217   The capacitive removal experiments in NaCl solutions: 65 mL of NaCl solution is

218   circulated through the electrode by a peristaltic pump at the speed of 40 mL/min at 1.2

219   V for 120 min. The conductivity of NaCl solution was recorded on-line by a

220   conductivity meter (Seven Multi of Mettler Toledo). The salt adsorption capacity (SAC)

221   was calculated by formula (Eq. S3) in theory:

222
$$SAC = \frac{(C_0 - C)V_b}{m} \tag{S3}$$

223   *SAC* stands for the deionized mass specific capacitance, C_0 stands for the initial

224   concentration, and C_t stands for the final concentration, V represents the solution

225   volume (L) and *m* stands for the quality of electrode material (g).

226   On the basis of following equation, the salt adsorption rate (SAR, mg g^{-1} min^{-1}) could

227   be calculated (Eq. S4):[1, 2]

228
$$SAR = \frac{SAC}{t} \tag{S4}$$

229   Where t (min) stands for the desalination time.

230   The average salt removal rate (ASAR, mg g^{-1} min^{-1}) is the average of all SAR values

231   obtained throughout the desalination period.[3, 4]

232   On the basis of following equation, for constant-voltage, the specific energy

233   consumption (SEC^{-1}, mg J^{-1}) could be calculated (Eq. S5):[5, 6]

234
$$SEC^{-1} = \frac{(C_0 - C_t)V}{V_d \int_0^t I dt} \tag{S5}$$

235   Where I (A) and V_d (V) respectively stand for the time dependent current and applied

236   voltage.

237   On the basis of following equation, the charge efficiency (Λ, %) could be calculated

238   (Eq. S6):[7]

$$\Lambda = \frac{\Gamma \times F}{\Sigma} \qquad \text{(S6)}$$

240   Where Γ, F and Σ respectively stand for deionization capacity, Faraday constant and

241   obtained by integrating current.

242   On the basis of following equation, the energy consumption (EC, Wh g^{-1}) could be

243   calculated (Eq. S7):[8]

$$EC = \frac{V_d \int_0^t I dt}{m} \qquad \text{(S7)}$$

245   On the basis of following equation, the water recovery (WR, %) could be calculated

246   (Eq. S8):[6, 8]

$$WR = \frac{V_1 t_1}{V_1 t_1 + V_2 t_2} \qquad \text{(S8)}$$

248   Where V_1, t_1, V_2 and t_2 stand for the volume of initial NaCl solution, the time of NaCl

249   removed in one cycle, the volume of recuperative initial NaCl solution and the time of

250   recuperating initial NaCl solution. There is concentration recycle, resulting in $V_1=V_2$.

251   On the basis of following equation, the product water-specific Gibbs free energy ($\triangle$g,

252   J g^{-1}) could be calculated (Eq. S9):[9]

$$\triangle g = 2RT \left\{ \frac{C_0}{WR} \ln \left[\frac{C_0 - C_t WR}{C_0(1-WR)} \right] - C_t \ln \left[\frac{C_0 - C_t WR}{C_t(1-WR)} \right] \right\} \qquad \text{(S9)}$$

254   Where R and T stand for the ideal gas constant and the absolute temperature.

255   On the basis of following equation, the energy efficiency (EE, %) could be calculated

256   (Eq. S10):[9]

$$EE = \frac{\triangle g}{EC} \qquad \text{(S10)}$$

258

259 The removal efficiency (C) was calculated by formula (Eq. S11) in theory:

$$C = \frac{c_0 - c_t}{c_t} \qquad \text{(S11)}$$

261 C stands for the removal efficiency, C_0 stands for the initial concentration, and C_t stands

262 for the final concentration.

263 The capacitive removal experiments in the binary-component heavy metal ions and

264 NaCl solutions: 10 mg/L Pb(NO$_3$)$_2$ and 100 mg/L NaCl solution, 10 mg/L Fe(NO$_3$)$_3$ and

265 100 mg/L NaCl solution, 10 mg/L Ni(NO$_3$)$_2$ and 100 mg/L NaCl solution, 10 mg/L

266 Cr(NO$_3$)$_3$ and 100 mg/L NaCl solution, 10 mg/L Cd(NO$_3$)$_2$ and 100 mg/L NaCl solution,

267 10 mg/L Co(NO$_3$)$_2$ and 100 mg/L NaCl solution, 10 mg/L Cu(NO$_3$)$_2$ solution and 100

268 mg/L NaCl solution, 50 mg/L Pb(NO$_3$)$_2$ and 100 mg/L NaCl solution, 50 mg/L

269 Fe(NO$_3$)$_3$ and 100 mg/L NaCl solution, 50 mg/L Ni(NO$_3$)$_2$ and 100 mg/L NaCl solution,

270 50 mg/L Cr(NO$_3$)$_3$ and 100 mg/L NaCl solution, 50 mg/L Cd(NO$_3$)$_2$ and 100 mg/L NaCl

271 solution, 50 mg/L Co(NO$_3$)$_2$ and 100 mg/L NaCl solution, 50 mg/L Cu(NO$_3$)$_2$ solution

272 and 100 mg/L NaCl solution were configured respectively. Those solutions (65 mL)

273 were circulated through the electrode by a peristaltic pump at the speed of 40 mL/min

274 at 1.2 V for 120 min, respectively. The concentration of heavy metal ions in the solution

275 after 120 min was tested by ICP-OES.

276 The capacitive removal experiments in a variety of single-component heavy metal ion

277 solutions and the multi-component heavy metal ion solution: 10 mg/L Pb(NO$_3$)$_2$, 10

278 mg/L Fe(NO$_3$)$_3$ solution, 10 mg/L Ni(NO$_3$)$_2$ solution, 10 mg/L Co(NO$_3$)$_2$ solution, 10

279 mg/L Cu(NO$_3$)$_2$ solution, 10 mg/L Cr(NO$_3$)$_3$ solution, 10 mg/L Cd(NO$_3$)$_2$ solution; 50

280 mg/L $Pb(NO_3)_2$, 50 mg/L $Fe(NO_3)_3$ solution, 50 mg/L $Ni(NO_3)_2$ solution, 50 mg/L

281 $Co(NO_3)_2$ solution, 50 mg/L $Cu(NO_3)_2$ solution, 50 mg/L $Cr(NO_3)_3$ solution, 50 mg/L

282 $Cd(NO_3)_2$ solution and 10 mg/L $Pb(NO_3)_2$, 10 mg/L $Fe(NO_3)_3$, 10 mg/L $Ni(NO_3)_2$, 10

283 mg/L $Co(NO_3)_2$, 10 mg/L $Cu(NO_3)_2$, 10 mg/L $Cr(NO_3)_3$, 10 mg/L $Cd(NO_3)_2$, 100 mg/L

284 NaCl mixed solutions; 10 mg/L $Pb(NO_3)_2$, 10 mg/L $Fe(NO_3)_3$, 10 mg/L $Ni(NO_3)_2$, 10

285 mg/L $Co(NO_3)_2$, 10 mg/L $Cu(NO_3)_2$, 10 mg/L $Cr(NO_3)_3$, 10 mg/L $Cd(NO_3)_2$, 500 mg/L

286 NaCl mixed solutions; 50 mg/L $Pb(NO_3)_2$, 50 mg/L $Fe(NO_3)_3$, 50 mg/L $Ni(NO_3)_2$, 50

287 mg/L $Co(NO_3)_2$, 50 mg/L $Cu(NO_3)_2$, 50 mg/L $Cr(NO_3)_3$, 50 mg/L $Cd(NO_3)_2$, 100 mg/L

288 NaCl mixed solutions; 50 mg/L $Pb(NO_3)_2$, 50 mg/L $Fe(NO_3)_3$, 50 mg/L $Ni(NO_3)_2$, 50

289 mg/L $Co(NO_3)_2$, 50 mg/L $Cu(NO_3)_2$, 50 mg/L $Cr(NO_3)_3$, 50 mg/L $Cd(NO_3)_2$, 500 mg/L

290 NaCl mixed solutions; 10 mg/L $Pb(NO_3)_2$, 10 mg/L $Fe(NO_3)_3$, 10 mg/L $Ni(NO_3)_2$, 10

291 mg/L $Co(NO_3)_2$, 10 mg/L $Cu(NO_3)_2$, 10 mg/L $Cr(NO_3)_3$, 10 mg/L $Cd(NO_3)_2$, 20 mg/L

292 methyl blue solutions, 100 mg/L NaCl mixed solutions; 10 mg/L $Pb(NO_3)_2$, 10 mg/L

293 $Fe(NO_3)_3$, 10 mg/L $Ni(NO_3)_2$, 10 mg/L $Co(NO_3)_2$, 10 mg/L $Cu(NO_3)_2$, 10 mg/L

294 $Cr(NO_3)_3$, 10 mg/L $Cd(NO_3)_2$, 20 mg/L aniline solutions, 100 mg/L NaCl mixed

295 solutions; 10 mg/L $Pb(NO_3)_2$, 10 mg/L $Fe(NO_3)_3$, 10 mg/L $Ni(NO_3)_2$, 10 mg/L

296 $Co(NO_3)_2$, 10 mg/L $Cu(NO_3)_2$, 10 mg/L $Cr(NO_3)_3$, 10 mg/L $Cd(NO_3)_2$, 100 mg/L $CaCl_2$

297 mixed solutions; 10 mg/L $Pb(NO_3)_2$, 10 mg/L $Fe(NO_3)_3$, 10 mg/L $Ni(NO_3)_2$, 10 mg/L

298 $Co(NO_3)_2$, 10 mg/L $Cu(NO_3)_2$, 10 mg/L $Cr(NO_3)_3$, 10 mg/L $Cd(NO_3)_2$, 500 mg/L $CaCl_2$

299 mixed solutions were configured respectively.

300　Those solution (65 mL) were circulated through the electrode by a peristaltic pump at

301　the speed of 40 mL/min at 1.2 V for 120 min, respectively. The concentration of heavy

302　metal ions in the solution after 120 min was measured by ICP-OES.

303　An asymmetric capacitive deionization (CDI) system was used to explore the ability of

304　$W_{18}O_{49}$/Graphene electrode to adsorb sodium ions in the NaCl solutions. In the

305　asymmetric capacitive deionization system, $W_{18}O_{49}$/Graphene and $W_{18}O_{49}$/C materials

306　were used as the cathode and AC as the anode. In contrast, AC was used as both the

307　cathode and the anode in a symmetric capacitive deionization system. The asymmetric

308　$W_{18}O_{49}$/Graphene‖AC, $W_{18}O_{49}$/C‖AC and the symmetric AC‖AC were first tested in a

309　1000 mg/L NaCl solution at 1.2 V. The results show that $W_{18}O_{49}$/Graphene has the

310　largest salt adsorption capacity (SAC) which is up to 78 mg/g (Figure S18). This is

311　because the layered structure of $W_{18}O_{49}$/Graphene can provide a fast channel for ion

312　transfer from the electrolyte, which is helpful to improve the ion implantation ability.

313　The SAC of $W_{18}O_{49}$/Graphene electrode has reached a higher level compared with

314　many reported values in literature (Table S4). Furthermore, the desalination ability of

315　$W_{18}O_{49}$/Graphene electrode is studied at different voltages in the 1000 mg/L NaCl

316　solution (Figure S19). The results show that the $W_{18}O_{49}$/Graphene electrode can obtain

317　a higher SAC at 1.2 V. Meanwhile, the SAC of $W_{18}O_{49}$/Graphene electrode increases

318　with the increase of NaCl concentration (Figure S20). In addition, the salt adsorption

319　rate is also used to measure the desalination performance of the electrode in different

320　concentration NaCl solutions. The $W_{18}O_{49}$/Graphene electrode has a higher salt

321　adsorption rate than other electrodes in the 1000 mg/L NaCl solutions (Figure S21-22).

322   The corresponding maximum salt adsorption rate of the $W_{18}O_{49}$/Graphene electrode is

323   0.22 mg/g/s in a 1000 mg/L NaCl solution at a constant voltage of 1.2 V. At the same

324   time, the average salt adsorption rate is 0.032 mg/g/s. The high desalting ability and

325   fast salt adsorption rate are mainly attributed to the electro-adsorption behavior of the

326   electrode. From the Ragone curve, it can be seen that the increase of concentration will

327   make the curve shift to the upper right corner, which indicates that salt adsorption rate

328   (SAR) and SAC increase with the increase of concentration (Figure S23-24). The

329    $W_{18}O_{49}$/Graphene electrode also showed the higher charge efficiency than other

330   electrodes in different NaCl solutions at a constant voltage of 1.2 V (Figure S25). The

331   charge efficiency of $W_{18}O_{49}$/Graphene electrode can be maintained at 84%~90% in

332   100~1000 mg/L NaCl solutions at a constant voltage of 1.2 V. The specific energy

333   consumption (SEC^{-1}) of the electrodes was observed. It displayed an intrinsic trade-off

334   between SEC^{-1} and SAR. The $W_{18}O_{49}$/Graphene electrode had the highest salt

335   adsorption rate in the same energy consumption in the 1000 mg/L NaCl solution,

336   indicating that the electrode could absorb more ions at the same energy consumption

337   (Figure S26-27). At the same time, the energy consumption of $W_{18}O_{49}$/Graphene

338   electrode is reduced to 0.34 Wh g^{-1} in a 1000 mg/L NaCl solution at a constant voltage

339   of 1.2 V, which is lower than that of traditional capacitive deionization (0.37-3.8 Wh g^{-1}

340   )[10]. The energy efficiency of the $W_{18}O_{49}$/Graphene can also reach 30% in a 1000 mg/L

341   NaCl solution at a constant voltage of 1.2 V.

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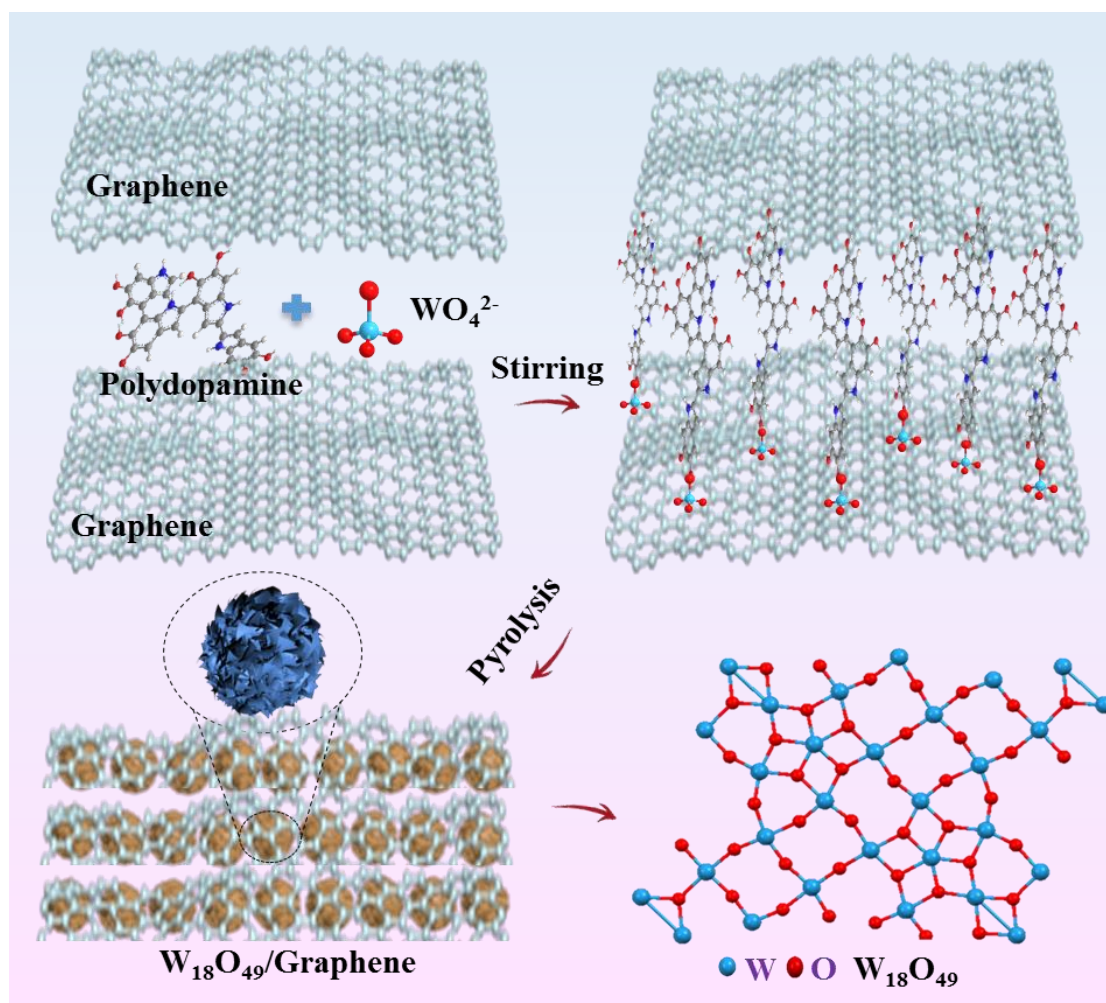
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344   Figure S1. Schematic illustration of the synthesis route of the $W_{18}O_{49}$/Graphene.

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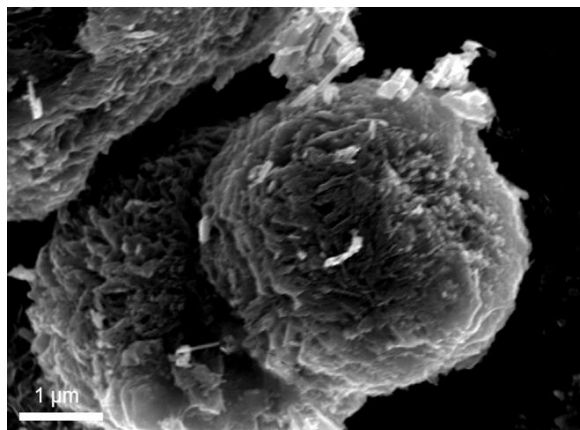
347   Figure S2. SEM image of the $W_{18}O_{49}/C$.

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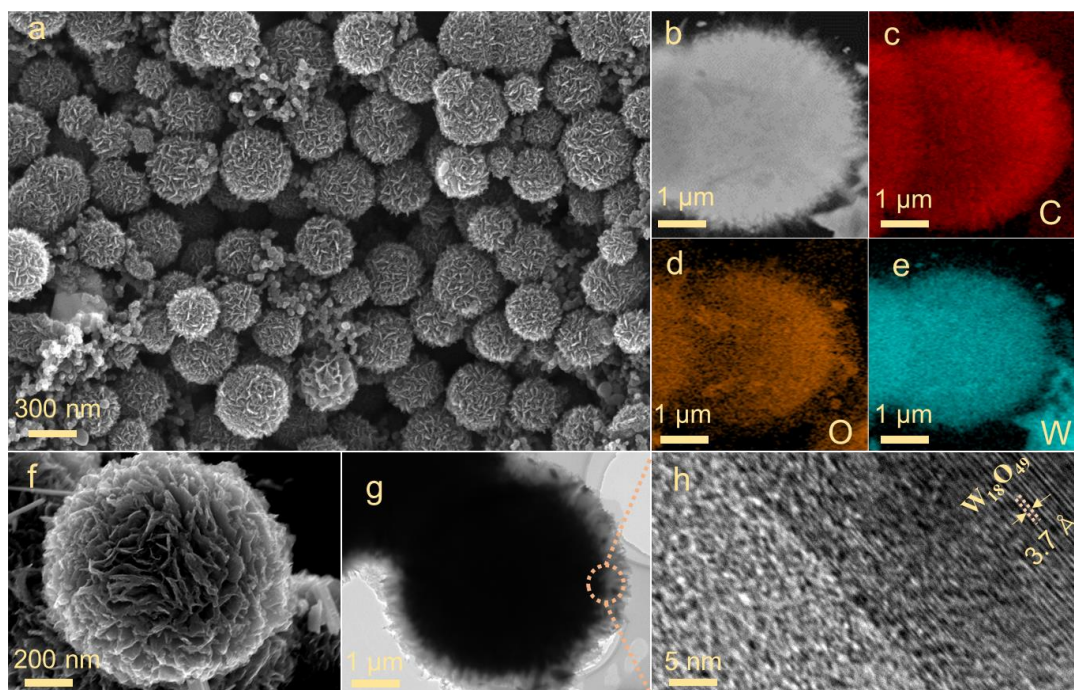
Figure S3. (a) SEM image, (b-e) EDS mapping, (f) SEM image, (g) TEM image and (h)

HRTEM image of the $W_{18}O_{49}$/Graphene.

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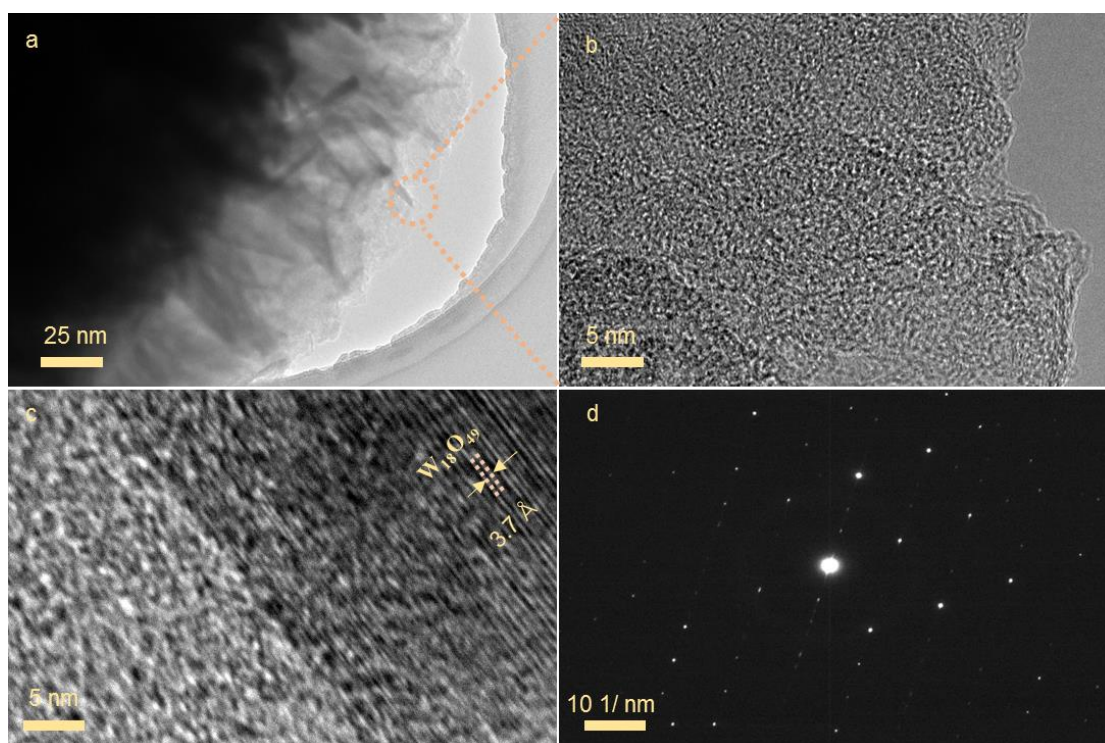
Figure S4. (a) TEM image, (b, c) HRTEM and (d) SAED patterns of the W$_{18}$O$_{49}$/Graphene.

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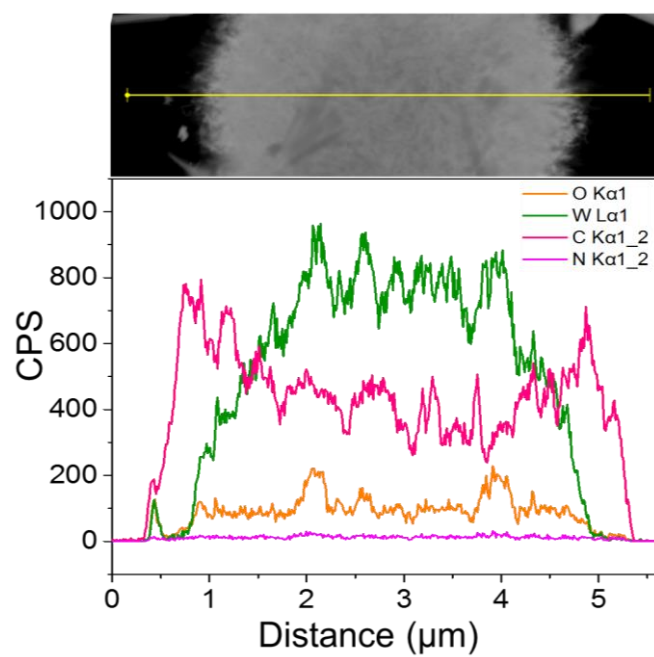
Figure S5. EDS line scans of the $W_{18}O_{49}$/Graphene.

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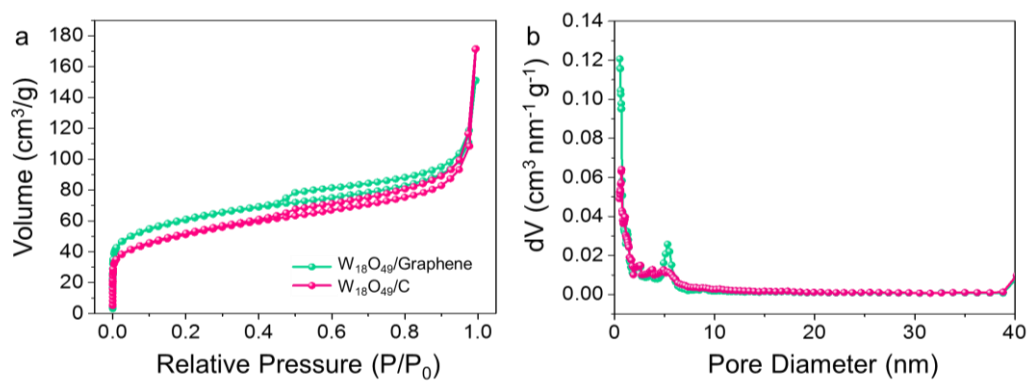
362 Figure S6. (a) Nitrogen sorption isotherms of the $W_{18}O_{49}$/Graphene and $W_{18}O_{49}$/C. (b)

363 DFT pore size distribution curves of the $W_{18}O_{49}$/Graphene and $W_{18}O_{49}$/C.

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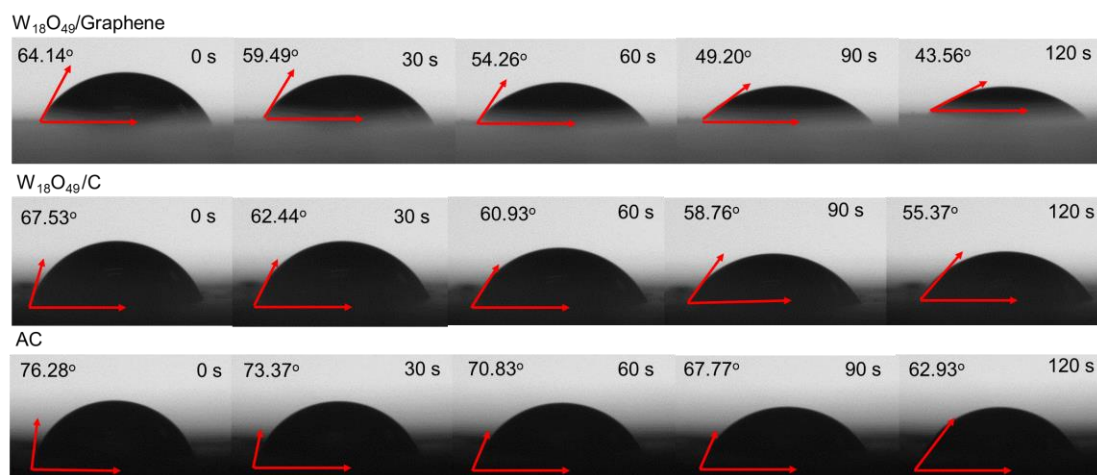
Figure S7. Dynamic water contact angle analysis of the $W_{18}O_{49}$/Graphene, $W_{18}O_{49}$/C and AC.

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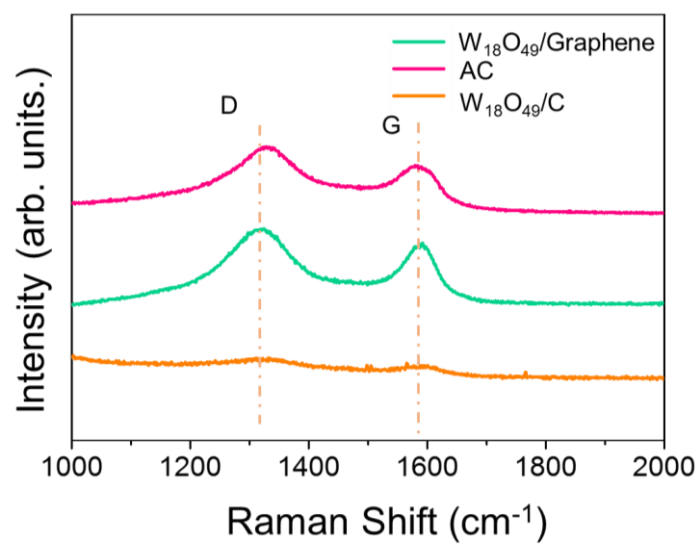
Figure S8. Raman spectra of the $W_{18}O_{49}$/Graphene, $W_{18}O_{49}$/C and AC.

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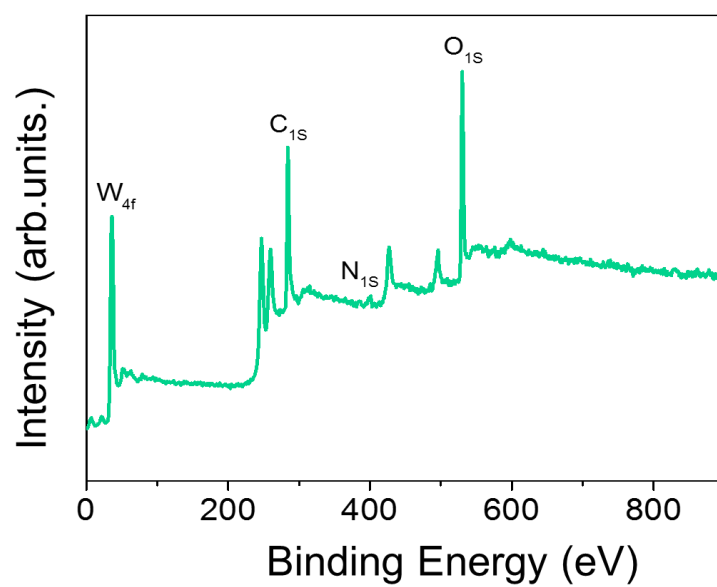
Figure S9. XPS spectra of the $W_{18}O_{49}$/Graphene.

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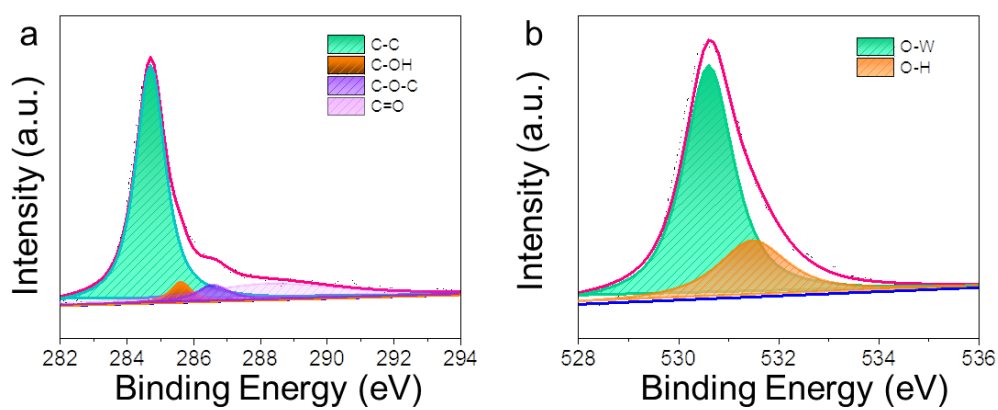
378   Figure S10. (a) C 1s and (b) O 1s spectra of the $W_{18}O_{49}$/Graphene.

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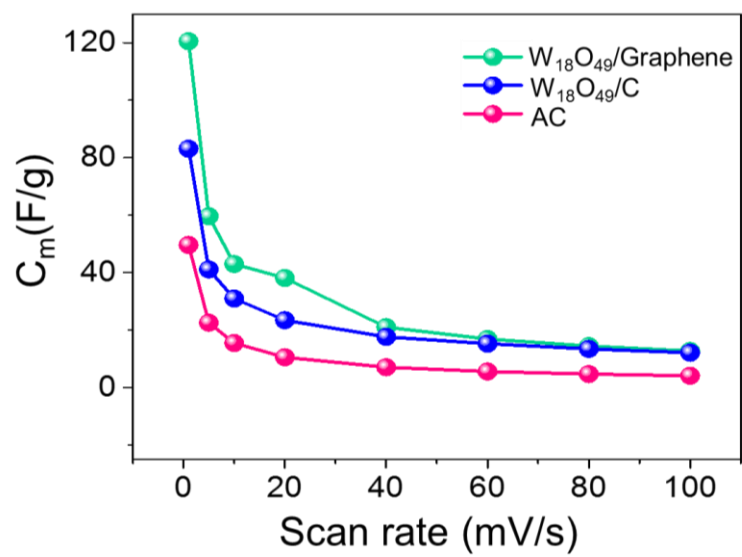
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381   Figure S11. Plots of specific capacitance *versus* scanning rates for $W_{18}O_{49}$/Graphene,

382    $W_{18}O_{49}$/C, and AC in a 1000 mg/L NaCl solution.

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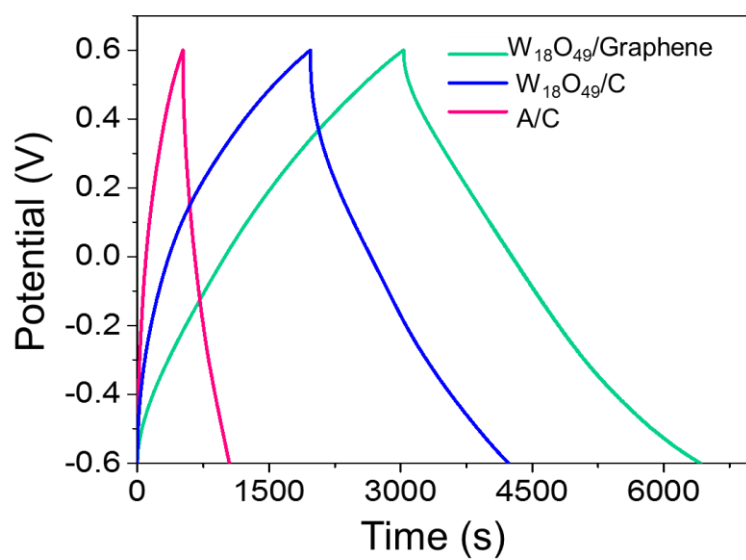
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385 Figure S12. Charge-discharge curves of $W_{18}O_{49}$/Graphene, $W_{18}O_{49}$/C, and AC at 0.2

386 A/g in a 1000 mg/L NaCl solution.

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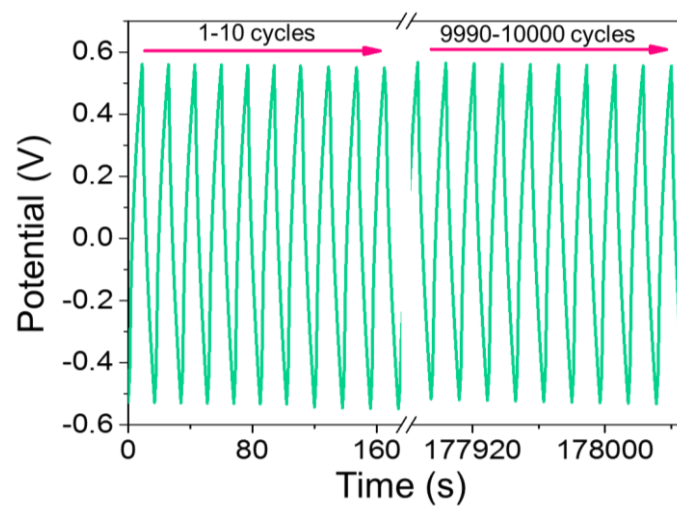
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389 Figure S13. Cycle stability plots of the $W_{18}O_{49}$/Graphene electrode at 10 A/g in a 1000

390 mg/L NaCl solution.

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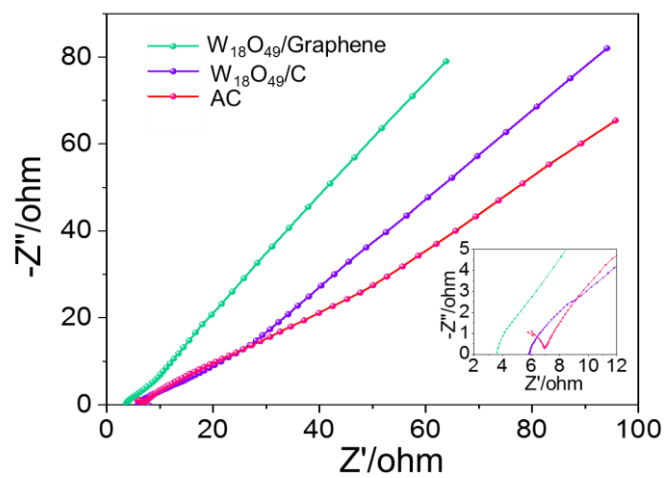
Figure S14. Impedance spectra of $W_{18}O_{49}$/Graphene, $W_{18}O_{49}$/C, and AC in a 1000 mg/L

NaCl solution.

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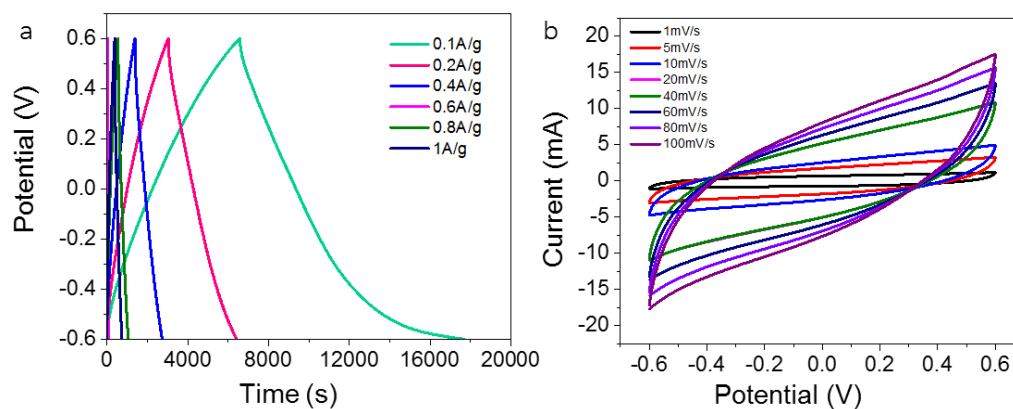
Figure S15. (a) Charge-discharge curves of the $W_{18}O_{49}$/Graphene electrodes in a 1000 mg/L NaCl solution. (b) CV curves of the $W_{18}O_{49}$/Graphene electrodes in a 1000 mg/L NaCl solution.

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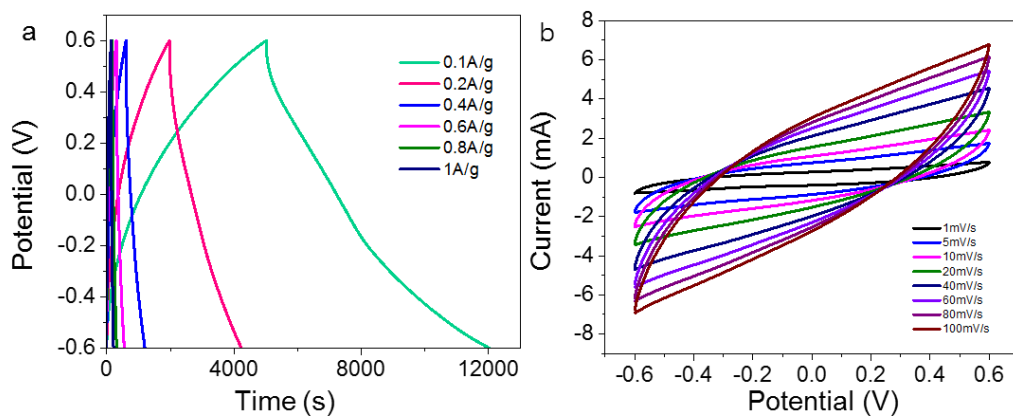
403 Figure S16. (a) Charge-discharge curves of the $W_{18}O_{49}/C$ electrodes in a 1000 mg/L

404 NaCl solution. (b) CV curves of the $W_{18}O_{49}/C$ electrodes in a 1000 mg/L NaCl solution.

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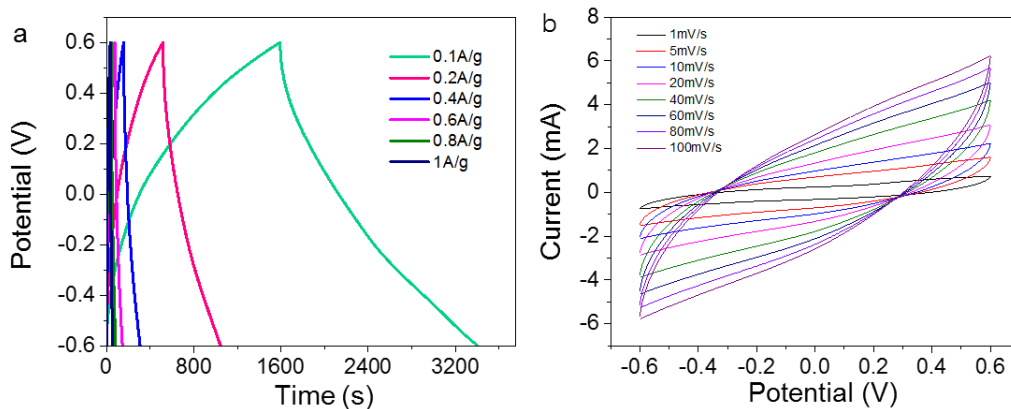
Figure S17. (a) Charge-discharge curves of the AC electrodes in a 1000 mg/L NaCl solution. (b) CV curves of the AC electrodes in a 1000 mg/L NaCl solution.
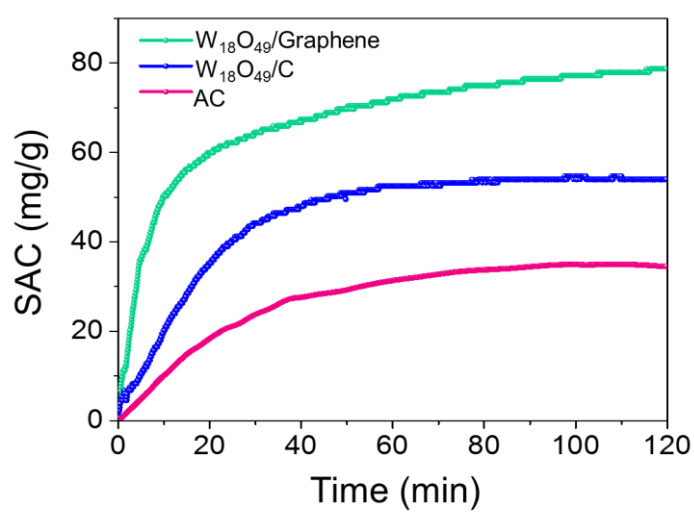
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411   Figure S18. Plots of salt adsorption capacity of $W_{18}O_{49}$/Graphene, $W_{18}O_{49}$/C and AC

412   *versus* time in a 1000 mg/L NaCl solution at 1.2 V.

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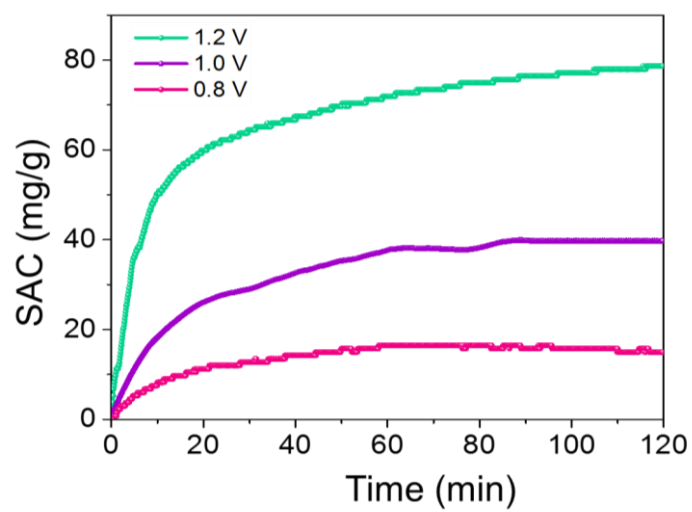
Figure S19. Plots of salt adsorption capacity of $W_{18}O_{49}$/Graphene *versus* time in a 1000

mg/L NaCl solution at different voltages.

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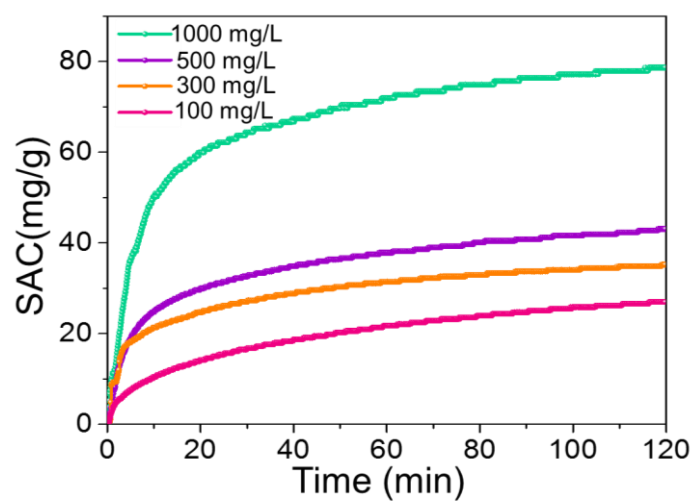
Figure S20. Plots of salt adsorption capacity of $W_{18}O_{49}$/Graphene *versus* time in

different concentrations of NaCl solutions at 1.2 V.

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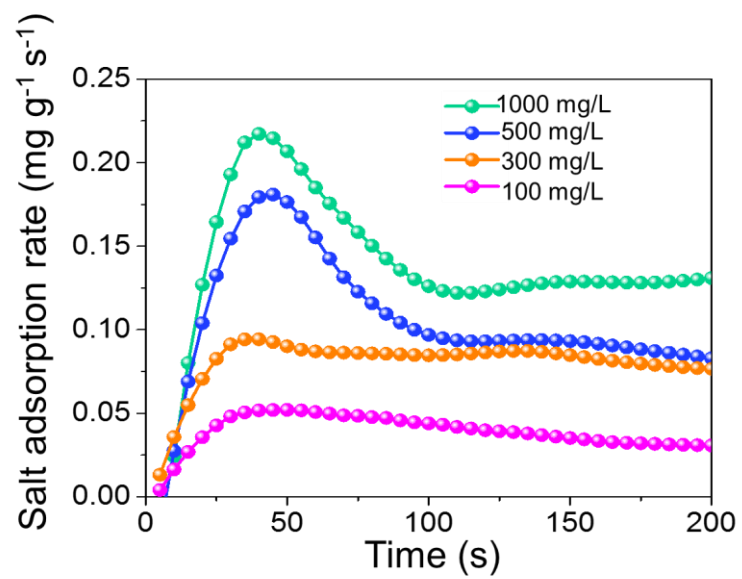
Figure S21. Plots of salt adsorption rate of $W_{18}O_{49}$/Graphene *versus* time in different

concentrations of NaCl solutions.

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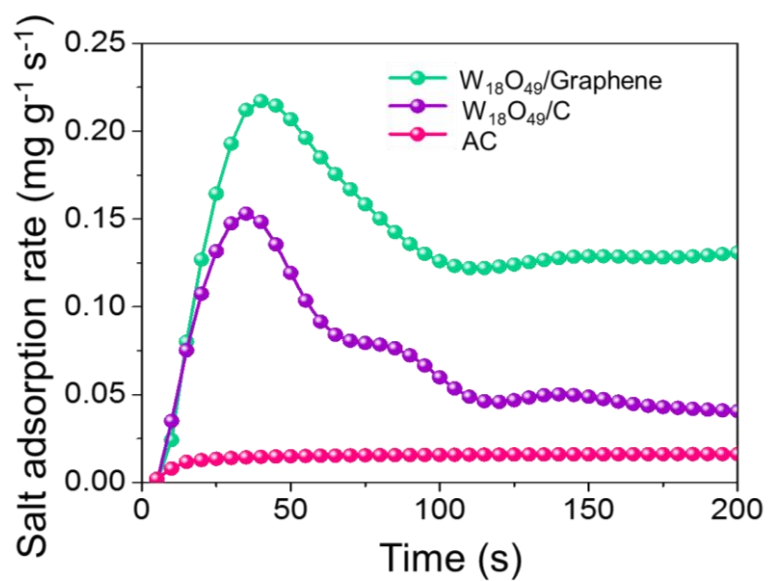
Figure S22. Plots of salt adsorption rate of $W_{18}O_{49}$/Graphene, $W_{18}O_{49}$/C and AC *versus*

time in a 1000 mg/L NaCl solution at 1.2 V.

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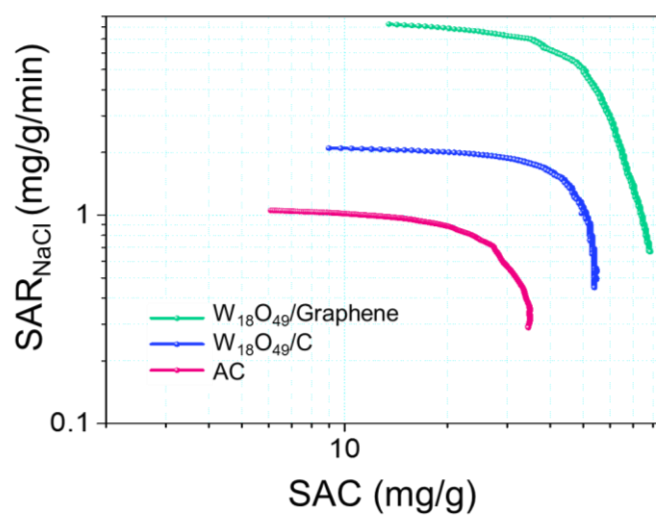
433

434 Figure S23. Ragone plots of SAR *versus* SAC of $W_{18}O_{49}$/Graphene, $W_{18}O_{49}$/C and AC

435 time in a 1000 mg/L NaCl solution at 1.2 V.

436

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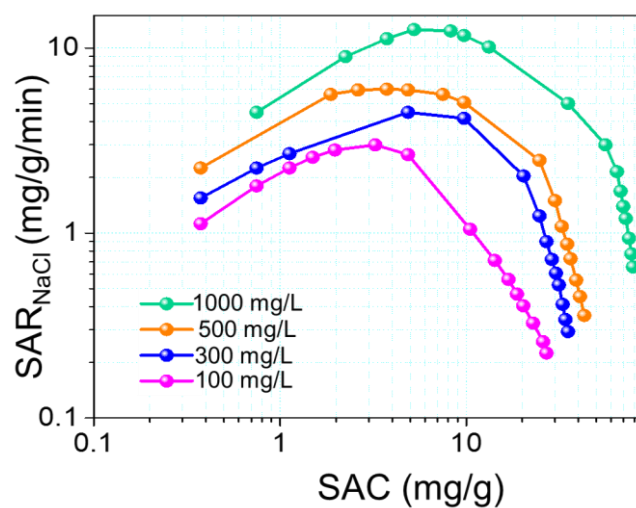
Figure S24. Ragone plots of SAR *versus* SAC of $W_{18}O_{49}$/Graphene in different

concentrations of NaCl solutions.

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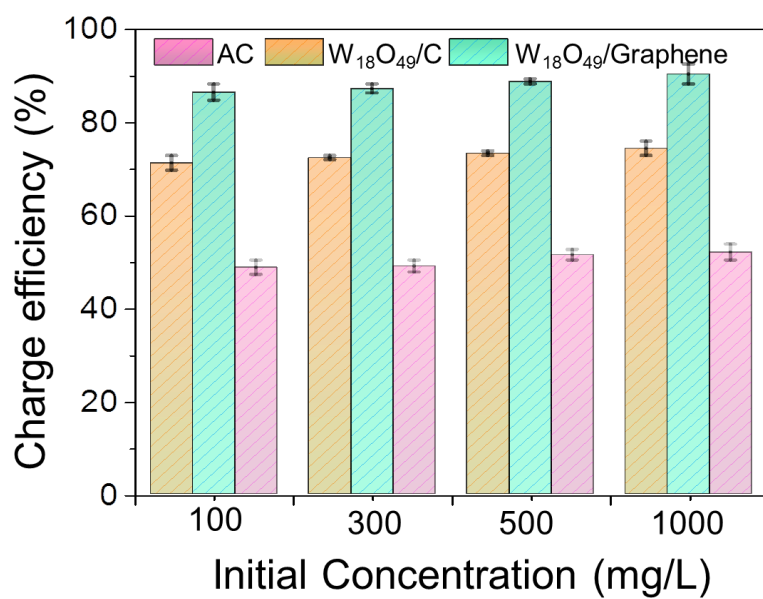
Figure S25. Plots of charge efficiency of $W_{18}O_{49}$/Graphene, $W_{18}O_{49}$/C and AC in

different concentrations of NaCl solutions at 1.2 V.

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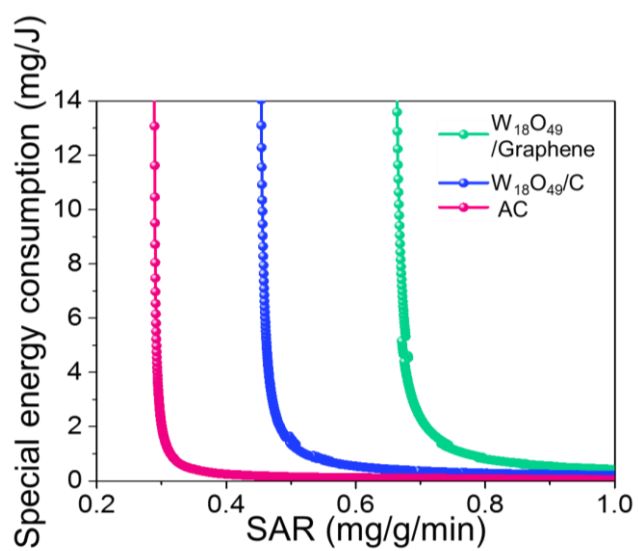
446   Figure S26. Plots of specific energy consumption of the $W_{18}O_{49}$/Graphene, $W_{18}O_{49}$/C

447   and AC electrode *versus* SAR in a 1000 mg/L NaCl solution at 1.2 V.

448
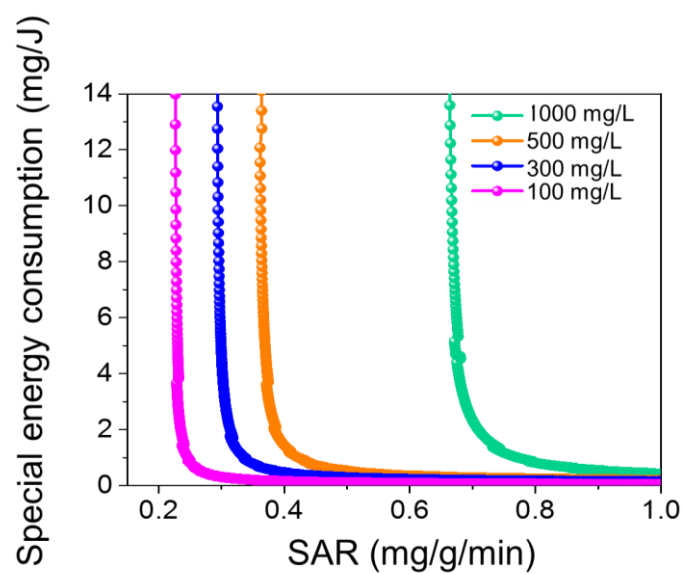
449

450   Figure S27. Plots of specific energy consumption of the $W_{18}O_{49}$/Graphene *versus* SAR

451   in different concentrations of NaCl solutions.

452
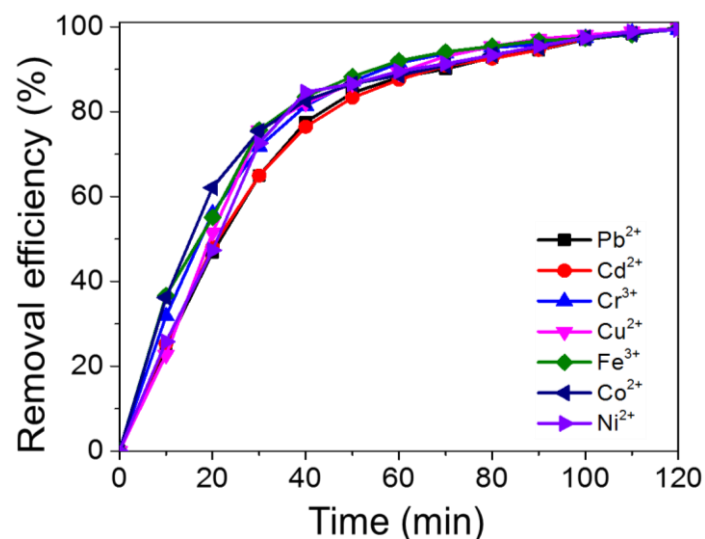
Figure S28. Plots of removal efficiency of heavy metal ions with the $W_{18}O_{49}$/Graphene electrode *versus* different times in the multi-component solution containing all the seven metal nitrates (10 mg/L for each) and NaCl (100 mg/L) at 1.2 V.
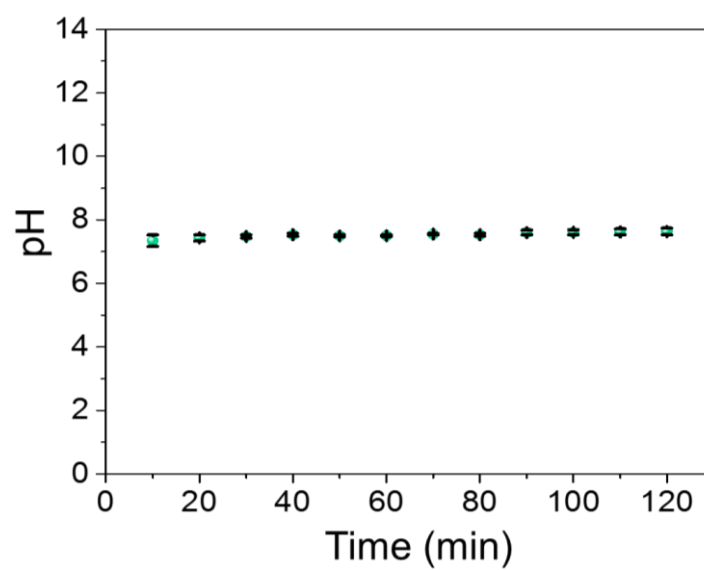
458

459 Figure S29. Plot of pH value *versus* deionization time of $W_{18}O_{49}$/Graphene in the multi-

460 component solution containing all the seven metal nitrates (10 mg/L for each) and 100

461 mg/L NaCl at 1.2 V.

462

463
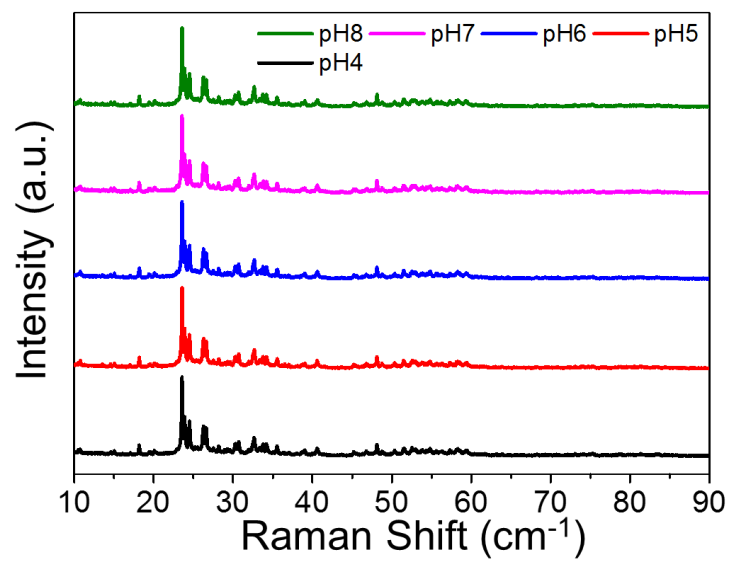
Figure S30. XRD patterns of materials after soaking in solutions with different pH

values.
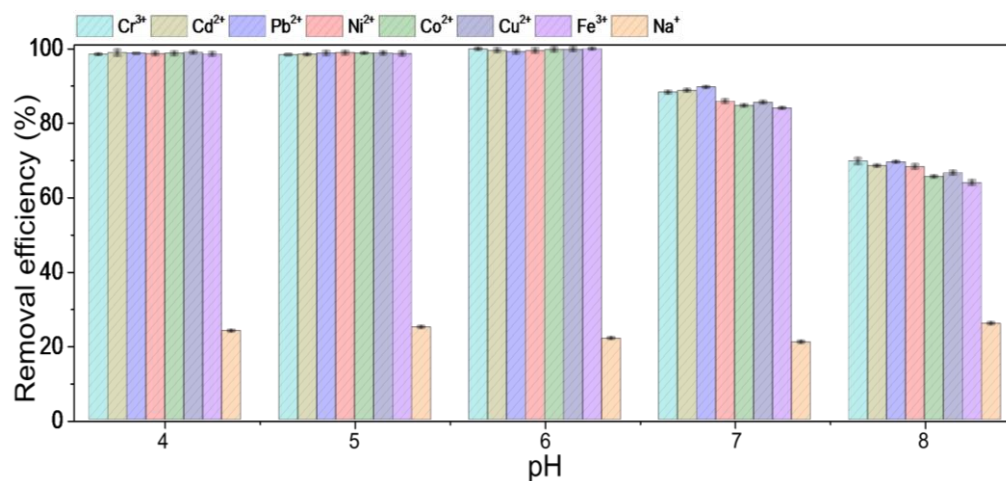
467   Figure S31. Plots of removal efficiency of heavy metal ion *versus* pH values in the

468   multi-component solution containing all the seven metal nitrates (10 mg/L for each)

469   and 100 mg/L NaCl at 1.2 V.

470

471
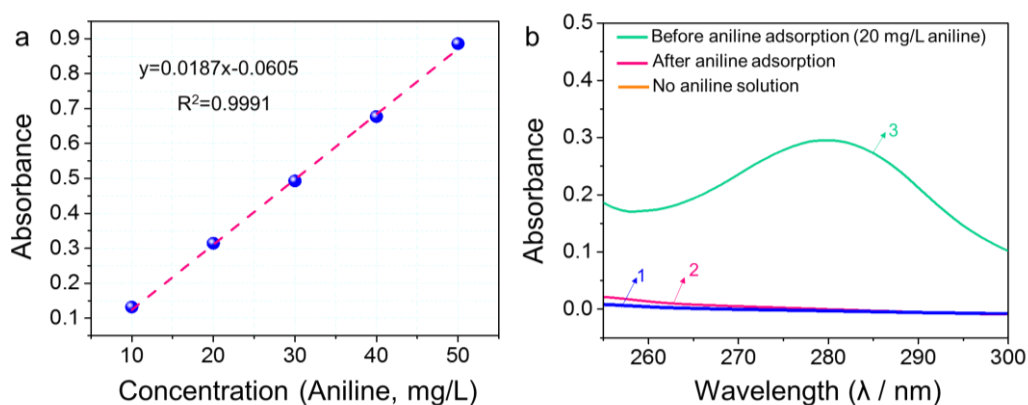
472 Figure S32. (a) Plots of absorbance *versus* aniline concentration. (b) Absorbance curves

473 in the multi-component solution containing all the seven metal nitrates (10 mg/L for

474 each) and 100 mg/L NaCl (Line 1). Absorbance curves after aniline adsorption in the

475 multi-component solution containing all the seven metal nitrates (10 mg/L for each), 20

476 mg/L aniline and 100 mg/L NaCl (Line 2). Absorbance curves before aniline adsorption

477 in the multi-component solution containing all the seven metal nitrates (10 mg/L for

478 each), 20 mg/L aniline and 100 mg/L NaCl (Line 3).

479

480

Figure S33. (a) Plots of absorbance *versus* methyl blue concentration. (b) Absorbance

curves in the multi-component solution containing all the seven metal nitrates (10 mg/L

for each) and 100 mg/L NaCl (Line 1). Absorbance curves after methyl blue adsorption

in the multi-component solution containing all the seven metal nitrates (10 mg/L for

each), 20 mg/L aniline and 100 mg/L NaCl (Line 2). Absorbance curves before methyl

blue adsorption in the multi-component solution containing all the seven metal nitrates

(10 mg/L for each), 20 mg/L methyl blue and 100 mg/L NaCl (Line 3).
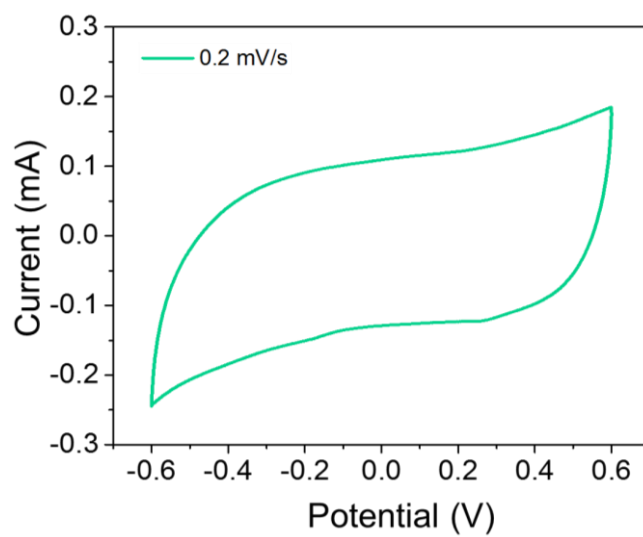
489

490   Figure S34.CV curves of the $W_{18}O_{49}$/Graphene electrodes at 0.2 mV/s in 100 mg/L

491    $CaCl_2$ at a constant voltage of 1.2 V.

492

493
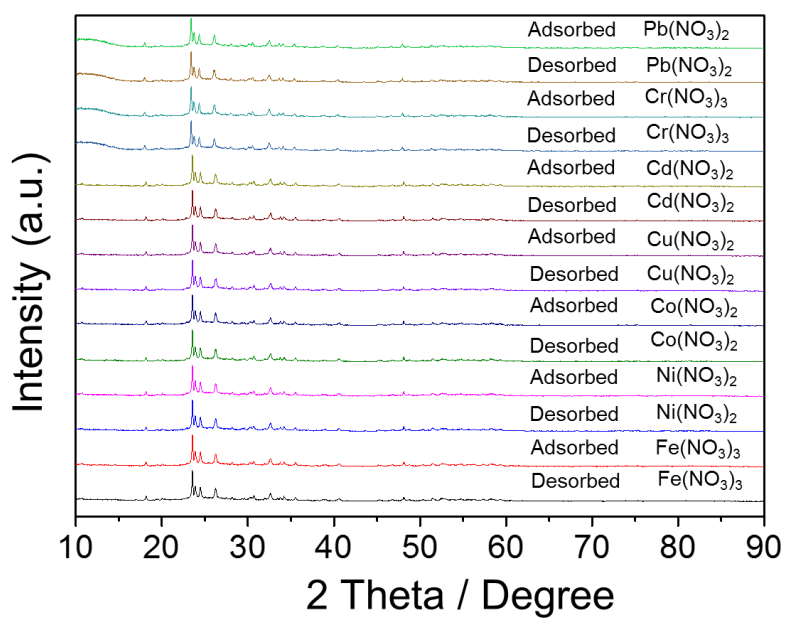
Figure S35. XRD patterns of $W_{18}O_{49}$/Graphene before and after heavy metal ion

adsorption in single-component metal nitrate solution solutions (metal nitrate (10 mg/L).

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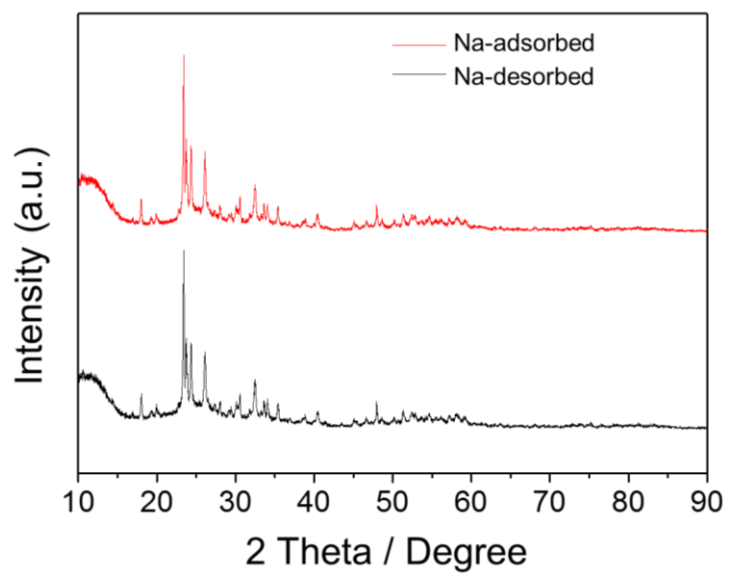
497

498   Figure S36. XRD patterns of $W_{18}O_{49}$/Graphene after Na-adsorbed and Na-desorbed in

499   100 mg/L NaCl solutions.

500
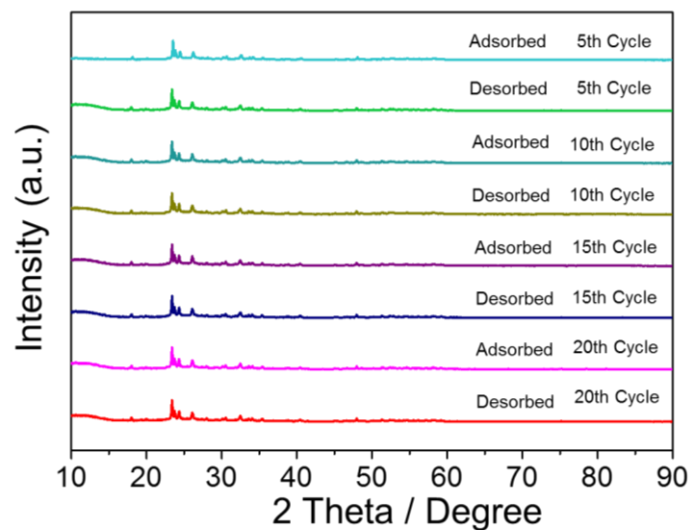
501

502 Figure S37. XRD patterns of $W_{18}O_{49}$/Graphene before and after heavy metal ion

503 adsorption in the multi-component solution containing all the seven metal nitrates (10

504 mg/L for each) and 100 mg/L NaCl at a constant voltage of 1.2 V.
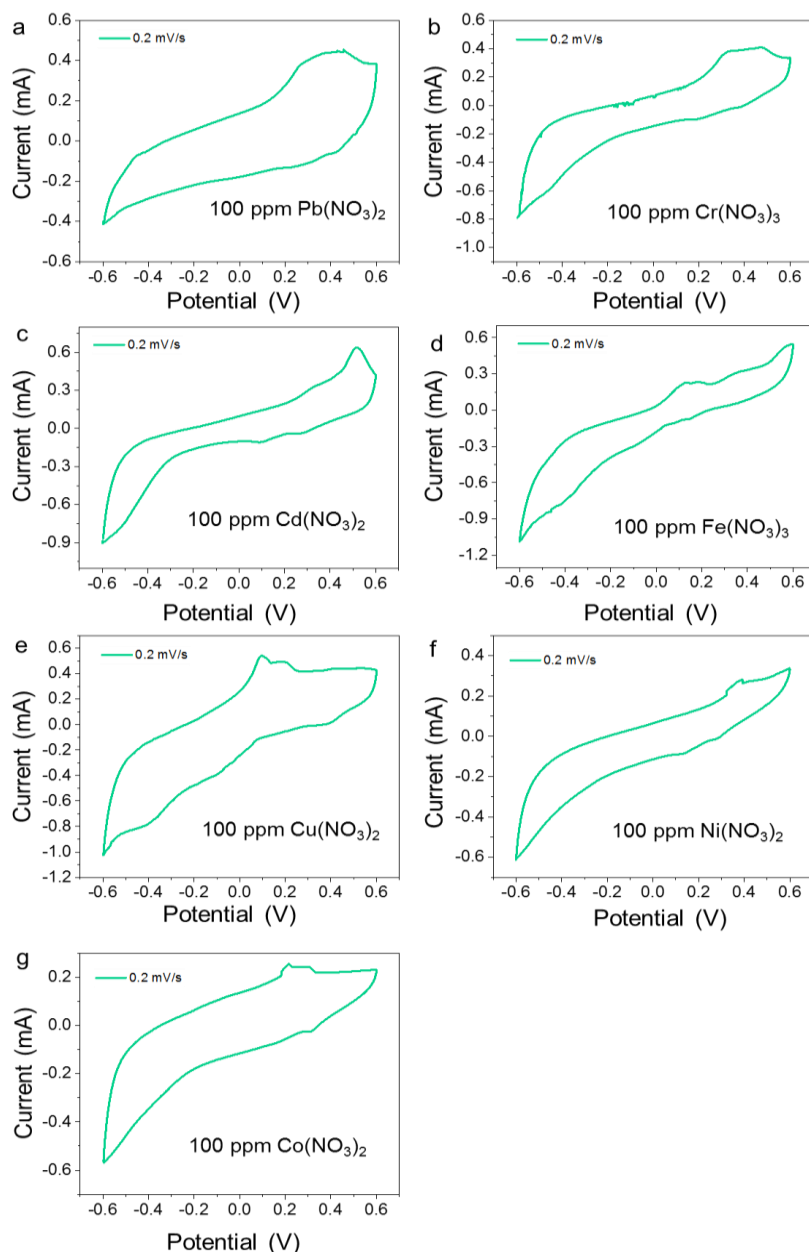
Figure S38. (a) CV curves at a scanning rate of 0.2 mV/s in 100 mg/L Pb(NO$_3$)$_2$ solutions, (b) CV curves at a scanning rate of 0.2 mV/s in 100 mg/L Cr(NO$_3$)$_3$ solutions, (c) CV curves at a scanning rate of 0.2 mV/s in 100 mg/L Cd(NO$_3$)$_2$ solutions, (d) CV curves at a scanning rate of 0.2 mV/s in 100 mg/L Fe(NO$_3$)$_3$ solutions, (e) CV curves at a scanning rate of 0.2 mV/s in 100 mg/L Cu(NO$_3$)$_2$ solutions, (f) CV curves at a scanning rate of 0.2 mV/s in 100 mg/L Ni(NO$_3$)$_2$ solutions, (g) CV curves at a scanning rate of 0.2 mV/s in 100 mg/L Co(NO$_3$)$_2$ solutions.

513
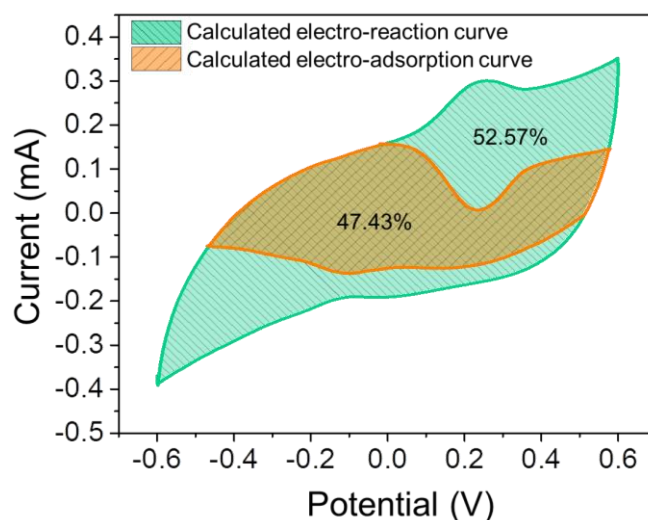
Figure S39. CV curves at a scanning rate of 0.2 mV/s in the multi-component solution

containing all the seven metal nitrates (10 mg/L for each) and 100 mg/L NaCl.

The proportion of contribution of electro-adsorption and electro-reaction were

calculated according to the Eq (12).[11]

$$i(V) = k_1 v + k_2 v^{0.5} \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots(12)$$

where the i is the current (A), the v is the scanning rate (mV/s), k_1 and k_2 are

constant values at a fixed potential. $k_1 v$ is related to the capacitive current raised

from electro-adsorption and $k_2 v^{0.5}$ is related to electro-reaction.

CV curves at 0.2 and 0.5 mV/s have been measured, respectively. Based on the

Eq (12), at a given potential P, two known different current values i_1 and i_2 are

obtained at two scanning rates v_1 (0.2 mV/s) and v_2 (0.5 mV/s), thus obtaining a

binary equations as follow:[11]

$$i_1(P) = 0.2\, k_1 + \sqrt{0.2}\, k_2 \dots\dots\dots\dots\dots\dots\dots\dots\dots(13)$$

$$i_2(P) = 0.5\, k_1 + \sqrt{0.5}\, k_2 \dots\dots\dots\dots\dots\dots\dots\dots\dots(14)$$

k_1 and k_2 at P potential can be obtained by solving the abovementioned binary

equations consisting Eq (13) and Eq (14). A CV cycle contains a series of potential

530   values, so a series of k_1 and k_2 values can be obtained. For the same material, k_1

531   and k_2 are fixed at a given potential. Therefore, at the scanning rate of 0.2 mV/s,

532   the current derived from electro-adsorption can be obtained by the Eq (15).[11]

533 $$i_{electro-adsorption}(V) = 0.2\, k_1 \dots\dots\dots\dots\dots\dots\dots\dots\dots(15)$$

534   Where $i_{electro-adsorption}$ is the current derived from the electro-adsorption. These

535      $i_{electro-adsorption}$ points can be linked to form a closed CV curve, which is the shaded

536   part in Figure S39. The area of shaded part as a percentage of the area of the

537   measured CV curve is the percentage of the contribution of the electro-

538   adsorption. The rest is the electro-reaction contribution. The yellow shadow area

539   is corresponding to the contribution of the electro-adsorption at 0.2 mV/s (Figure

540   S39), which takes a proportion of 47.43%. The result demonstrates that electro-

541   adsorption contributes 47.43% and the electro-reaction contributes 52.57%.

542

543   Table S1. Summary of properties of the materials.

Materials	S_{BET}[a] [m^2 g^{-1}]	V_{total}[b] [cm^3 g^{-1}]	$V_{Micropore}$ [c] [cm^3 g^{-1}]	$V_{macro\&meso}$[d] [cm^3 g^{-1}]
W$_{18}$O$_{49}$/Graphene	218	0.26	0.045	0.215
W$_{18}$O$_{49}$/C	181	0.23	0.065	0.165

544   [a] Brunuaer–Emmett–Teller surface area. [b] Calculated by single-point adsorption at a

545   relative pressure of 0.98. [c] Calculated by V–t plot method. [d] Calculated by DFT method

546   from the desorption isotherm linear plot.

547

548 Table S2. Summary of relative intensity ratios of all materials in Raman spectra.

Materials	Integral Area / D band	Integral Area / G band	I_D/I_G
$W_{18}O_{49}$/Graphene	244719.25158	103373.78731	2.37
$W_{18}O_{49}$/C	2142.78762	5060.35489	0.42
AC	312977.03653	141618.5685	2.21

549

550   Table S3. Elemental contents of the synthesized materials determined by XPS spectra.

Materials	C (%)	N (%)	O (%)	W (%)
$W_{18}O_{49}$/Graphene	64.09	3.03	24.43	8.44

551

552   Table S4. Comparison of the $W_{18}O_{49}$/Graphene materials with the state-of-the-art

553   electrode materials.

Materials	Cell configuration	voltage (V)	NaCl (mg/L)	SAC (mg/g)	Desalination rate(mg/g/s)$_{max}$	Ref
MoS_2-Graphene	HCDI	1.2	500	19	/	11
$Na_4Ti_9O_{20}$	HCDI	1.4	250	23	/	12
Na-birnessite	HCDI	1.2	880	31	/	13
Fe-NC	CDI	1.2	500	36	/	1
MNPC	CDI	1.2	500	24	/	2
$Na_2FeP_2O_7$	HCDI	1.2	1000	30	0.081	14
PHCs//HCs@MnO_2	HCDI	1.2	500	30	0.130	15
PCNSs	CDI	1.1	500	15	0.017	16
$Na_{0.44}MnO_2$	HCDI	1.2	585	31	0.066	17
SnS_2@GP	CDI	1.2	500	30	/	18
GPCSs	CDI	1.2	500	19	/	19
MoC@CNFA1	CDI	1.2	3000	37	0.200	20
rGO/TiO_2	CDI	0.8	300	9	/	21
$W_{18}O_{49}$/Graphene	CDI	1.2	1000	78	0.220	This work
$W_{18}O_{49}$/Graphene	CDI	1.2	500	43	0.179	This work
$W_{18}O_{49}$/Graphene	CDI	1.2	300	35	0.094	This work
$W_{18}O_{49}$/Graphene	CDI	1.2	100	27	0.052	This work

554

555 Table S5. Removal efficiency after 120 min of capacitive adsorption in the complex

556 binary-component solutions [metal nitrate (10 mg/L) and NaCl (100 mg/L)] at 1.2 V by

557 ICP-OES tested.

	C_0 (mg/L)	C_t (mg/L)	Removal efficiency (%)
10 mg/L Pb(NO$_3$)$_2$ and 100 mg/L NaCl	10 (Pb^{2+})	0.031 (Pb^{2+})	99.7
10 mg/L Cr(NO$_3$)$_3$ and 100 mg/L NaCl	10 (Cr^{3+})	0.990 (Cr^{3+})	99.0
10 mg/L Cd(NO$_3$)$_2$ and 100 mg/L NaCl	10 (Cd^{2+})	0.113 (Cd^{2+})	98.9
10 mg/L Fe(NO$_3$)$_3$ and 100 mg/L NaCl	10 (Fe^{3+})	0.125 (Fe^{3+})	98.8
10 mg/L Co(NO$_3$)$_2$ and 100 mg/L NaCl	10 (Co^{2+})	0.142 (Co^{2+})	98.6
10 mg/L Ni(NO$_3$)$_2$ and 100 mg/L NaCl	10 (Ni^{2+})	0.134(Ni^{2+})	98.7
10 mg/L Cu(NO$_3$)$_2$ and 100 mg/L NaCl	10 (Cu^{2+})	0.131 (Cu^{2+})	98.7

558

559 Table S6. Removal efficiency after 120 min of capacitive adsorption in the complex

560 binary-component solutions [metal nitrate (50 mg/L) and NaCl (100 mg/L)] at 1.2 V by

561 ICP-OES tested.

	C_0 (mg/L)	C_t (mg/L)	Removal efficiency (%)
50 mg/L $Pb(NO_3)_2$ and 100 mg/L NaCl	50 (Pb^{2+})	0.079 (Pb^{2+})	99.8
50 mg/L $Cr(NO_3)_3$ and 100 mg/L NaCl	50 (Cr^{3+})	1.371(Cr^{3+})	97.2
50 mg/L $Cd(NO_3)_2$ and 100 mg/L NaCl	50 (Cd^{2+})	5.006 (Cd^{2+})	90.0
50 mg/L $Fe(NO_3)_3$ and 100 mg/L NaCl	50 (Fe^{3+})	3.016 (Fe^{3+})	93.9
50 mg/L $Co(NO_3)_2$ and 100 mg/L NaCl	50 (Co^{2+})	3.386 (Co^{2+})	93.2
50 mg/L $Ni(NO_3)_2$ and 100 mg/L NaCl	50 (Ni^{2+})	4.800 (Ni^{2+})	90.4
50 mg/L $Cu(NO_3)_2$ and 100 mg/L NaCl	50 (Cu^{2+})	0.864 (Cu^{2+})	98.3

562

563 Table S7. Removal efficiency after 120 min of capacitive adsorption in the multi-

564 component solution containing all the seven metal nitrates (10 mg/L for each) and 100

565 mg/L NaCl at a constant voltage of 1.2 V by ICP-OES tested.

Metal ions	C_0 (mg/L)	C_t (mg/L)	Removal efficiency (%)
Pb^{2+}	10	0.024	99.7
Cr^{3+}	10	0.026	99.7
Cd^{2+}	10	0.032	99.6
Fe^{3+}	10	0.011	99.8
Co^{2+}	10	0.043	99.5
Ni^{2+}	10	0.017	99.8
Cu^{2+}	10	0.090	99.1
Na^+	100	74.00	26.0

566

567 Table S8. Removal efficiency after 120 min of capacitive adsorption in the multi-

568 component solution containing all the seven metal nitrates (10 mg/L for each) and 500

569 mg/L NaCl at a constant voltage of 1.2 V by ICP-OES tested.

Metal ions	C_0 (mg/L)	C_t (mg/L)	Removal efficiency (%)
Pb^{2+}	10	0.025	99.7
Cr^{3+}	10	0.019	99.8
Cd^{2+}	10	0.029	99.7
Fe^{3+}	10	0.010	99.9
Co^{2+}	10	0.016	99.8
Ni^{2+}	10	0.056	99.4
Cu^{2+}	10	0.032	99.6
Na^+	500	437.0	12.6

570

571   Table S9. Removal efficiency after 120 min of capacitive adsorption in the multi-

572   component solution containing all the seven metal nitrates (50 mg/L for each) and 100

573   mg/L NaCl at a constant voltage of 1.2 V by ICP-OES tested.

Metal ions	C_0 (mg/L)	C_t (mg/L)	Removal efficiency (%)
Pb^{2+}	50	2.137	95.7
Cr^{3+}	50	4.807	90.3
Cd^{2+}	50	3.313	93.3
Fe^{3+}	50	1.210	97.5
Co^{2+}	50	3.756	92.4
Ni^{2+}	50	4.281	91.4
Cu^{2+}	50	0.580	98.8
Na^+	100	72.00	28.0

574

575 Table S10. Removal efficiency after 120 min of capacitive adsorption in the multi-

576 component solution containing all the seven metal nitrates (50 mg/L for each) and 500

577 mg/L NaCl at a constant voltage of 1.2 V by ICP-OES tested.

Metal ions	C_0 (mg/L)	C_t (mg/L)	Removal efficiency (%)
Pb^{2+}	50	1.527	96.9
Cr^{3+}	50	2.687	94.6
Cd^{2+}	50	1.731	96.5
Fe^{3+}	50	1.110	97.8
Co^{2+}	50	2.154	95.7
Ni^{2+}	50	2.182	95.6
Cu^{2+}	50	0.456	99.1
Na^+	500	441.5	11.7

578

579   Table S11. Heavy metal ions concentration of 20 cycles after 120 min of capacitive

580   adsorption in the multi-component solution containing all the seven metal nitrates (10

581   mg/L for each) and 100 mg/L NaCl at a constant voltage of 1.2 V by ICP-OES tested.

Cycles`	1	5	10	15	20
Pb^{2+}(mg/L)	0.024	0.024	0.036	0.075	0.024
Cr^{3+}(mg/L)	0.026	0.021	0.031	0.021	0.043
Cd^{2+}(mg/L)	0.032	0.035	0.038	0.032	0.037
Fe^{3+}(mg/L)	0.011	0.030	0.053	0.074	0.070
Co^{2+}(mg/L)	0.043	0.044	0.042	0.047	0.051
Ni^{2+}(mg/L)	0.017	0.017	0.015	0.021	0.018
Cu^{2+}(mg/L)	0.090	0.064	0.075	0.015	0.086

582

583 Table S12. Removal efficiency after 120 min of capacitive adsorption in the multi-

584 component solution containing all the seven metal nitrates (10 mg/L for each) and 100

585 mg/L $CaCl_2$ at a constant voltage of 1.2 V by ICP-OES tested.

Metal ions	C_0 (mg/L)	C_t (mg/L)	Removal efficiency (%)
Pb^{2+}	10	0.035	99.6
Cr^{3+}	10	0.022	99.7
Cd^{2+}	10	0.018	99.8
Fe^{3+}	10	0.050	99.5
Co^{2+}	10	0.072	99.3
Ni^{2+}	10	0.077	99.2
Cu^{2+}	10	0.035	99.6
Ca^{2+}	100	79.00	21.0

586

587 Table S13. Removal efficiency after 120 min of capacitive adsorption in the multi-

588 component solution containing all the seven metal nitrates (10 mg/L for each) and 500

589 mg/L $CaCl_2$ at a constant voltage of 1.2 V by ICP-OES tested.

Metal ions	C_0 (mg/L)	C_t (mg/L)	Removal efficiency (%)
Pb^{2+}	10	0.097	99.0
Cr^{3+}	10	0.019	99.8
Cd^{2+}	10	0.016	99.8
Fe^{3+}	10	0.011	99.9
Co^{2+}	10	0.037	99.6
Ni^{2+}	10	0.031	99.7
Cu^{2+}	10	0.025	99.8
Ca^{2+}	500	449.0	10.2

590

591   Table S14. The area corresponding to the peak position of XPS.

	W^{6+}	W^{6+}	W^{5+}	W^{5+}	W^{4+}	W^{4+}
XPS	35.9 eV/Area	38.1 eV/Area	35.4 eV/Area	37.6 eV/Area	34.5 eV/Area	36.7 eV/Area
$W_{18}O_{49}$/Graphene	21225	19382	7554	7230	4577	5808
Adsorbed Na	19463	19691	7461	7184	4488	5685
Adsorbed heavy metal ion	19866	18803	7781	13224	4388	2959

592

REFERENCES

1. Wang, G.; Yan, T.; Zhang, J.; Shi, L.; Zhang, D., Trace-Fe-enhanced capacitive deionization of saline water by boosting electron transfer of electro-adsorption sites. *Environ. Sci. Technol.* **2020**, 54, 8411-8419.

2. Zhang, J.; Yan, T.; Fang, J.; Shen, J.; Shi, L.; Zhang, D., Enhanced capacitive deionization of saline water using N-doped rod-like porous carbon derived from dual-ligand metal-organic frameworks. *Environ. Sci-Nano.* **2020**, 7, 926-937.

3. Liu, T.; Serrano, J.; Elliott, J.; Yang, X.; Cathcart, W.; Wang, Z.; He, Z.; Liu, G., Exceptional capacitive deionization rate and capacity by block copolymer–based porous carbon fibers. *Sci. Adv.* **2020,** *6*, eaaz0906.

4. Tan, G.; Lu, S.; Xu, N.; Gao, D.; Zhu, X., Pseudocapacitive behaviors of polypyrrole grafted activated carbon and MnO_2 electrodes to enable fast and efficient membrane-free capacitive deionization. *Environ. Sci. Technol.* **2020,** *54*, 5843-5852.

5. Wang, L.; Lin, S., Intrinsic tradeoff between kinetic and energetic efficiencies in membrane capacitive deionization. *Water. Res.* **2018,** *129*, 394-401.

6. Patel, S. K.; Qin, M.; Walker, W. S.; Elimelech, M., Energy efficiency of electro-driven brackish water desalination: Electrodialysis significantly outperforms membrane capacitive deionization. *Environ. Sci. Technol.* **2020,** *54*, 3663-3677.

7. Zhang, H.; Zhang, W.; Shen, J.; Li, Y.; Yan, X.; Qi, J.; Sun, X.; Shen, J.; Han, W.; Wang, L.; Li, J., Ag-doped hollow ZIFs-derived nanoporous carbon for efficient hybrid capacitive deionization. *Desalination.* **2020,** *473*, 114173.

8. Hawks, S. A.; Ramachandran, A.; Porada, S.; Campbell, P. G.; Suss, M. E.;

615 Biesheuvel, P. M.; Santiago, J. G.; Stadermann, M., Performance metrics for the

616 objective assessment of capacitive deionization systems. *Water. Res.* **2019,** *152*, 126-

617 137.

618 9. Lin, S., Energy efficiency of desalination: Fundamental insights from intuitive

619 interpretation. *Environ. Sci. Technol.* **2020,** *54*, 76-84.

620 10. Dykstra, J.; Porada, S.; van der Wal, A.; Biesheuvel, P. Energy consumption in

621 capacitive deionization–Constant current versus constant voltage operation. *Water. Res.*

622 **2018**, 143, 367-375.

623 11. Han, J.; Yan, T.; Shen, J.; Shi, L.; Zhang, J.; Zhang, D., Capacitive deionization of

624 saline water by using MoS_2-graphene hybrid electrodes with high volumetric

625 adsorption capacity. *Environ. Sci. Technol.* **2019,** *53*, 12668-12676.

626 12. Zhou, F.; Gao, T.; Luo, M.; Li, H., Heterostructured graphene@$Na_4Ti_9O_{20}$

627 nanotubes for asymmetrical capacitive deionization with ultrahigh desalination capacity.

628 *Chem. Eng. J.* **2018,** *343*, 8-15.

629 13. Byles, B. W.; Hayes-Oberst, B.; Pomerantseva, E., Ion removal performance,

630 structural/compositional dynamics, and electrochemical stability of layered manganese

631 oxide electrodes in hybrid capacitive deionization. *ACS Appl. Mater. Inter.* **2018,** *10*,

632 32313-32322.

633 14. Kim, S.; Lee, J.; Kim, C.; Yoon, J., $Na_2FeP_2O_7$ as a novel material for hybrid

634 capacitive deionization. *Electrochim. Acta.* **2016,** *203*, 265-271.

635 15. Wang, S.; Wang, G.; Wu, T.; Li, C.; Wang, Y.; Pan, X.; Zhan, F.; Zhang, Y.; Wang,

636 S.; Qiu, J., Membrane-free hybrid capacitive deionization system based on redox

reaction for high-efficiency NaCl removal. *Environ. Sci. Technol.* **2019**, 53, 6292-6301.

16. Wu, T.; Wang, G.; Dong, Q.; Zhan, F.; Zhang, X.; Li, S.; Qiao, H.; Qiu, J., Starch derived porous carbon nanosheets for high-performance photovoltaic capacitive deionization. *Environ. Sci. Technol.* **2017,** *51*, 9244-9251.

17. Lee, J.; Kim, S.; Kim, C.; Yoon, J., Hybrid capacitive deionization to enhance the desalination performance of capacitive techniques. *Energy. Environ. Sci* .2014, 7, 3683-3689.

18. Wen, X.; Zhao, M.; Zhang, M.; Fan, X.; Zhang, D., Efficient capacitive deionization of saline water by an integrated tin disulfide nanosheet@graphite paper electrode via an in situ growth strategy. *ACS Sustain. Chem. Eng.* **2020,** *8*, 1268-1275.

19. Wang, H.; Yan, T.; Shen, J.; Zhang, J.; Shi, L.; Zhang, D., Efficient removal of metal ions by capacitive deionization with straw waste derived graphitic porous carbon nanosheets. *Environ. Sci-Nano.* **2020**, 7, 317-326.

20. Liu, Y.; Zhang, Y.; Zhang, Y.; Zhang, Q.; Gao, X.; Dou, X.; Zhu, H.; Yuan, X.; Pan, L., MoC nanoparticle-embedded carbon nanofiber aerogels as flow-through electrodes for highly efficient pseudocapacitive deionization. *J. Mater. Chem. A.* **2020,** *8*, 1443-1450.

21. El-Deen, A. G.; Choi, J.-H.; Kim, C. S.; Khalil, K. A.; Almajid, A. A.; Barakat, N. A. M., TiO$_2$ nanorod-intercalated reduced graphene oxide as high performance electrode material for membrane capacitive deionization. *Desalination.* **2015,** *361*, 53-64.