Electronic Supplementary Material (ESI) for Environmental Science: Nano.

Effects of pH and Electrolytes on the Sheet-to-Sheet Aggregation Mode of Graphene Oxide in Aqueous Solutions

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SI 1 Preparing methods for GO

Hummers method was used to produce GO.[1] 46 mL of concentrated sulfuric acid were cooled in a 500 mL beaker to 0 °C in an ice water bath. 2 g of natural graphite flakes and 1g anhydrous sodium nitrate were then added to the sulfuric acid. After stirring for 15 min, 6 g of $KMnO_4$ were slowly added to the mixture with stirring for 1h and further cooling to prevent the temperature from exceeding 20 °C. The mixture was then heated to 35±3°C and held at that temperature for 30 min under constant stirring. 92mL of deionized (DI) water were then added to the mixture and stirred for 15 minutes. Then, the reaction was terminated through addition of 280 mL of 50 ℃ DI water. Finally, 10 mL of 30% H_2O_2 solution was slowly added to the mixture and washed with 1.25 L of 1:10 HCl solution to remove metal ions and other contaminants. The mixture was then centrifuged at 300 r/min for 1 min to sediment the graphite flakes. Subsequently, the filtrate centrifuged for 10 min at 12000 rpm to sediment the GO, and the supernatant was decanted. This DI wash process was repeated many times until the GO was unable to be separated from water, and the final pH of the mixture was about ~6.5.

SI 2. System setups for DFT calculations

SI 2.1 Models of GOs for LOLIPOP index and polarizability

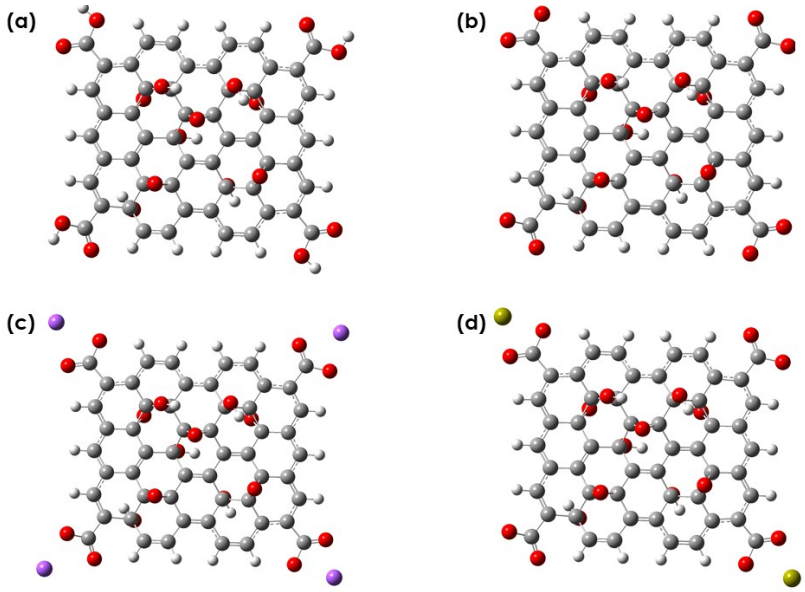

Fig. S1. Models of GOs used for LOLIPOP index and polarizability calculations under different conditions. (a) GO with all carboxyl groups protonated. (b) GO with all carboxyl groups deprotonated. (c) GO with all carboxyl groups deprotonated and the presence of Na^{+}. (d) GO with all carboxyl groups deprotonated and the presence of Ca^{2+}.

SI 2.2 System setup for the interaction between GO and water

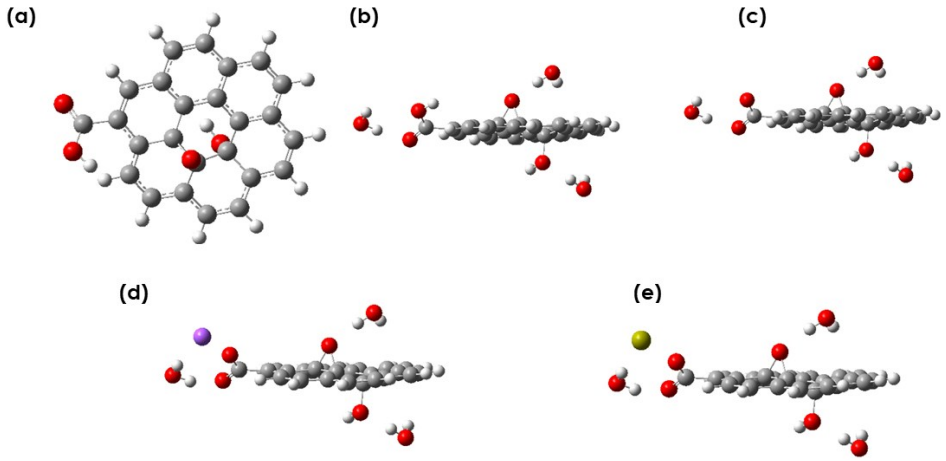

Fig. S2. (a)Basic model of GO used for the calculation of the interaction between GO and water. (b) Interaction between water and GO with carboxyl group protonated. (c) Interaction between water and GO with carboxyl group deprotonated. (d) Interaction between water and GO with carboxyl group deprotonated and the presence of Na^{+}. (e) Interaction between water and GO with carboxyl group deprotonated and the presence of Ca^{2+}.

SI 2.3 System setup for the H-bond interaction between GO

Simplified models of GO which only contain the relevant functional groups were used. The initial setup was similar for each system, and we didn't list all the figures for the setups.

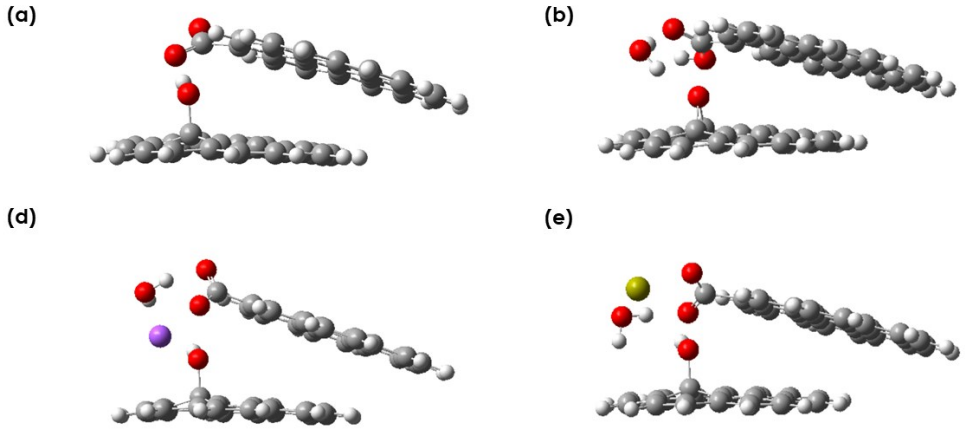

Fig. S3. (a) Direct H-bond between hydroxy and deprotonated carboxyl. (b) Water-bridged H-bond between epoxy and protonated carboxyl. (c) Water-bridged H-bond between hydroxy and deprotonated carboxyl with the presence of Na^{+}. (d) Water-bridged H-bond between hydroxy and deprotonated carboxyl with the presence of Ca^{2+}.

SI 2.4 System setup for the detailed edge-to-edge interaction

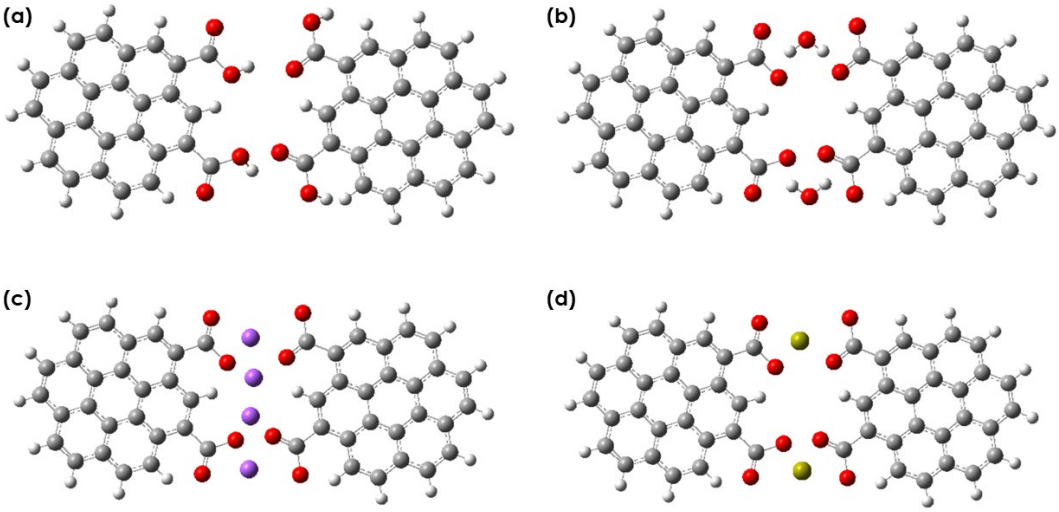

Fig. S4. (a) Edge-to-edge interaction facilitated by direct H-bond interaction between protonated carboxyl groups. (b) Edge-to-edge interaction facilitated by water-bridged H-bond interaction between deprotonated carboxyl groups and water molecules. (c) Edge-to-edge interaction facilitated by chelating between deprotonated carboxyl groups and Na^{+}. (d) Edge-to-edge interaction facilitated by chelating between deprotonated carboxyl groups and Ca^{2+}.

SI 3. AFM Characterizations of GO

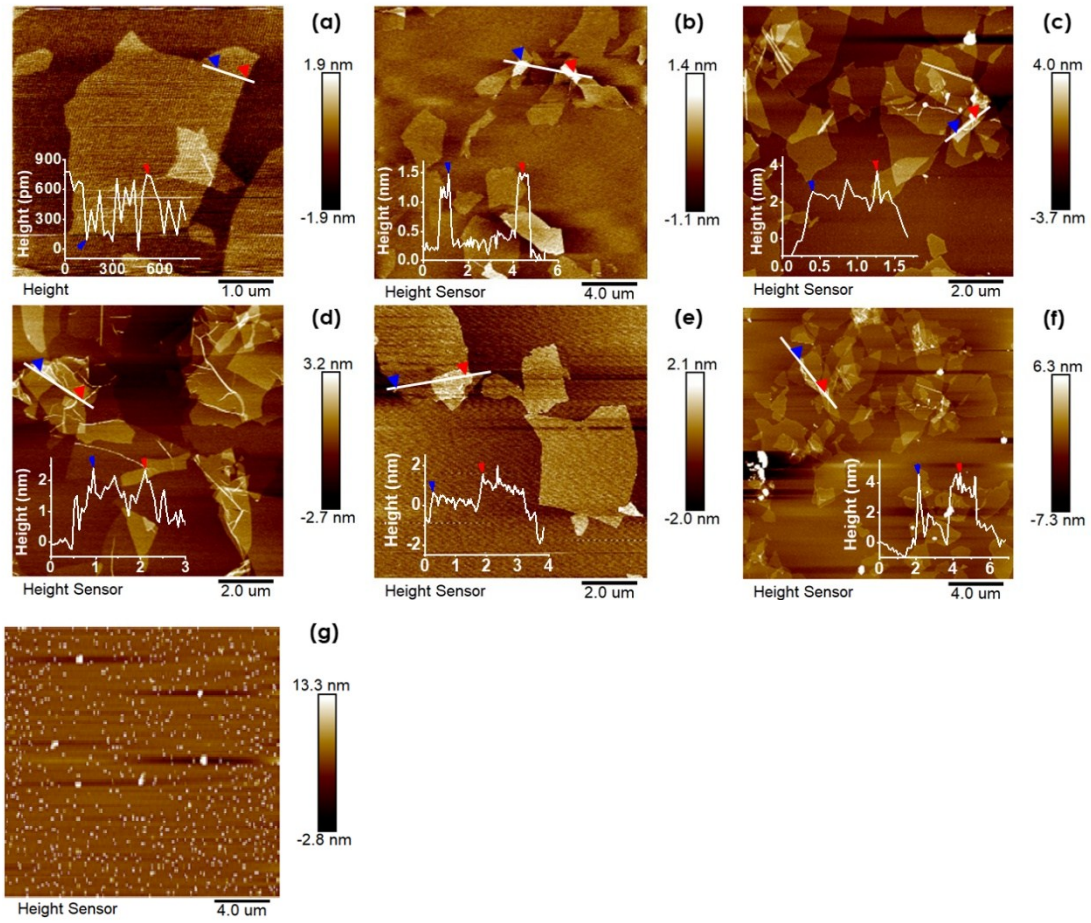

Fig. S5. (a) Thickness of GO palate. (b) Aggregation of GO at ~pH 6 with no metal ions. (c) Aggregation of GO at pH ~6 with 60 mM NaCl. (d) Aggregation of GO at pH ~9 with 60 mM NaCl. (e) Edge-to-Edge and partial face-to-face aggregation of GOs at pH ~9 with 1 mM $CaCl_2$. (f) Aggregation of GOs at pH ~6 with 5 mM $CaCl_2$. (g) Aggregation of GOs at pH ~6 with 200 mM NaCl.

AFM results of pH 6 with 5 mM $CaCl_2$ (Fig. S5(f)) agrees well with the MD results. However, when 200 mM NaCl (Fig. S5(f)) was added, AFM image is full of metal crystals and the GO flakes were hard to distinguish.

SI 4. MD Results of the Aggregation of GO

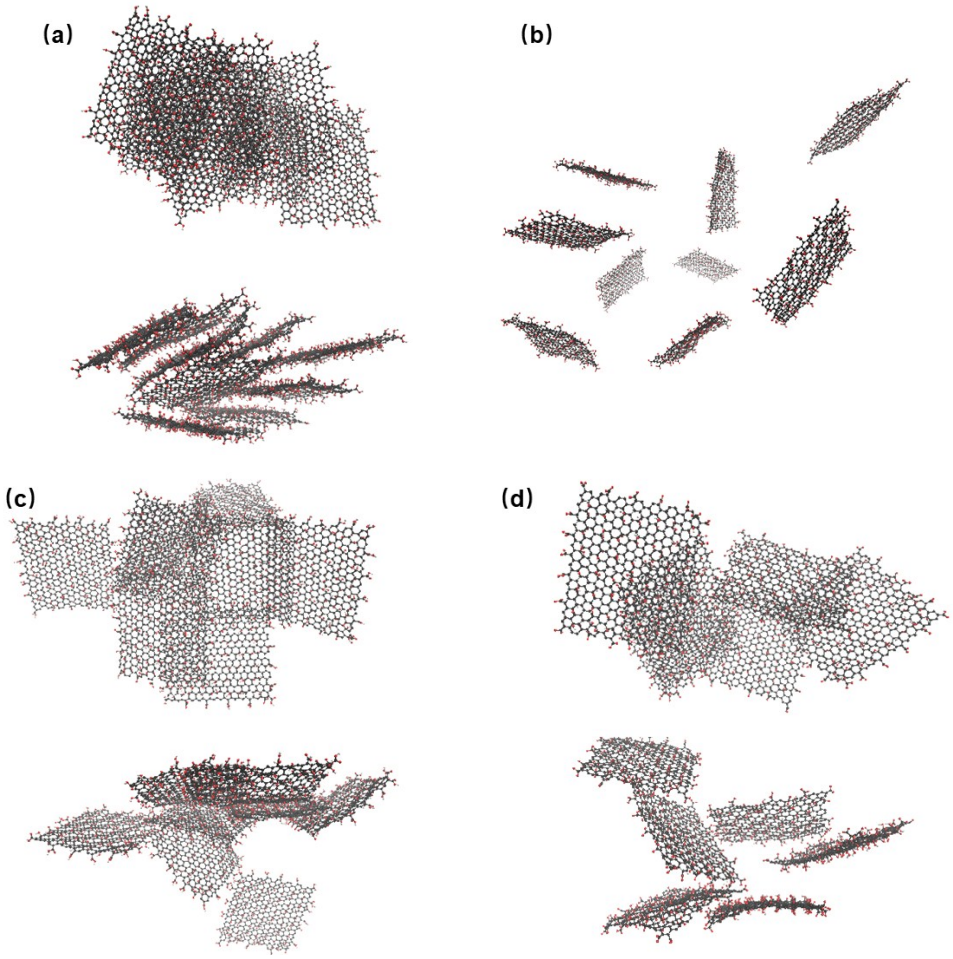

Fig. S6. Aggregation of GO under different aqueous chemistries. (a) pH ~3, (b) pH ~ 6 and no metal cations were added, (c) pH ~6 with 1 mM $CaCl_2$, (d) pH ~9 with 1 mM $CaCl_2$.

SI 5. Simulation Results of the Aggregate Morphology.

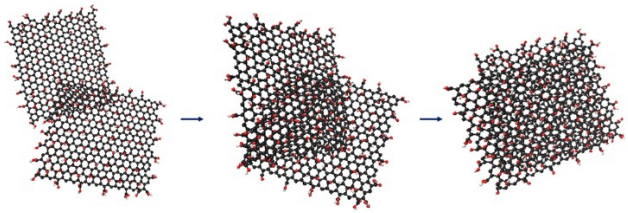

Fig. S7. The "bind and adjust" two-step process to obtain the face-to-face aggregation

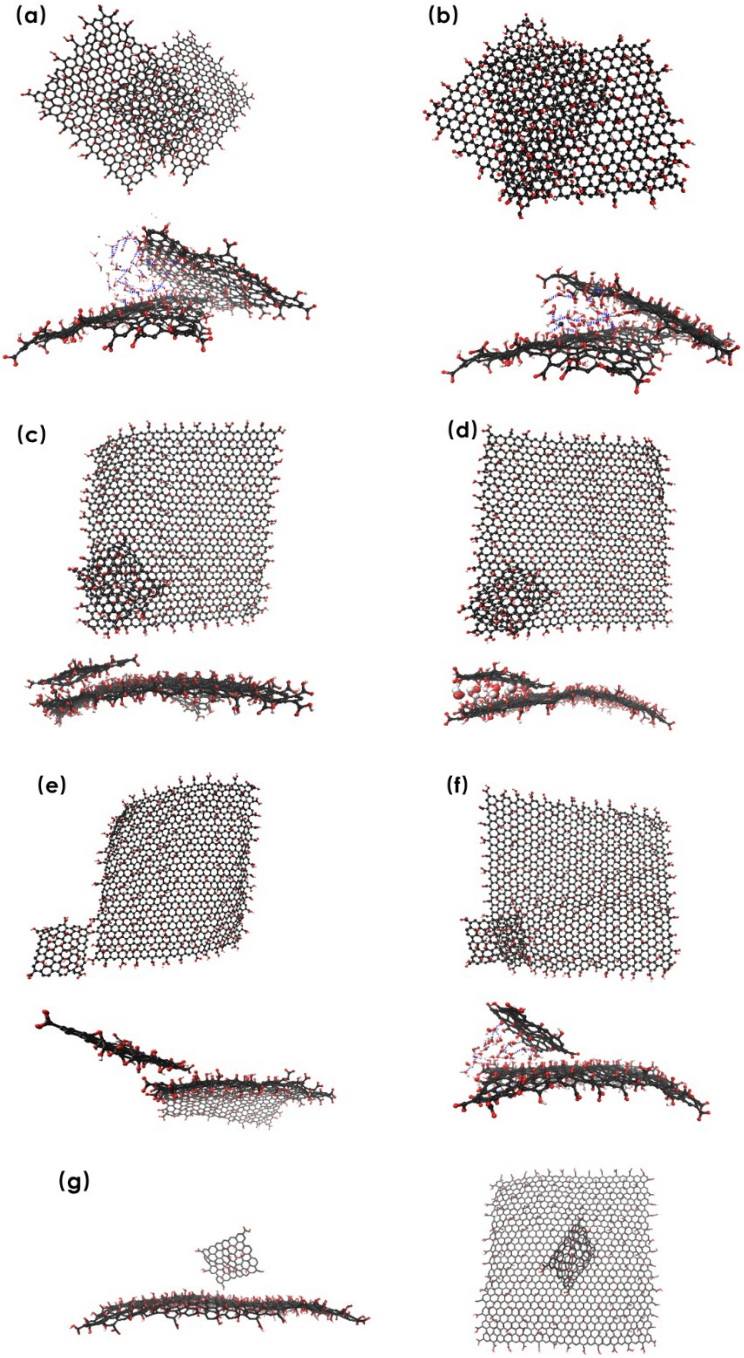

Fig. S8. (a) Partial face-to-face aggregation of GO at pH ~6 and 1 mM $CaCl_2$. (b) Partial face-to-face aggregation of GO at pH ~6 and 5 mM $CaCl_2$. (c) Face-to-face aggregation of GO with contrasting size

at pH ~6 and 1 mM $CaCl_2$. (d) Partial face-to-face aggregation of GO with contrasting size at pH ~6 and 1 mM $CaCl_2$. (e) Edge-to-edge aggregation of GO with contrasting size at pH ~9 and 1 mM $CaCl_2$. (f) Partial face-to-face aggregation of GO with contrasting size at pH ~9 and 1 mM $CaCl_2$. (g) Point-to-point aggregation of GO occurred on the basal plane at pH ~9 and 1 mM $CaCl_2$.

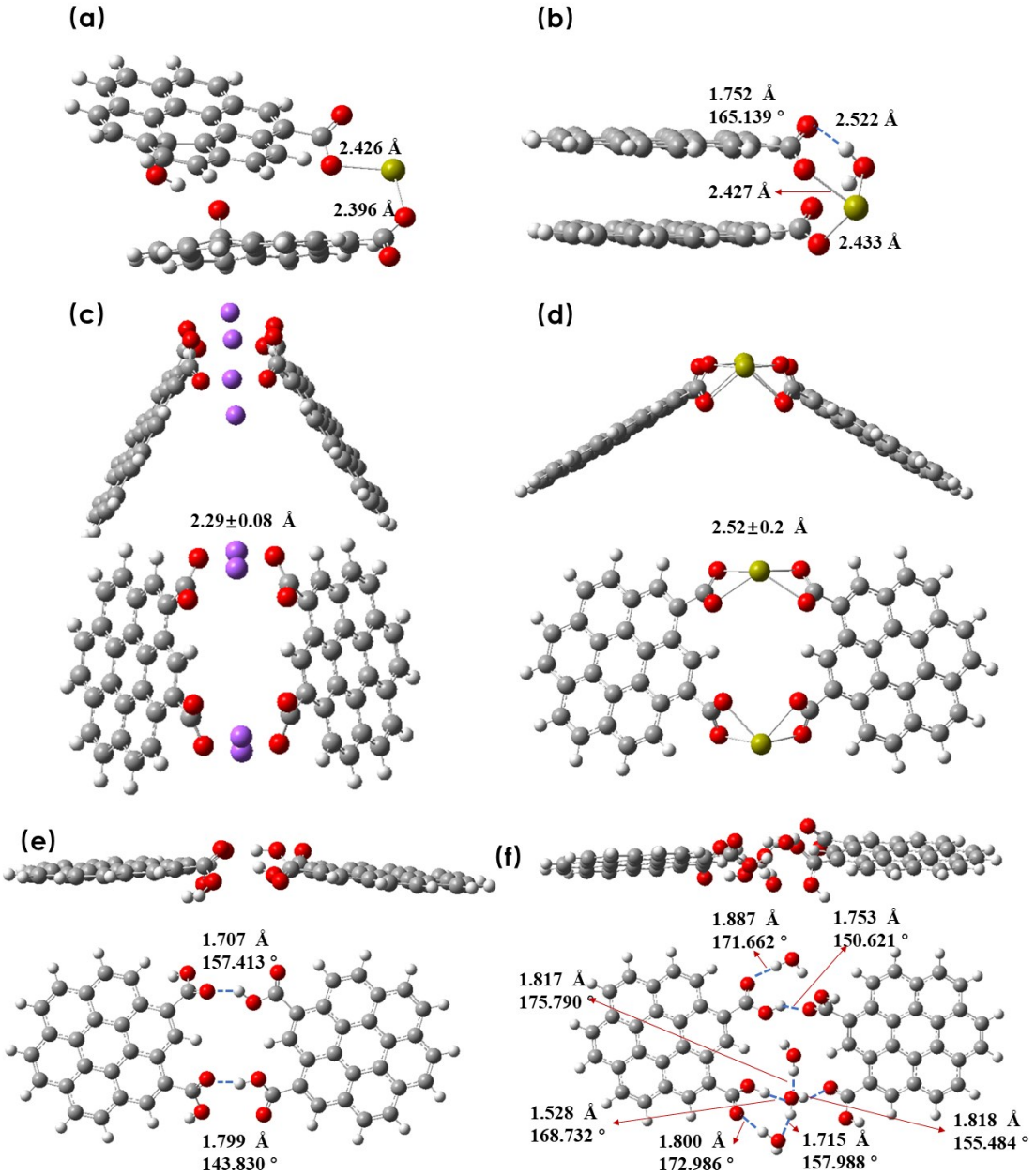

Fig. S9. Ca^{2+}-facilitated interactions in the face-to-face or partial face-to-face aggregation (a)(b). Edge-to-edge aggregation maintained by chelating interaction between carboxyl groups and Na^{+}(c) or Ca^{2+}(d). Edge-to-edge aggregation maintained by direct (e) or water-bridge H-bond (f) between carboxyl groups.

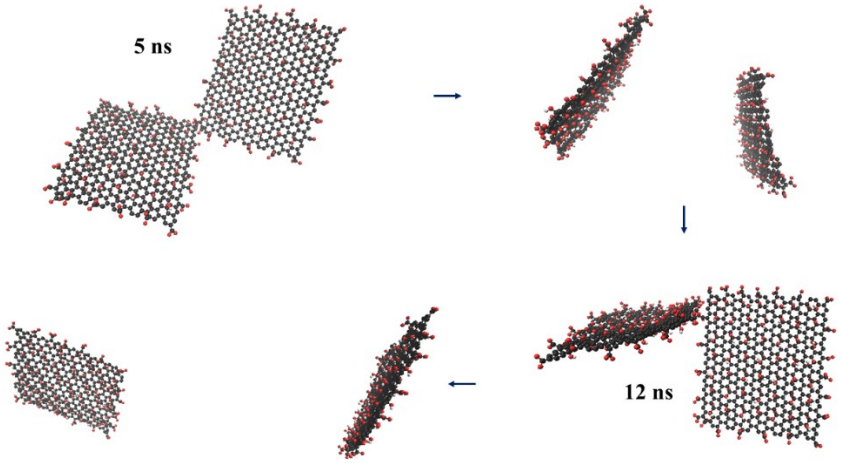

Fig. S10. Representative snapshots during the point-to-point aggregation of GO.

At 5 ns, two GOs aggregated and then dispersed in water; at 12 ns, two GOs aggregated again and shortly after dispersed in water.

SI 6. Polarizability of GO

Table S1. Effect of pH and coordination with metal ions on the polarizability of GO (a.u.).

	deprotonated GO	protonated GO	deprotonated GO with Ca^{2+}	deprotonated GO with Na^{+}
polarizability	226.186	291.8026	385.235	288.528

SI 7. DFT results of the H-bond Interaction

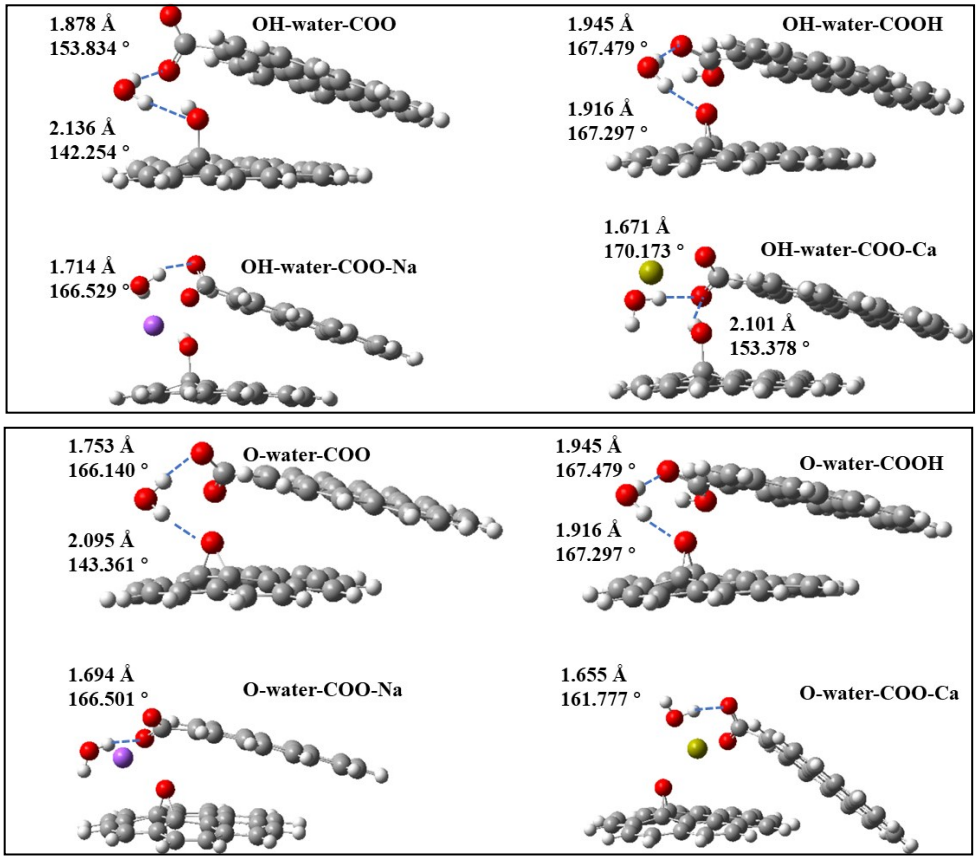

Fig. S11. Details of the direct and water-bridged H-bond formed during the aggregation of GO.

REFERENCES

1. Kovtyukhova, N. I.; Ollivier, P. J.; Martin, B. R.; Mallouk, T. E.; Chizhik, S. A.; Buzaneva, E. V.; Gorchinskiy, A. D., Layer-by-layer assembly of ultrathin composite films from micron-sized graphite oxide sheets and polycations. *Chem Mater* **1999,** *11*, (3), 771-778.