Electronic Supplementary Information for: Probing the influence of different oxygenated groups on graphene oxide's catalytic performance

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Experimental section

Synthesis of HGO

The GO sample was prepared as before. Then 20 ml deionized water was added into 2 ml GO slurry, after 30 minutes strong sonication, this solution was transferred into a Teflon-lined stainless autoclave with a volume of 30 ml and heated at 120℃ in an oven for one day. After cooling down to room temperature in nature, it was sonicated completely for catalytic test.

Synthesis of HGO-NaOH

2 g NaOH was dissolved in 4 ml deionized water, then 1 ml NaOH solution was picked out and added into 0.3 ml HGO solution. The obtained solution was heated at 80℃ for 1 hours, then it was washed with deionized water for three times to remove NaOH.

Catalytic reaction

50 mg $NaBH_4$ was dissolved in 25 ml deionized water first. Then 6 ml deionized water, 0.5 ml Nip (1 mM) and 2 ml $NaBH_4$ solution were mixed with their molar ration of 1:200. After for a while, we took out 3 ml solution and added 0.3 ml HGO (0.16 mg) for UV-vis absorbance spectroscope characterization.

Simulation

All of the calculations are completed on the Gaussian 09 software suit. The model of graphene discussed here contained 42 carbon and 16 hydrogen atoms, which was taken from Sidik's structure and has been used well in our previous work. The functional and basis set are B3LYP and 6-31G*, respectively, supplementing polarization functions to C, H, N and O atoms. All calculations are performed with a (75, 302) pruned grid, and there are no imaginary frequencies for all of these optimized groundstate structures, indicating they are all stable and reasonable. The adsorption energy is calculated as: $E_{ads} = E_{system} - E_{graphene} - E_{Nip}$, where E_{system}, $E_{graphene}$ and E_{Nip} are the total energies of Nip ion on graphene, free graphene and the isolated Nip ion, respectively. A more negative E_{ads} demonstrates that the interacting Nip-graphene is more stable.

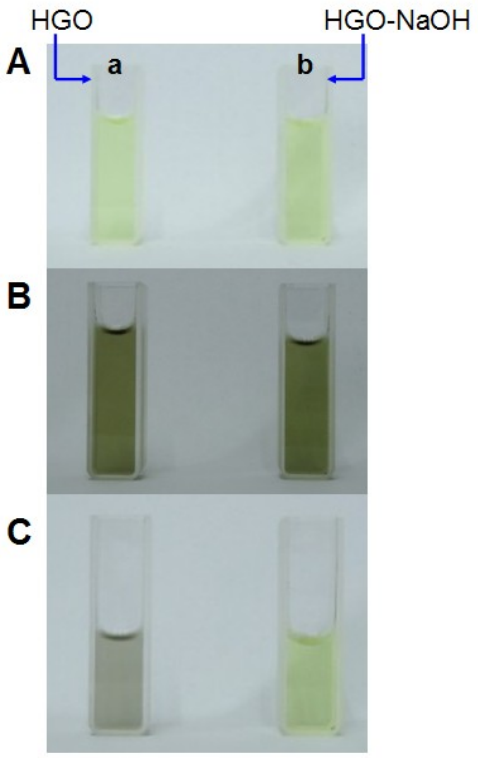

Fig. S1 The optical photos of the color change during the reaction for HGO (sample a) and HGO-NaOH (sample b). (A) The mixture of Nip and $NaBH_4$ solution with their mole ratio of 1: 200 before the catalytic reaction was carried out. (B) The catalysts were added. (C) The catalytic process has been carried out for half an hour to make sure the catalytic reaction was totally completed, and the catalysts were separated leaving the supernatant in the cuvettes. HGO-NaOH was centrifugated at 10000 rpm for 5 mins, while HGO was separated by filtration using PVDF membrane with pore size of 0.22 um because of its good solubility.

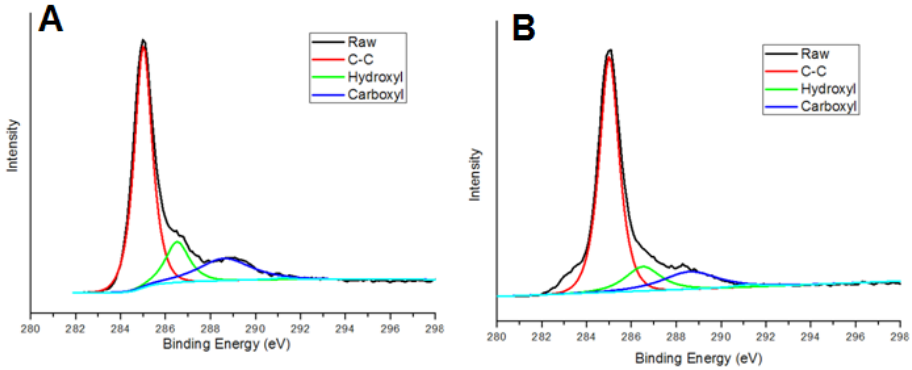

Fig. S2 XPS spectra of the prepared (A) HGO and (B) HGO-NaOH. The original XPS data was analyzed by a XPS peak software. The hydroxyl signal (green line) decreased obviously after the NaOH treatment. The small deviation between 282 and 284 eV of sample B might be due to the influence of the residual Na KLL. It didn't affect the analysis of hydroxyl groups.

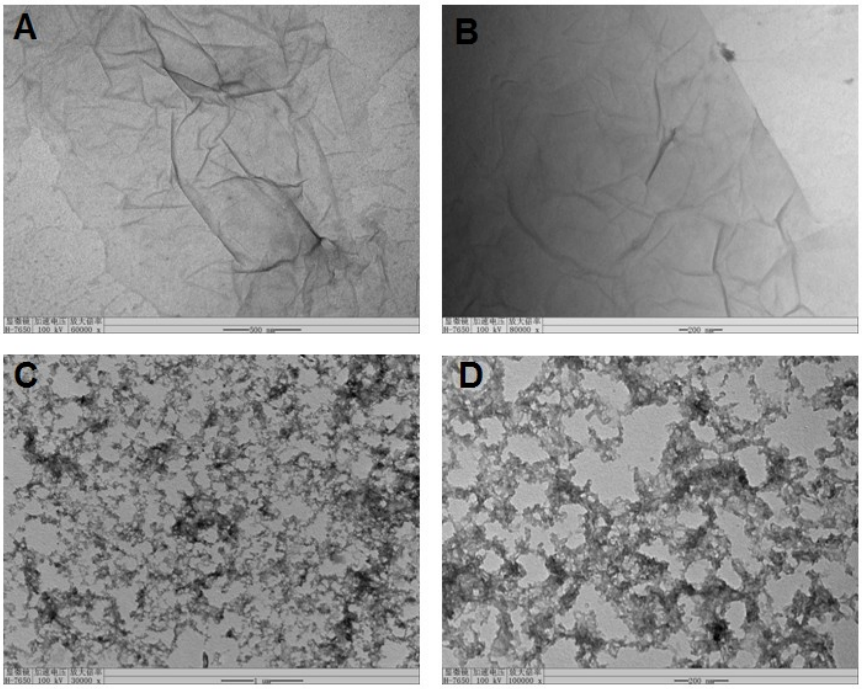

Fig. S3 TEM images of the prepared (A, B) GO and (C, D) HGO.

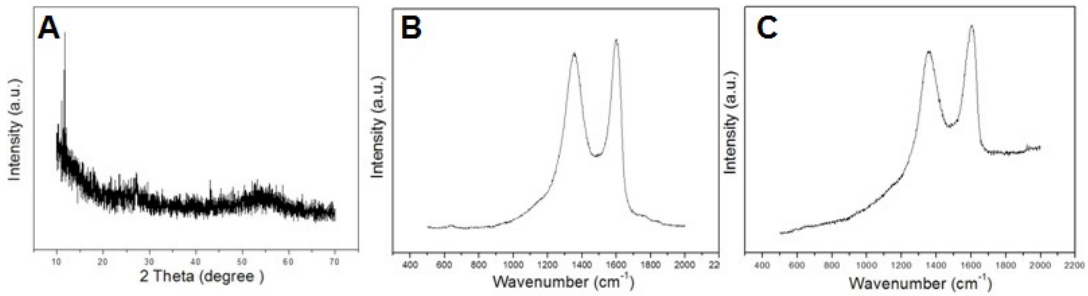

Fig. S4 (A) XRD pattern of HGO, (B) Raman spectrum of HGO and (C) Raman spectrum of GO. The Raman spectra were obtained with the incident wavelength of 514 nm.

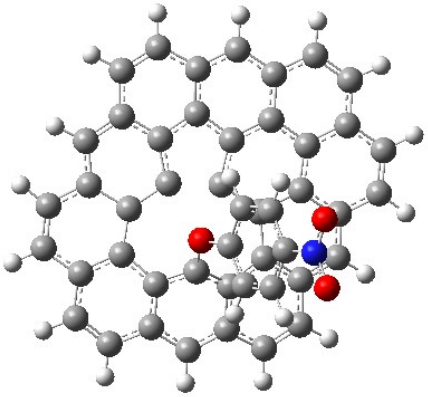

Fig. S5 The optimized structure of one Nip ion adsorbed on the mono-vacancy graphene in top view.

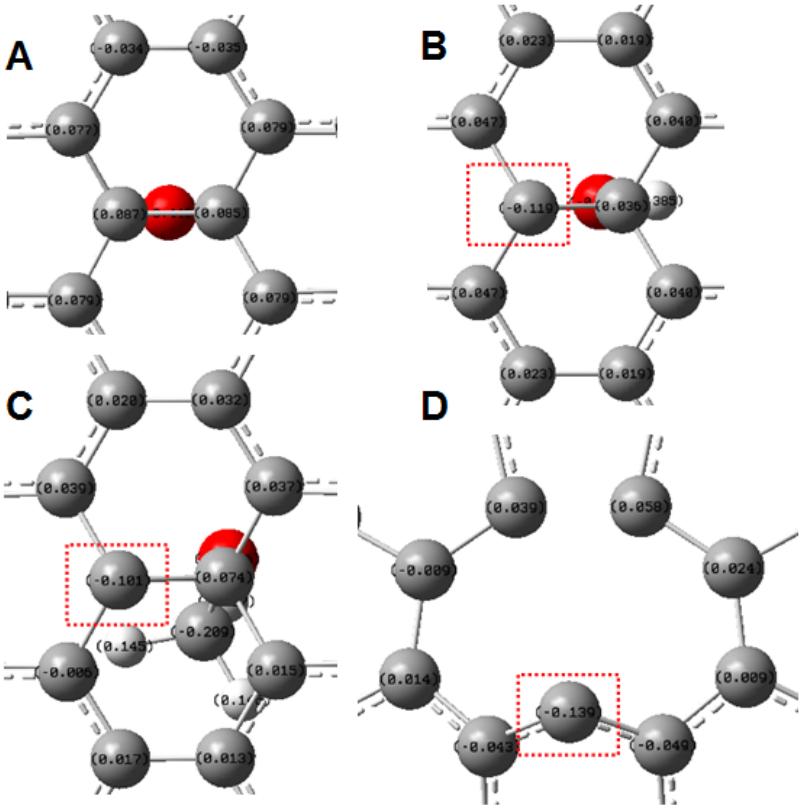

Fig. S6 The calculated Mulliken charge density distributions for (A) epoxy attached graphene, (B) hydroxyl attached graphene, (C) alkoxy attached graphene and (D) graphene with a mono-vacancy hole. The local high charge densities at the active sites have been marked directly.

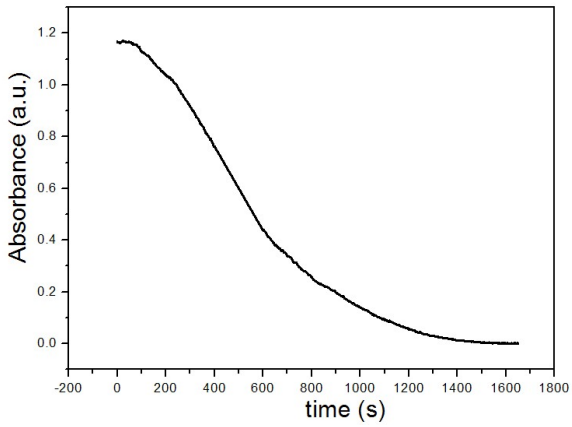

Fig. S7 The measured typical time curve of the absorbance at 400 nm for the HGO catalyst.

Model	Nip E_{ads} (Hartree)	d (Å)	Amp E_{ads} (Hartree)
pristine graphene	-0.0022	3.05	
epoxy attached graphene	-0.0028	2.83	
carboxyl attached graphene	-0.0050	3.31	
hydroxyl attached graphene	-0.0692	1.49	-0.0504
alkoxy attached graphene	-0.0645	1.50	-0.0456
graphene with a mono-vacancy hole	-0.1246	1.38	-0.1059

Table S1 The calculated adsorption energies and separated distances of Nip ions combined with different graphene models, and the adsorption energies of Amp ions on the three good substrates.