Supporting information

DFT investigation of NiO@Graphene composite as urea oxidation catalyst in alkaline electrolyte

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Number of Figure: 5

Number of Table: 2

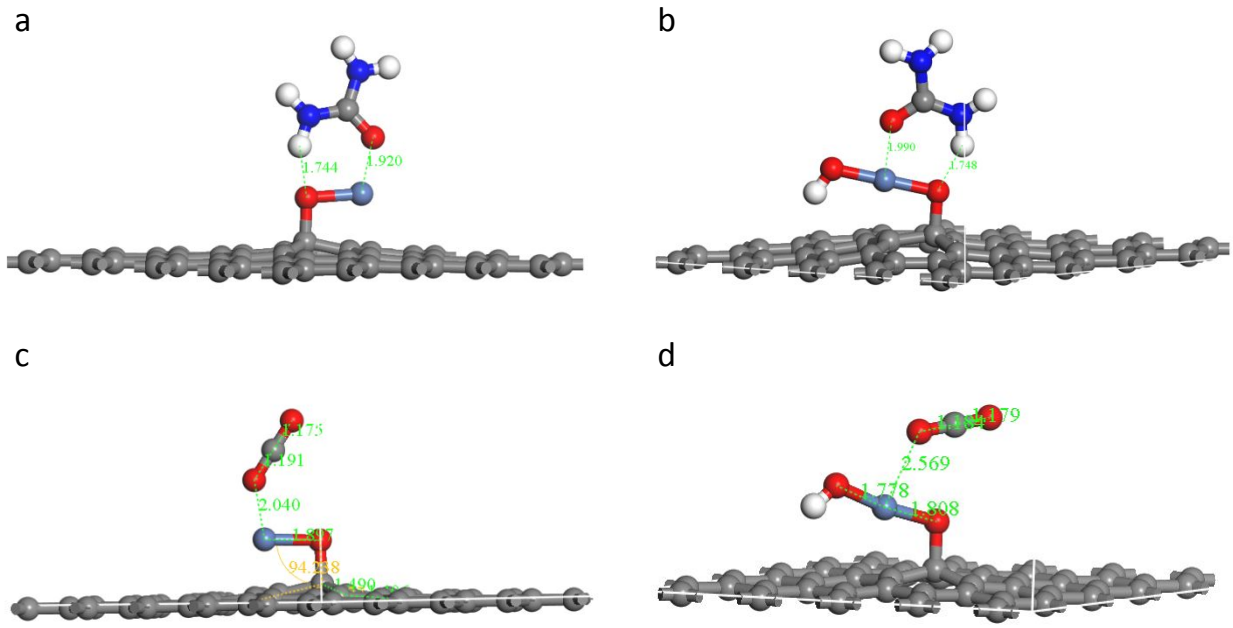

Figure S1. The shortest distance between urea and (a) NiO@Graphene, (b) NiOOH@Graphene, and (c) CO_2 and NiO@Graphene, (d) NiOOH@Graphene.

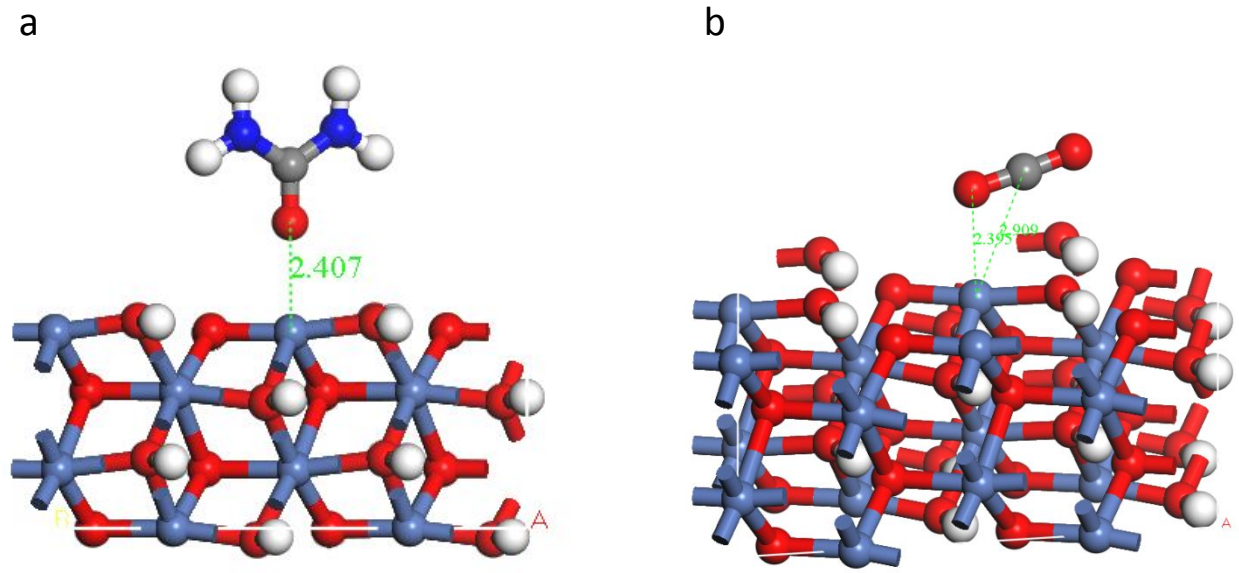

Figure S2. The shortest distance between (a) urea, (b) CO_2 and NiOOH.

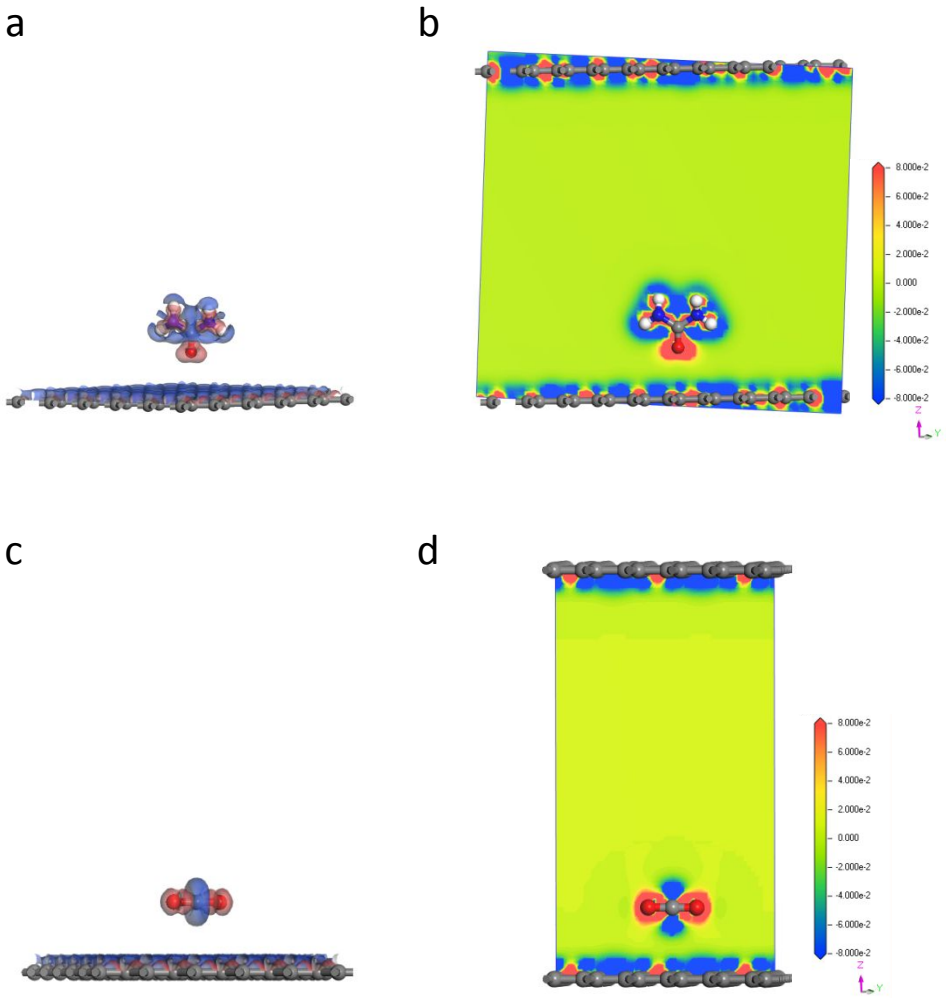

Figure S3. (a) The electron density difference of urea molecule adsorbed on the surface of Graphene. (b) Slice image of the adsorption of urea molecule on the surface of Graphene. (c) The electron density difference of CO_2 molecule adsorbed on the surface of Graphene. (b) Slice image of the adsorption of CO_2 molecule on the surface of Graphene. Note: (a, c) The red hooded face means enrichment of electrons while the blue means the deficiency of elections, (b, d) The contour around the atoms represents electron accumulation (red) or electron deletion (blue).

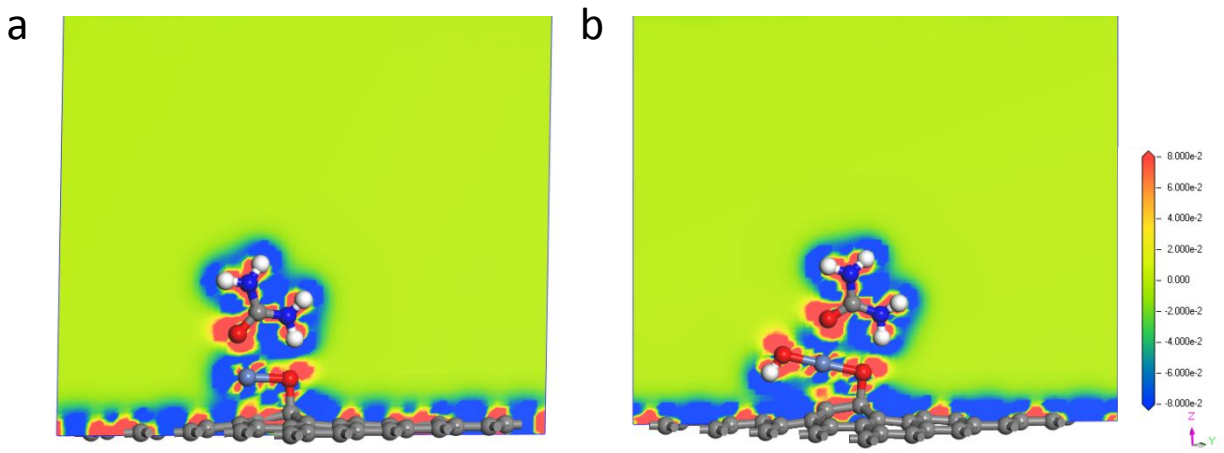

Figure S4. Slice images of the adsorption of urea molecule on the surface of (a) NiO@Graphene and (b) NiOOH@Graphene and the corresponding slice of the electron density difference. The contour around the atoms represents electron accumulation (red) or electron deletion (blue).

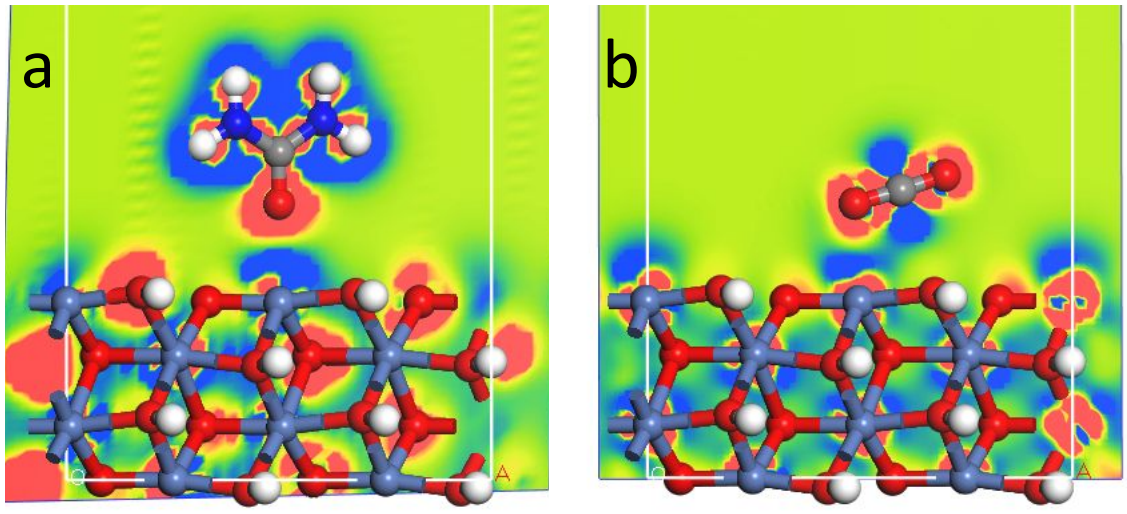

Figure S5. Slice images of the adsorption of (a) urea and (b) CO_2 molecule on the surface of NiOOH. The contour around the atoms represents electron accumulation (red) or electron deletion (blue).

Table S1 Gibbs energies (ΔG) for the possible steps on M (M = NiOOH).[1]

Reactions	ΔG/kJ mol^{-1}
$CO(NH_2)_2 + M \rightarrow [M{\cdot}CO(NH_2)_2]_{ads}$	66.2
$[M{\cdot}CO(NH_2)_2]_{ads} + OH^- \rightarrow [M{\cdot}CO(NH_2{\cdot}NH)]_{ads} + H_2O + e^-$	-28.9
$[M{\cdot}CO(NH_2{\cdot}NH)]_{ads} + OH^- \rightarrow [M{\cdot}CO(NH_2{\cdot}N)]_{ads} + H_2O + e^-$	-185.1
$[M{\cdot}CO(NH_2{\cdot}N)]_{ads} + OH^- \rightarrow [M{\cdot}CO(NH{\cdot}N)]_{ads} + H_2O + e^-$	75.4
$[M{\cdot}CO(NH{\cdot}N)]_{ads} + OH^- \rightarrow [M{\cdot}CO(N{\cdot}N)]_{ads} + H_2O + e^-$	-178.2
$[M{\cdot}CO(N{\cdot}N)]_{ads} + OH^- \rightarrow [M{\cdot}CO{\cdot}OH)]_{ads} + N_2 + e^-$	392.7
$[M{\cdot}CO{\cdot}OH)]_{ads} + OH^- \rightarrow [M{\cdot}CO_2)]_{ads} + H_2O + e^-$	-156.6
$[M{\cdot}CO_2)]_{ads} \rightarrow M + CO_2$	1242.2
Total	1227.7

Table S2 The optimized energy for the adsorption of CO_2 and urea on the surface of NiO@Graphene and NiOOH@Graphene, respectively, based on our model.

Species	Optimized energy/eV
CO_2	-1028.03939
Urea	-2077.79804
NiO@Graphene	-9540.52016
NiOOH@Graphene	-9994.29777

Reference

1. Daramola, D. A.; Singh, D.; Botte, G. G., Dissociation rates of urea in the presence of NiOOH catalyst: a DFT analysis. *J. Phys. Chem. A* **2010,** *114* (43), 11513-11521.