Supporting Information

Grafting chelating groups on 2D carbon for selective heavy metal adsorption

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S1. The selective removal of heavy metals by iminodiacetic acid (IDA)

IDA has been employed as a chelating group to remove heavy metals. Many studies have been reported so far, but most of them employ single metal species. In nature, multiple metals are present. Here we searched for selective metal removal from multiple metal-contained solutions (Table S1).

Table S1. Metal selectivity comparison of several adsorbent[1–4]

Adsorbent	Metals contained in the solution	Selectivity	Removal efficiency (%)	Ref.
Ox-MWCNTs	Cu, Zn, Pb, Cd, Co	Pb	N.D.	[1]
MWCNTs–SeP(O)(O-t-Bu)$_2$	Pb, Cd, Zn, Cu, Ni, Co	Pb	87	[2]
GO-SBA-15	Li, Na, K, Ca, Mg, Cd, Cr, Co, Hg, Fe, As, Pb Mn, Ni, Zn	Pb	99	[3]
CHI-APSGO	Pb, Cu, Cr, Ni	Pb	99	[4]
GO	Al, As, B, Cd, Cr, Cu, Mg, Pb, Se, Zn	Pb	95	This work
GO-C$_6$-IDA	Al, As, B, Cd, Cr, Cu, Mg, Pb, Se, Zn	Cu	65	This work

S2. Optimization of epoxy ring-opening amination

Alkylamine was employed as a model compound for the GO surface functionalization. Reaction temperature (Table S2), the amount of amine (Table S3), and pH (Table S4) were investigated.

Table S2. Elemental analysis of GO-amine prepared under different temperatures.

Temperature	C%	N%	O%
rt	75.3	3.1	1.3
40 °C	79.2	3.8	17.0
80 °C	84.1	5.1	10.8

Table S3. Elemental analysis of GO-amine prepared by different weight ratios.

GO : hexylamine	C%	O%	N%
1 : 0.2	65.3	32.0	1.02
1 : 0.4	66.7	28.1	1.22
1 : 0.6	68.9	29.7	1.44
1 : 1	74.7	23.7	1.60
1 : 2	82.7	15.6	1.68

Table S4. Elemental analysis of GO-amine with different pH.

pH	C%	H%	N%
5	52.6	3.2	0.7
7	55.5	3.0	0.9
9	55.8	3.0	1.2

S3. Additional structure analysis of GO-C_6-IDA

C-N bonding accounts for 14% in GO-C_6-IDA as determined by XPS (Figure 1d). We calculated the ratio of secondary amine and tertiary amine from XPS analysis at N 1s region (Figure S1). The ratio of secondary amine (orange line in Figure S2): tertiary amine (blue line in Figure S2) is 1: 1 in the ideal GO-C_6-IDA structure (Figure S2a); however, XPS analysis revealed secondary amine: tertiary amine is 3: 2.

Nitrogen connected to GO is calculated following the considerations below.

1. Nitrogen on the side not attached to GO transforms into IDA and becomes a tertiary amine.
2. A part of hexanediamine is crosslinked or reacted in the same GO plane to become secondary amine (yellow line in Figure S2b). The extra 1 (= 3 - 2) of nitrogen atoms are supposed to be in these forms. Thus, amine molecule of 0.5 (= 1/2) is in an undesirable structure.

Based on the above analysis, we consider the estimated structure of GO-C_6-IDA (Figure 2b). There are 24 C-N, of which 4 are GO-N with the desired structure. In other words, the ratio is 1/6, and the amount is $14 \times \frac{1}{6} = 2.3\%$.

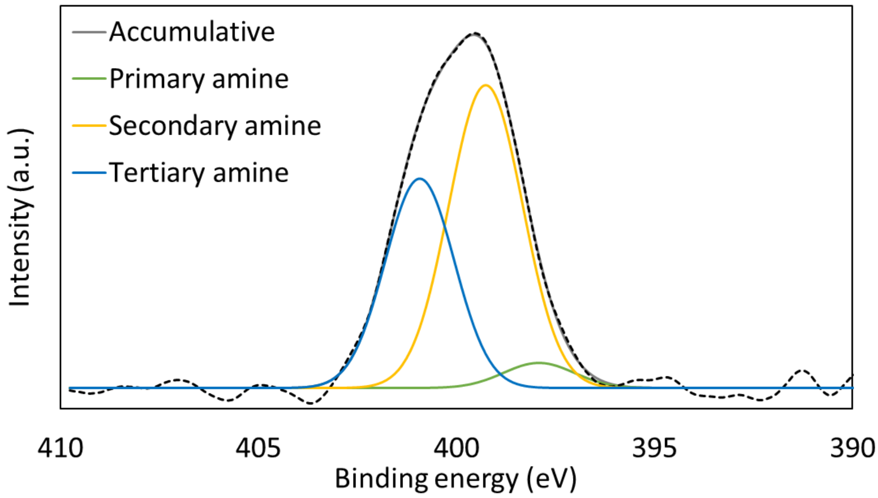

Figure S1. XPS analysis at N 1s region of GO-C_6-IDA.

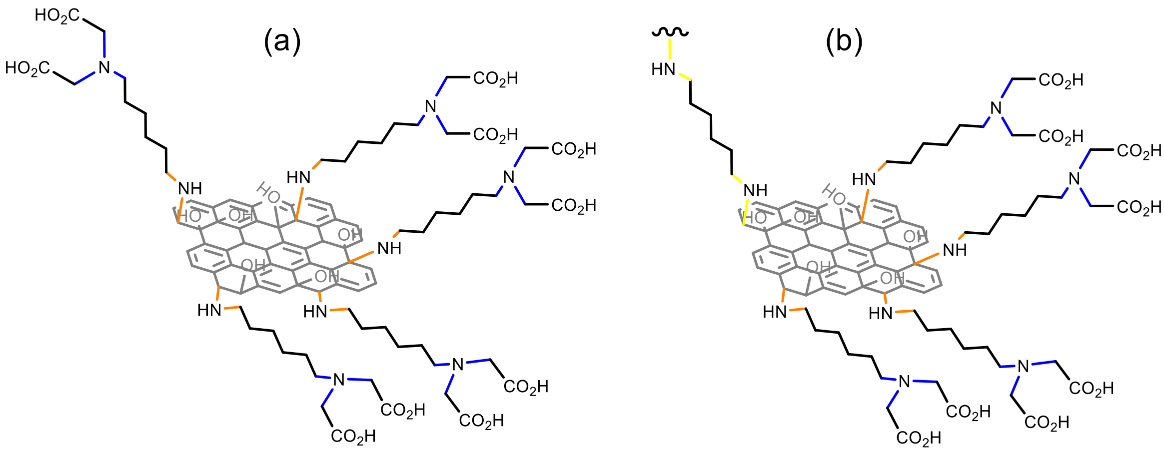

Figure S2 (a) Ideal and (b) estimated structures of GO-C_6-IDA.

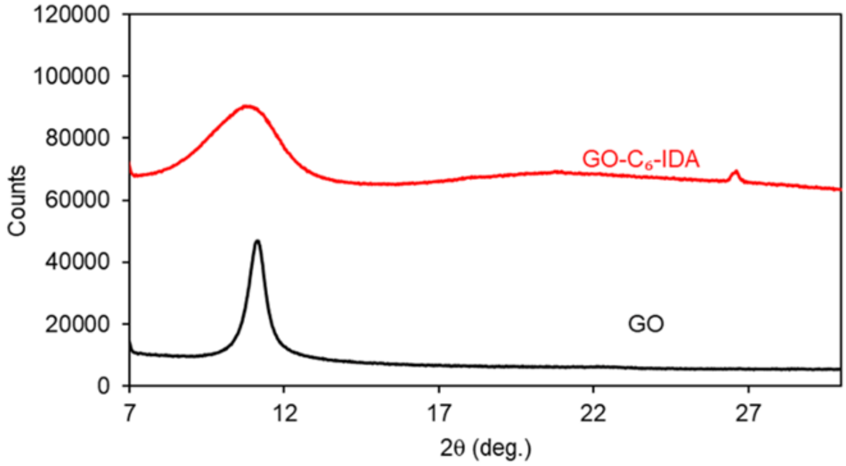

Figure S3. XRD patterns of GO/GO-C_6-IDA

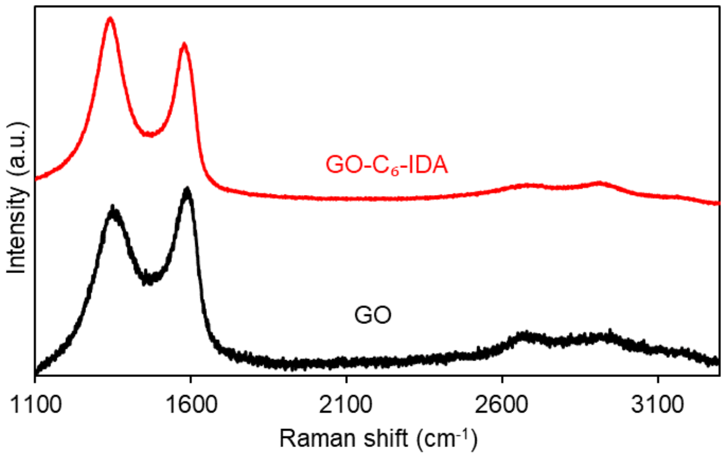

Figure S4. Raman spectra of GO/GO-C_6-IDA

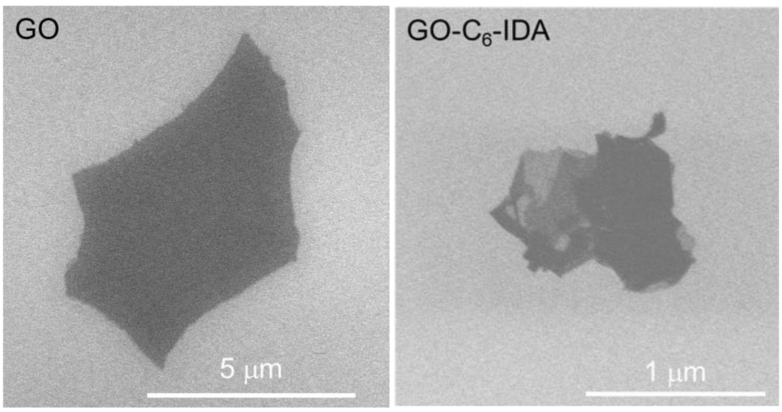

Figure S5. SEM images of GO/GO-C_6-IDA

S4. The metal selectivity of IDA moiety

After the formation of the C_0-IDA complex, metal adsorption by GO was carried out (Figure S3). The metal- C_0-IDA complex (C_0-IDA-M) was not adsorbed on GO, since no nitrogen was detected (Table S5). the stability constants of the corresponding IDA complexes for metal ions: Cu> B> Cr> Cd≈Pb

Table S5. The reactivity of GO and C_0-IDA chelate (C_0-IDA-M).

	C%	H%	N%
C_0-IDA-M + GO	48.8	2.7	-

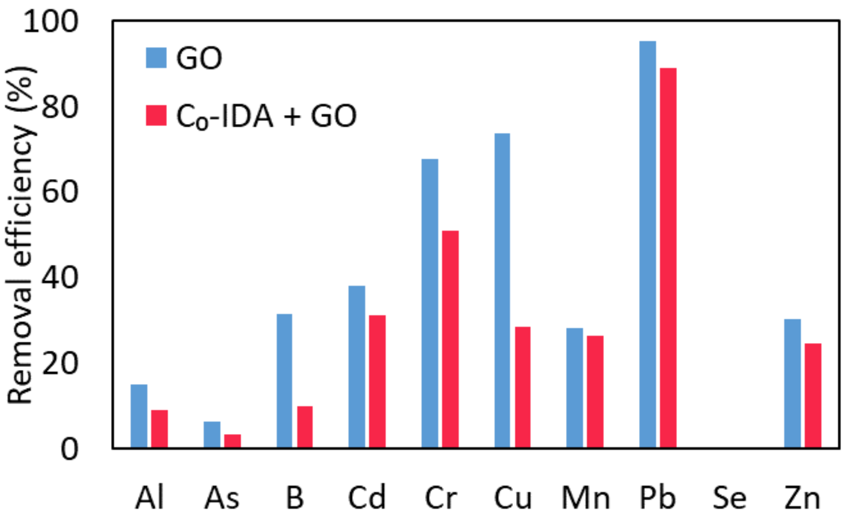

Figure S6. Metal removal efficiency of GO (blue) and C_0-IDA with GO (red).

S5. DFT calculation

Each optimization structure of a.Cu-C_0-IDA(b3lyp/N, C, O, H, O: 6-311+g(df,pd), Cu: lanl2dz), b.Cu-C_3-IDA(b3lyp/N, C, O, H, O: 6-311+g(df,pd), Cu: lanl2dz), c.Cu-C_6-IDA(b3lyp/N, C, O, H, O: 6-311+g(df,pd), Cu: lanl2dz), d.Cu-C_{12}-IDA(b3lyp/N, C, O, H, O: 6-311+g(df,pd), Cu: lanl2dz) from DFT calculations.[5]

Table S6. Cu-C_x-IDA chelating energy by DFT calculations.

Alkyl chain	0	3	6	12
E_{CnIDA}	-1345387	-1655204.886	-1964953.699	-2584451.154
E_{ion}	-512145	-512144.9843	-512144.9843	-512144.9843
$E_{chelate}$	-1857391	-2170189.57	-2479939.192	-3099436.777
ΔE (kJ/mol)	141.28	-2839.7	-2840.5	-2840.6

Table S7. CHN elemental analysis of adsorbents with different alkyl chain lengths.

Adsorbent	C	H	N
GO-C_0-IDA	57	2.7	0.30
GO-C_3-IDA	57	3.2	4.5
GO-C_6-IDA	60	4.4	5.2
GO-C_{12}-IDA	62	4.6	2.8

S6. Adsorption experiments

30 mg of adsorbent GO-C_6-IDA was prepared in a centrifuge tube, and 5 mL of copper sulfate[6] was added to the adsorbent. Then it was mixed by centrifugation. The supernatant solution was collected with a plastic syringe and filtered with a filter. The filtrate was measured by UV-visible absorption (UV-vis), and the change in concentration was analyzed (Figure S4). A calibration curve was created from each standard concentration (Figure S3).

In addition, it was determined the concentration in experiments investigating metal selectivity by ICP-AES. Calibration curves were prepared for each of the 10 types of metals (Table S7).

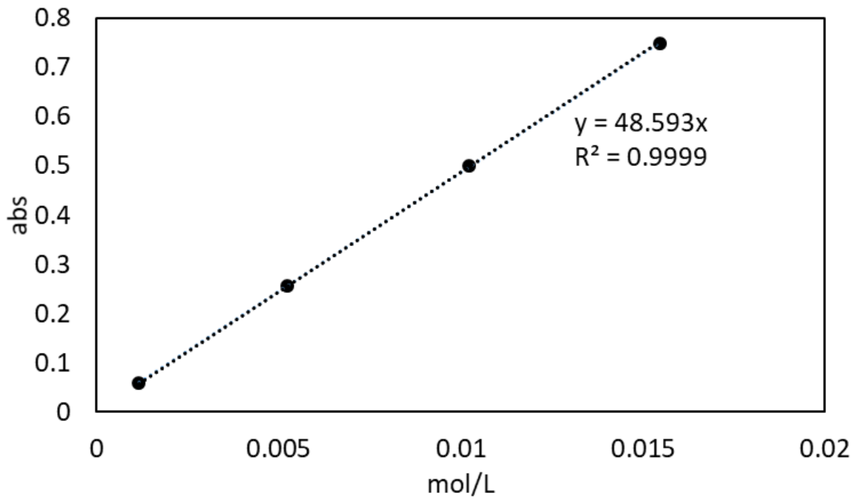

Figure S7. UV-vis calibration curve of copper(Ⅱ) sulfate.

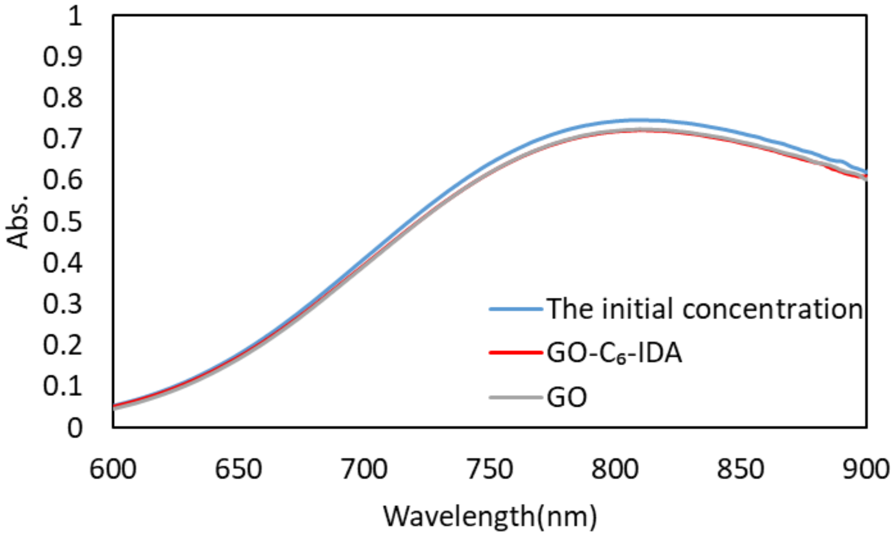

Figure S8. UV-vis spectra of copper adsorption by GO-C_6-IDA and GO.

Table S8. Calibration curve of each metal species derived by ICP-AES.

Metal	Concentration range (mg/L)	R^2	Gradient	Wavelength (nm)
Al	0.01 - 1	0.9915	6237	396
As	0.01 - 1	0.9934	35.29	235
B	0.01 - 1	0.9550	1298	250
Cd	0.01 - 1	0.9888	500.2	214
Cr	0.01 - 1	0.9995	968.7	268
Cu	0.01 - 1	0.9912	4482	327
Mn	0.01 - 1	0.9903	8137	258
Pb	0.01 - 1	0.9782	90.19	220
Se	0.01 - 1	0.9887	53.39	196
Zn	0.01 - 1	0.9882	1368	214

S7. Calculation of the utilization efficiency of IDA

We calculated the rate of C_6-IDA in GO-C_6-IDA. By CHN elemental analysis, nitrogen was found to be 5.2%. The one with the desired structure is 4/5 in the nitrogen. Since there are two types of nitrogen in one C_6-IDA moiety, the number of moles is halved.

$$5.2 \times \frac{4}{5} \div 2 \times \frac{232}{14} = 34.5 \text{ wt\%}$$

The substance amount of the chelate ligand was calculated from the amount of nitrogen from the elemental analysis data (Table 1). The metal removal effect of the chelate ligand was investigated by determining the amount of metal adsorbed on the chelate ligand present in GO-C_6-IDA. The metal concentration (C) adsorbed on the chelate ligand calculated as the difference between the metal concentration adsorbed on GO (C_{GO}) and the metal concentration adsorbed on GO-C_6-IDA ($C_{GO\text{-}C6\text{-}IDA}$) as shown in eq. (4).

$$C(mol/L) = C_{GO-C6-IDA}(mol/L) - C_{GO}(mol/L) \quad (4)$$

In the adsorption of copper, it was found that the chelating ligands on GO-C_6-IDA adsorbed 97% of copper (Table S8).

Table S9. Adsorption of copper.

	Cu ×10^{-2} (mol/L)	IDA : Cu	The amount of chelate ligand ×10^{-2} (mmol)
GO-C_6-IDA	2.65	1 : 0.97	5.38
GO	1.61	-	

S8. The adsorption state analysis

Copper adsorbed on GO-C_6-IDA or GO did not show the specific peak by UV-vis (Figure S5) because of the low concentration for copper or different chemical structure of copper on GO. Therefore, we found UV-vis analysis is not suitable for the chemical state analysis of copper on the adsorbents.

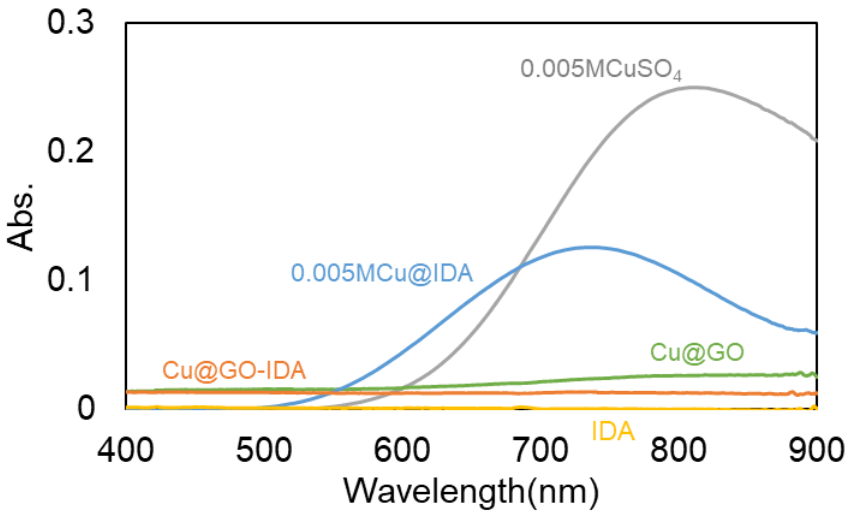

Figure S9. UV absorption of Cu@GO-C_6-IDA, Cu@GO, and Cu@IDA and UV-vis spectra of copper sulfate and IDA

XPS was carried out using an Mg (Kα) source. Carbon tape was used for the characterization of GO and GO-C_6-IDA. For the analysis of metal adsorption state, a dispersion of GO-C_6-IDA with copper adsorbed was placed on a Si substrate and spun at 1000 rpm for 60 seconds. Copper(II) sulfate pentahydrate was dispersed in ethanol and placed on a Si substrate. It was heated on a hot plate at 200 °C. Copper(II) acetate monohydrate was dissolved in water and spin coated at 2000 rpm for 60 seconds.

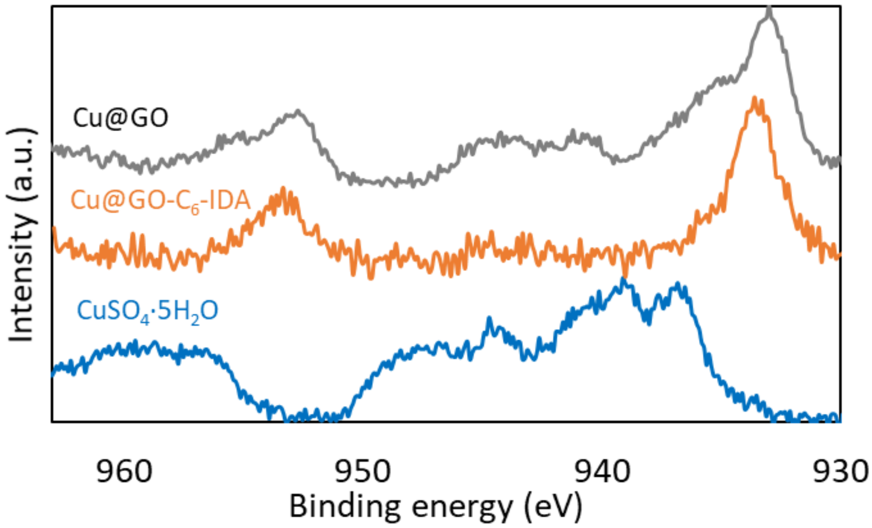

Figure S10. XPS analysis for Cu adsorbed on GO (Cu@GO), on GO-C_6-IDA (Cu@ GO-C_6-IDA), and $CuSO_4$.

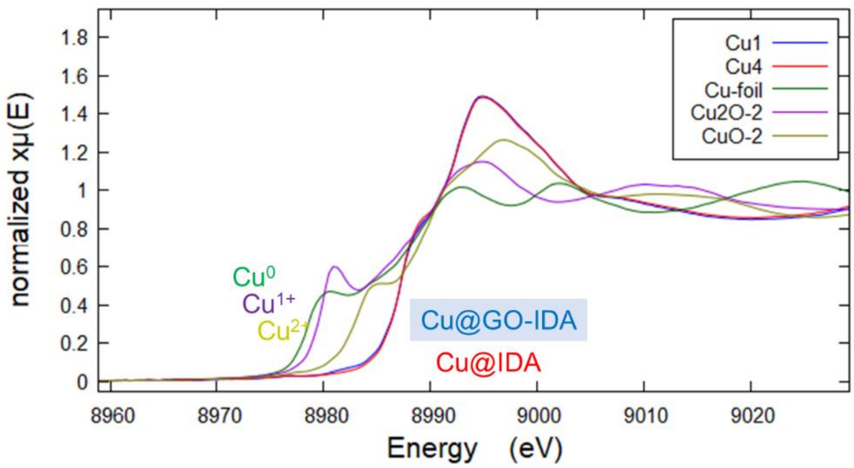

Figure S11. XANES spectra of copper. Cu1: Copper adsorbed on GO-C_6-IDA, Cu4: Copper bound to IDA, Cu-foil: zero-valent copper metal, Cu2O-2: Cu_2O, CuO-2: CuO.

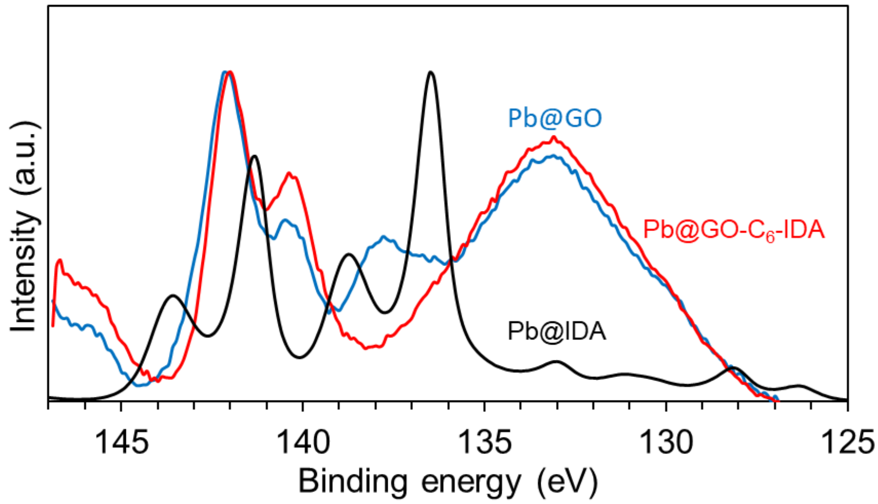

Figure S12. XPS analysis of Pb on GO, GO-C_6-IDA, and IDA.

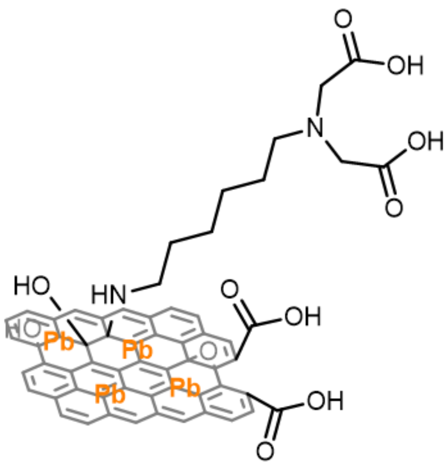

Figure S13. The estimated structure of Pb adsorbed on GO-C_6-IDA.

Reference

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