

Direct/Alternating Current Electrochemical Method for Removing and Recovering Heavy Metal from Water Using Graphene Oxide Electrode

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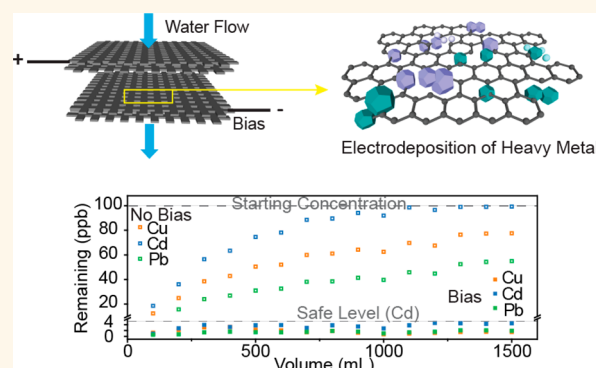
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Supporting Information

ABSTRACT: Treatment of heavy-metal pollution in both point-of-use water and industrial wastewater is critical in protecting human health and the environment. Current methods for heavy-metal treatment in both sources have limitations. For point-of-use water, current methods usually suffer from limited capacity and difficulties in spontaneously removing multiple heavy metals. For industrial wastewater, current methods greatly reduce the value of heavy metal by precipitating them as sludge which requires further treatment. Here we developed an electrochemical method that can treat both low-concentration and high-concentration heavy-metal pollution using either direct current (DC) or alternating current (AC) electrodeposition with graphene-oxide-modified carbon felt electrode (CF-GO). The graphene oxide provides a high density of surface functional groups to assist the electrodeposition. The electrodeposition method showed 2 orders of magnitude higher capacity (>29 g heavy metal for 1 g of graphene oxide) compared with traditional adsorption methods. For low levels of heavy-metal pollution in point-of-use water, DC electrodeposition with a CF-GO electrode can reduce single heavy-metal ion pollution (Cu, Cd, and Pb) as well as multiple ion mixtures to below safe water drinking levels. This method can tolerate a much wider range of heavy-metal pollution in point-of-use water than traditional adsorption methods. For high-level pollution in industrial wastewater, AC electrodeposition can recover >99.9% heavy-metal ions. By tuning the AC frequency and voltage, the electrodeposition method can further selectively recover Cu, Cd, and Pb separately, which adds values to the heavy-metal removal process.

KEYWORDS: heavy metal, water, pollution, electrochemistry, graphene oxide



Industry development imposes negative impacts on water and environment, and one serious issue is heavy-metal pollution.^{1–3} Wastewater containing a high concentration of heavy-metal ions from industries, such as metal plating facilities, mining operations, and tanneries, is directly or indirectly discharged into the environment.^{4,5} This causes serious pollution to surface and groundwater. Since heavy metals tend to accumulate in living organisms, even trace amounts of heavy-metal exposure could lead to illness and diseases such as tremors, renal lesions, or even cancer.^{6–9}

To remove heavy metal from water, different methods are adopted according to the pollution level (heavy-metal ion concentration). When the starting pollution concentration is

high, such as in industrial wastewater, chemical precipitation is effective with a removal efficiency as high as 99%.^{10–12} However, this method generates sludge with mixed pollutants as secondary pollution which needs further separation or treatment. This not only adds complexity for treatment but also reduces the value of heavy metal if recovered from the wastewater. On the other hand, when pollution concentration is low, such as in point-of-use water, chemical precipitation is

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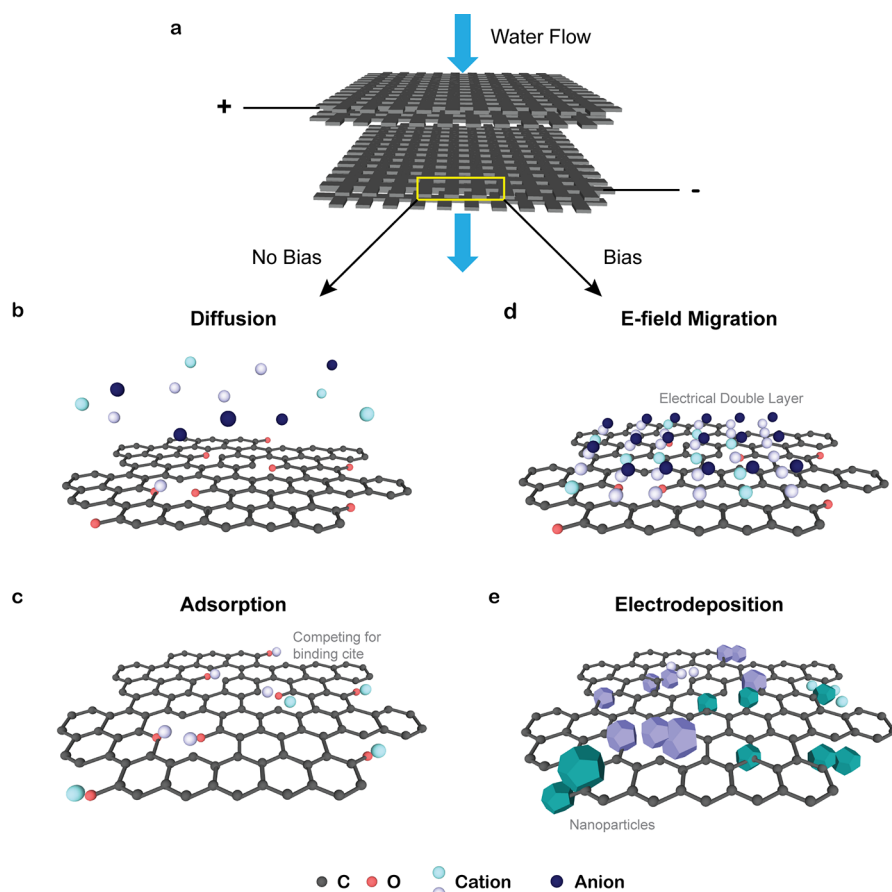


Figure 1. Schematics showing the difference between adsorption and electrochemical deposition. During adsorption, ions diffuse to the surface of the sorbent (b) and bind to the functional groups on the sorbent materials (c). By comparison, in the electrodeposition process, ions migrate to the electrode to form an electrical double layer (d) and then be reduced to a metal form on the electrode (e).

not feasible due to the large input of precipitation chemicals. There are several methods to remove trace amounts of heavy-metal pollution from water such as adsorption and ion exchange.^{13–18} A number of studies have investigated high surface area nanomaterials for heavy-metal adsorption and thus removal, and the removal efficiency can reach above 90%.^{19–21} The constraint associated with the adsorption method is that the capacity is intrinsically limited by the surface adsorption sites, so the treated water volume is small and the performance decays over time. More importantly, since adsorption relies on the strength of binding between sorbents' surface sites to heavy-metal ions when multiple ions coexist in the polluted water, strong binding ions dominate the surface binding sites and largely decrease the adsorption of weak binding heavy-metal ions.^{22,23} This makes treating multiple ions simultaneously from polluted water difficult. There is also some work using an electrochemical deionization method to remove heavy-metal ions from water. The kinetics is faster than pure adsorption, and the capacity of heavy-metal removal can be increased more than pure adsorption through a redox-based pseudocapacitor mechanism. However, the capability of separation of different heavy-metal ions is still challenging.^{24,25}

Here we developed a direct current (DC)/alternating current (AC) electrochemical method to treat both high and low concentrations of heavy-metal pollution. The DC electrochemical method was used to remove low-concentration heavy-metal ions from point-of-use water, and the AC electrochemical method was used to recover high-concen-

tration heavy-metal ions from industrial wastewater. Both DC and AC electrochemical methods use three-dimensional (3D) electrodes made from graphene oxide. The 3D graphene oxide ensures high-density surface binding sites initially anchor the heavy-metal ions to facilitate the nucleation, owing to the high specific area of graphene oxide, $>2000 \text{ m}^2/\text{g}$.^{15,26,27} The electrochemical deposition-based mechanism for removing heavy metal has several advantages (Figure 1): (1) Fast removal enabled by electric-field migration instead of random diffusion. This effect is more obvious in lower initial heavy-metal concentration. (2) High capacity owing to the electrodeposition nature to reduce heavy-metal ions to its zerovalent metal. (3) Treating multiple heavy-metal ions at the same time and selectively recovering heavy-metal ions in series from polluted water. The electrochemical deposition method showed a 2 orders of magnitude higher capacity compared to adsorption using the same graphene oxide electrode. The DC/AC electrochemical methods showed high efficiency in both point-of-use water treatment and industrial waste heavy-metal recovery.

RESULTS

The 3D graphene oxide electrode (CF-GO) was synthesized by electrophoretic deposition of graphene oxide onto conductive carbon felt (CF) substrates.^{28,29} A 5 mg/mL graphene oxide water solution was used. Graphene oxide was deposited onto the CF substrate at 5 V for 2 h (see [Materials and Methods](#)). With graphene oxide coating, the CF electrode

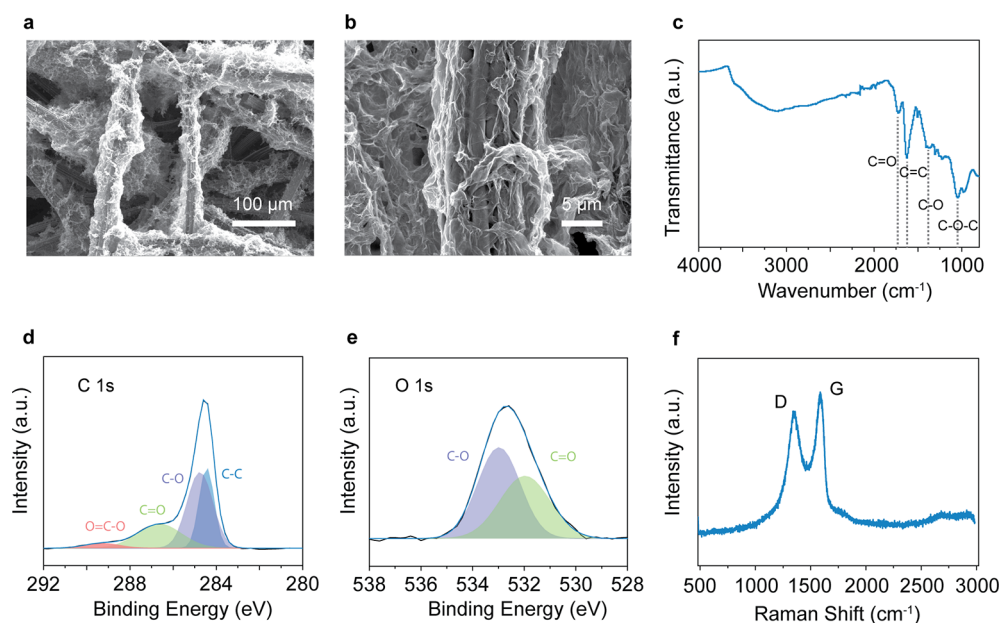


Figure 2. Characterization of CF-GO electrode. (a, b) SEM images of the CF-GO electrode made by electrophoretic deposition. (c) FTIR spectra of the CF-GO electrode showing the functional groups of graphene oxide. (d, e) XPS characterization of the CF-GO electrode showing the C 1s and O 1s peak analysis. (f) Raman spectra of CF-GO electrode showing the D band and G band of graphene oxide.

shows a much better hydrophilicity (Supplementary Figure 1). The morphology of the graphene oxide electrode was characterized by scanning electron microscope (SEM) and is shown in Figure 2a,b. The deposited graphene oxide formed flower-like 3D structures surrounding each of the CF fibers. This 3D CF-GO electrode has a surface area of 18 m²/g compared to bare CF of 2.9 m²/g (pore distribution shown in Supplementary Figure 2). This ensures a high-density exposure of surface functional groups for heavy-metal ions to bind. The as-synthesized CF-GO electrode was characterized by Fourier transform infrared spectroscopy (FTIR). The spectrum (Figure 2c) shows the characteristic absorption peak from graphene oxide at 1730, 1620, 1387, and 1045 cm⁻¹ for C=O, C=C, C-O, and C-O-C, respectively. Comparing to the pristine graphene oxide, the ratio of C=C increased after electrophoretic deposition (Supplementary Figure 3). To further analyze the functional groups on graphene oxide, X-ray photoelectron spectroscopy (XPS) was used for characterization. The spectra of C 1s and O 1s are shown in Figure 2d,e. All carbon species were observed in the C 1s spectrum including C=C, C-O, C=O, and O=C-O. The O 1s spectrum shows two peaks indicating the existence of C-O and C=O functional groups. A Raman spectrum was then used to characterize the quality of the graphene oxide on the electrode (Figure 2f). The graphene oxide on the electrode exhibits both a D peak at 1347 cm⁻¹ and a G peak at 1581 cm⁻¹. The integrity of graphene can be characterized by measuring the ratio of these two peaks. A ratio of zero means no defect at all, and a higher ratio means a high defect content of the graphene oxide. The I_D/I_G for the graphene oxide deposited on CF is 0.89 and similar to pristine graphene oxide (Supplementary Figure 4). This indicates a sufficient amount of functional groups.

The DC electrochemical deposition method was first evaluated to remove trace amounts of heavy-metal pollution, as in point-of-use water. The test was carried out in a flow device. The polluted water was fed to the inlet of the flow

device, and treated water was collected from the outlet. CF-GO was used as the negative electrode and bare CF as the positive electrode. The two electrodes were cut into a 1 cm² piece each and put into a device chamber with two layers of Kimwipes tissue paper in between as a separator to prevent electric contact. During operation, as water flows through the device, an external voltage was applied to the two electrodes. Cu, Cd, and Pb were chosen to represent the heavy-metal pollutants, and an initial concentration of ~100 ppb was used. The remaining heavy metal concentrations in the effluent are shown in Figure 3. The remaining concentration measured at 0 V is equivalent to the case of adsorption. The adsorption ability for CF-GO showed an increasing trend as Cd < Cu < Pb. When an external voltage was applied, the remaining concentration further decreased with increasing voltage. At 20 V, the remaining concentrations of Cu, Cd, and Pb were 1.3, 2.3, and 0.74 ppb, respectively. They are all below the safe drinking level (US EPA) which is 1 ppm for Cu, 5 ppb for Cd, and 15 ppb for Pb. This is in sharp contrast to the adsorption method which can only reduce Cu, Cd, and Pb to 42.9, 53.2, and 29.5 ppb. The flow dependence was also studied by comparing the water flow rates of 5 mL/min to 10 mL/min. The CF-GO electrode showed a slight decrease in removal efficiencies of heavy-metal ions at a faster flow rate of 10 mL/min compared to 5 mL/min, but it can still remove heavy-metal ions to a safe drinking level at 20 V. The effectiveness of graphene oxide to provide a high density of surface binding sites was proven by comparing a CF-GO electrode to a bare CF electrode. The bare CF electrode also showed the same trend that the remaining heavy-metal ion concentration decreased with an increase of the applied voltage. However, comparing to the CF-GO electrode, the removing efficiency of the bare CF electrode was much lower. Mass loading effect was also investigated for the CF-GO electrode, and the result is shown in Supplementary Figure 5.

Further, the ability for the CF-GO electrode to remove multiple heavy-metal ions simultaneously was investigated.

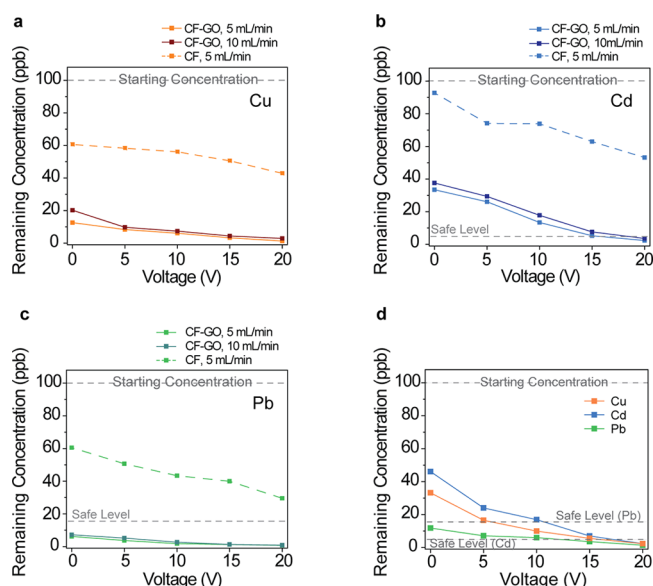


Figure 3. Performances of dilute heavy-metal removal using DC electrodeposition with a CF-GO electrode. (a–c) Remaining Cu, Cd, and Pb concentrations in the effluent at different applied voltages and filtration speeds using a CF-GO electrode compared to a bare CF electrode. All three solutions only contain a single contaminant. Safe drinking levels for Cd and Pb are drawn in the figure. Since Cu has a safe drinking level of 1 ppm, it is not indicated in the figure. (d) Performance showing the ability of the CF-GO electrode to remove a mixed pollution with Cu, Cd, and Pb. Remaining concentrations of Cu, Cd, and Pb are shown at different applied voltages.

The starting pollution contains all three types of heavy-metal ions (Cu, Cd, and Pb) with each one of ~ 100 ppb in concentration and the flow rate was 5 mL/min. At the condition of adsorption (0 V), due to the adsorption ability difference of CF-GO to Cu, Cd, and Pb, less Cd and Cu was removed with the presence of Pb. The remaining concentrations were 33.2, 46.1, and 11.8 ppb for Cu, Cd, and Pb, respectively. This implies that the adsorption cannot effectively remove multiple ions simultaneously. Since Pb has the highest binding ability to graphene oxide, it interferes with the removal of coexisting Cu and Cd. For the electrodeposition method, as the applied voltage increased, the remaining ion concentrations decreased for all three ions. At 20 V, the remaining concentrations were 2.2, 2.4, and 1.4 ppb for Cu, Cd, and Pb, respectively, which are all below the safe drinking level. This result indicates a success for the electrodeposition method in removing multiple heavy-metal ions simultaneously.

The difference between electrochemical deposition and adsorption was even larger in long-term testing for simultaneously removing Cu, Cd, and Pb together. The 20 V electrodeposition condition was chosen to compare to the adsorption method for the long-term test. 1500 mL of polluted water was flowed through the filter, and the concentrations of Cu, Cd, and Pb in the effluent were monitored. The remaining concentration of Cu, Cd, and Pb is shown in Figure 4a. The adsorption method showed a dramatic removal efficiency decay over the 1500 mL test. After flowing 1000 mL of polluted water, adsorption barely removed any Cd from the influent water. The remaining concentration of Cd was approaching 100 ppb. At the end of the 1500 mL test, the remaining concentrations of Cu, Cd, and Pb were 77.5, 99.2,

and 54.8 ppb, respectively. By sharp contrast, for the 1500 mL test, Cu, Cd, and Pb were all below 5 ppb in the electrochemical deposition case, and they were all below the safe drinking level. A higher pollution level of multiple ions in point-of-use water was also tested using the flow device. As the initial concentrations of the three ions increased to 1000 ppb and 10,000 ppb, the adsorption method showed a drastic decay in ion removal efficiency, especially for the most weakly adsorbed Cd, as shown in Figure 4b. The Cd removal efficiencies dropped to 6.9% and 0.43% for an initial concentration of 1000 ppb and 10,000 ppb, respectively. On the other hand, the electrochemical deposition method can still tolerate high initial concentrations up to 10,000 ppb. The removal efficiencies for Cu, Cd, and Pb were 97.7%, 97.3%, and 98.5% for the 1000 ppb case and 96.5%, 94.8%, and 98.5% for the 10,000 ppb case at 20 V. Therefore, the electrochemical deposition method showed a much better performance than adsorption for point-of-use heavy-metal pollution treatment, owing to its longer lifetime, treatment compatibility for multiple coexisting ions, and also concentration variation tolerance.

After the long-term test, the CF-GO electrode was characterized to identify the chemical species of removed Cu, Cd, and Pb. First, the CF-GO electrode was characterized by SEM, and the images are shown in Figure 4c,d. After the long-term test, the graphene oxide surfaces were densely covered by nanoparticles which could result from electrodeposition of Cu, Cd, and Pb. The electrodeposited nanoparticles were then proven to be metal with native oxide by XPS, as shown in Figure 4e–g. The XPS spectra of Cu 2p showed a major peak at 932.6 eV for Cu metal and a shoulder peak at 932.2 eV for Cu^+ as in the native oxide, Cu_2O . The Pb 4f spectra also showed both signals from Pb metal (136.8 eV) and Pb^{2+} (138.2 eV). The Cd 3d spectra showed peaks at 405.3 and 412.2 eV. Since the characteristic peak for Cd metal and Cd^{2+} are too close, the peak could be from both metal and native oxide of Cd.

Besides point-of-use heavy-metal removal, the electrochemical deposition method can also be used for industrial wastewater treatment to recover the heavy-metal ions as valuable metals. Since wastewater usually has high heavy-metal ion concentration (high conductivity), the DC electrochemical deposition would induce severe water splitting which not only wastes energy but also induces local pH increase in the negative electrode, leading to precipitation of metal hydroxide that blocks further electrodeposition. To solve this problem, we have adopted the AC electrochemical deposition method to recover heavy-metal ions from wastewater. The details for AC electrodeposition are shown in the Materials and Methods section. Compared to the hydrogen evolution reaction, metal ion electrodeposition happens at a much higher kinetic rate; therefore, by limiting the duration of electron transfer, one can eliminate the hydrogen evolution reaction as we demonstrated in our previous study.³⁰ First, the capacity of the CF-GO electrode for recovering heavy-metal ions from heavily polluted water was tested (Figure 5a–c). Using an initial concentration of ~ 1000 ppm, the adsorption method showed capacities of 0.24 g/g, 0.27 g/g, and 0.42 g/g for Cu, Cd, and Pb, respectively. In contrast, the AC electrodeposition method achieves the capture capacities for all three ions of >29 g/g, and no saturation was observed. The capacities for AC electrodeposition comparing to adsorption were 2 orders of magnitude higher for Cu and Cd and 69 times higher for Pb.

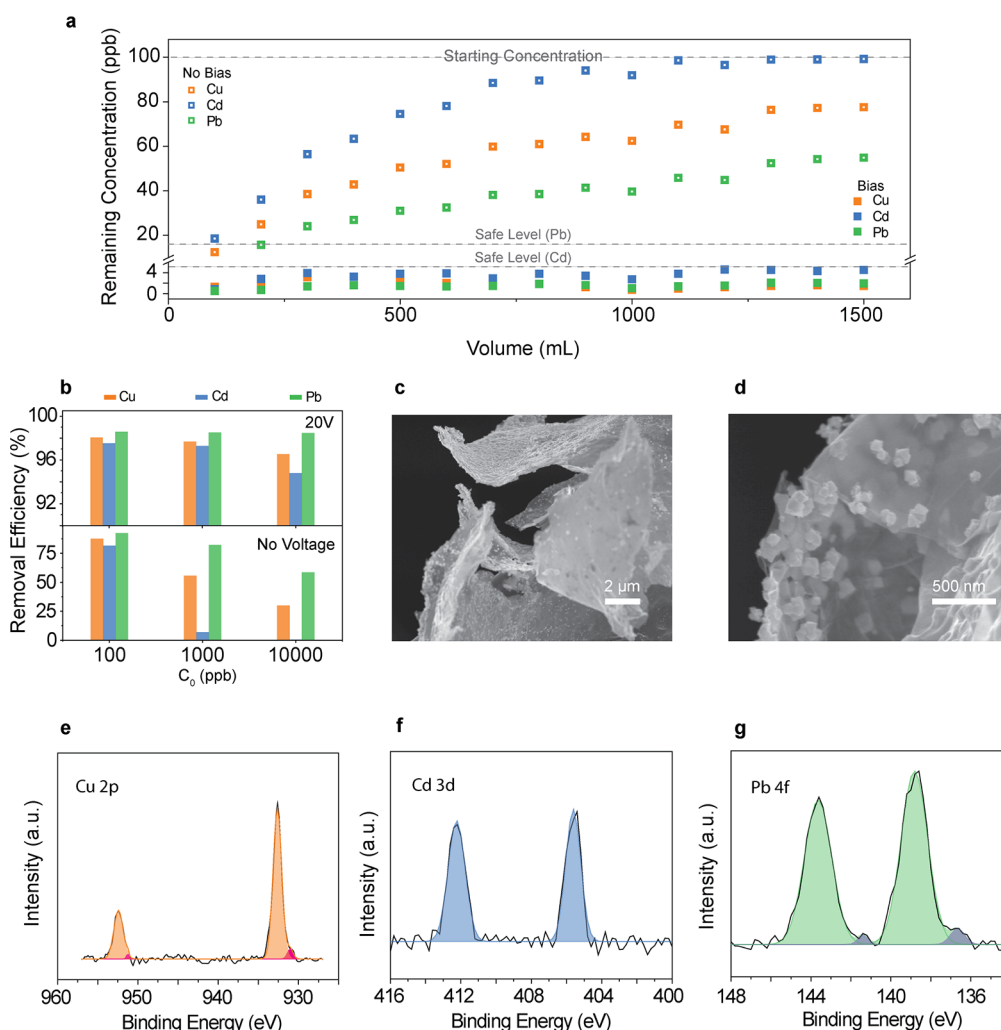


Figure 4. (a) Long-term performance comparison of CF-GO electrode with and without bias in removing mixed heavy-metal pollution with Cu, Cd, and Pb of 100 ppb each initially. (b) Removal efficiency comparison of the CF-GO electrode with and without bias using different concentrations of mixed ion polluted water. C_0 is the initial concentration of each ion in the mixed pollution. (c, d) SEM images showing the morphologies of CF-GO after a long-term filtration performance under bias. Heavy-metal particles are formed on the surface of graphene oxide. (e–g) XPS analysis of the Cu, Cd, and Pb deposited on the CF-GO electrode after a long-term filtration test under bias.

The AC electrodeposited Cu, Cd, and Pb were characterized by SEM and X-ray diffraction (XRD), as shown in [Supplementary Figures 6–11](#). In all three cases, ions are deposited as metals from the XRD pattern. In the case of Cd, CdCO_3 was also detected owing to the reaction of Cd metal with dissolved CO_2 as CO_3^{2-} . The effect of pH and temperature was studied, and the results are shown in [Supplementary Figures 12 and 13](#). Also, the CF-GO was regenerated by electrochemically dissolving the metal species, and reuse performance was tested using the Cu solution (shown in [Supplementary Figure 14](#)).

More importantly, by tuning the AC amplitude, frequency, and offset, we can selectively recover metal ions one by one from a mixture of pollution. This can save enormous time and effort for the subsequent refinement. As shown in [Figure 5d](#), the starting solution contains all three heavy-metal ions, Cu, Cd, and Pb of $\sim 1,000$ ppm each. In the beginning, (-3.5 V, $+1$ V) AC voltage was applied at a frequency of 50 Hz, and only Pb was removed from the pollution. After 8 h of operation, $>99.9\%$ of Pb was recovered at the electrode, while the loss of Cu and Cd from solution was $<1\%$ and $<0.1\%$, respectively. After recovering Pb, Cu was then recovered at (-4 V, 0 V) at

50 Hz, and $>99.9\%$ of Cu was recovered with $<0.1\%$ of Cd loss. Finally, Cd was recovered at (-5 V, -2 V) at 4 MHz. The successful recovery of metal ions separately added great value to the heavy-metal treatment process compared to a traditional precipitation method, which only produces mixed content sludge as a secondary pollution.

CONCLUSION

In conclusion, we have developed a DC/AC electrodeposition method to remove and recover heavy metals from point-of-use water and industrial wastewater with graphene oxide electrodes. The electrochemical method showed a 2 orders of magnitude higher capacity ($>29\text{g/g}$) for Cu, Cd, and Pb than the traditional adsorption method. At the point-of-use water treatment, the DC electrodeposition method can simultaneously remove all three heavy-metal ions to below safe drinking levels. In high-concentration pollution, the AC electrodeposition can selectively recover Pb, Cu, and Cd in series.

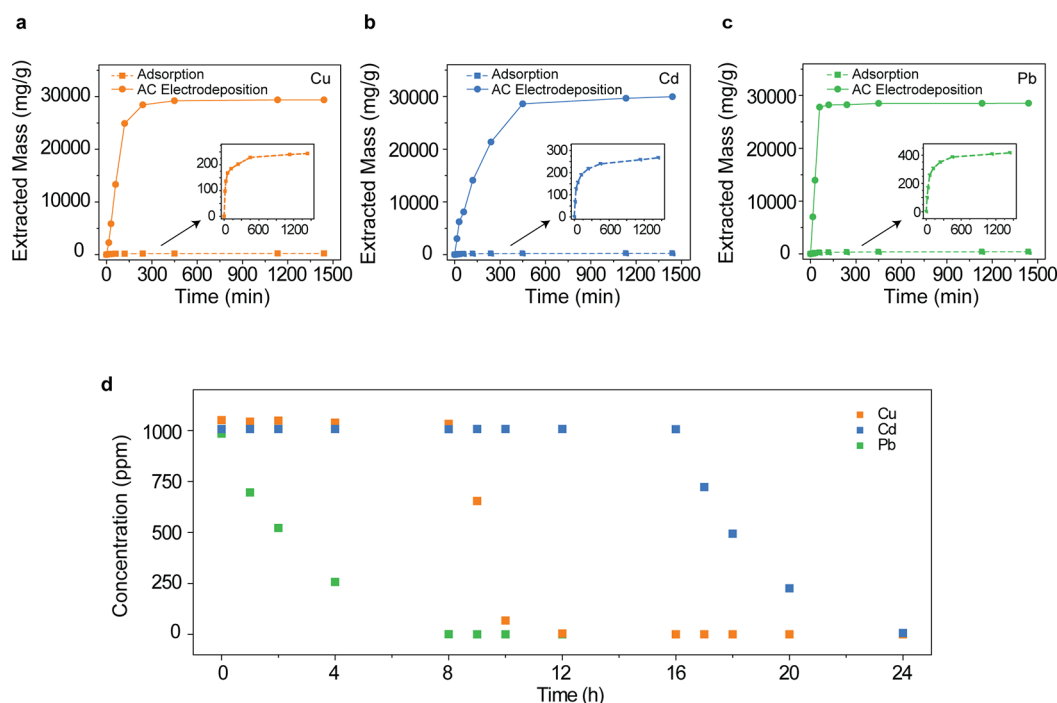


Figure 5. (a–c) The removal capacity of Cu, Cd, and Pb was compared between the AC electrodeposition method and adsorption using the CF-GO electrode. Plots show the recovered metal mass on the CF-GO electrode during the 24 h test for both AC electrodeposition and adsorption. All three solutions only contain a single contaminant. (d) Selective recovery of Pb, Cu, and Cd in series from heavily polluted water with mixed pollution using different AC bias and frequency.

MATERIALS AND METHODS

CF-GO Electrode Fabrication. The graphene oxide electrode was synthesized by an electrophoretic deposition method. Carbon felt (Alfa Aesar) was used as the negative electrode and graphite rod (Sigma-Aldrich) as the positive electrode. An ~ 5 mg/mL graphene oxide (Graphene Supermarket) and sulfuric acid (pH ~ 1) aqueous solution was used as the electrolyte. A 5 V voltage was applied for 2 h during the electrophoretic deposition. The CF-GO electrode was then washed with DI water and dried in vacuum.

Heavy-Metal Ion Removal Experiment. $\text{Cu}(\text{NO}_3)_2$, $\text{Cd}(\text{NO}_3)_2$, and $\text{Pb}(\text{NO}_3)_2$ were dissolved in DI water to make different concentrations of Cu, Cd, and Pb polluted water. For diluted pollution in the case of point-of-use water, a flow device was made (schematics shown in [Supplementary Figure 15](#)). The device had a 1 cm \times 1 cm \times 0.2 cm chamber with electric wire connections. CF-GO and bare CF were used as the negative and positive electrodes, respectively. For the AC electrochemical deposition to recover heavy metals, the CF-GO electrode (1 cm \times 1 cm \times 0.2 cm) was used as the negative electrode and a graphite rod as the counter electrode. A function generator (Rigol DG1022A) was used to apply different AC voltages. 15 mL of polluted water was treated each time, and the remaining concentrations of ions were monitored for 24 h. A 200 μL solution was taken out and diluted to 5 mL and then measured by ICP-MS.

Characterization. Scanning electron microscopy (SEM, FEI Nova NanoSEM 450) with beam energies of 5 kV was used for imaging. Fourier transform infrared spectroscopy (FTIR, Nicolet iS50) was carried out in the attenuated total reflectance mode. XRD (PANalytical Material Research Diffractometer) was carried out using Cu $K\alpha$ radiation. X-ray photoelectron spectroscopy (XPS, SSI SProbe XPS spectrometer) was carried out using an Al ($K\alpha$) source. Raman spectroscopy (WITTEC Raman spectrometer) was conducted using a 532 nm excitation laser.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.nano.8b09301.

Wettability and pore distribution of the electrode, FTIR and Raman of pristine graphene oxide, electrodeposited Cu, Cd, and Pb characterization, graphene oxide mass loading, and pH- and temperature-dependent performance ([PDF](#))

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Author Contributions

[†]These authors contributed equally to this work. C.L., T.W., and Y.C. conceived the concept. C.L. synthesized the CF-GO

electrode and conducted SEM and FTIR characterization. C.L. and T.W. measured the performances. P.-C. H. helped with XRD characterization. J. Xie helped with the Raman characterization. J.Z. helped with XPS characterization. Z. Ye helped with the performance measurement. J.T. helped with the BET test. K.L., J.S., J. Xu, D.L. provided important experimental insights. C.L., T.W., and Y.C. analyzed the data and cowrote the paper. All of the authors discussed the whole paper.

Notes

The authors declare no competing financial interest.

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