Supporting Information

Self-Limiting Growth of Single-Layer N-Doped Graphene Encapsulating Nickel Nanoparticles for Efficient Hydrogen Production

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Scheme S1. Schematic illustration of graphene growth on Ni nanoparticles (a) and on SiO₂imbedded Ni nanoparticles (b), respectively.



Figure S1. SEM images of (a, b) SiO₂ particles, (c, d) nickel silicate and (e, f) SiO₂-Ni.



Figure S2. XRD spectra of SiO₂, nickel silicate, SiO₂-Ni, SiO₂-Ni@SG-800, and SiO₂-Ni@SNG-800.



Figure S3. TEM images of (a) SiO₂-Ni and (b) the magnified area from the red box of (a).



Figure S4. TEM images of (a-c) SiO₂-Ni@SG at different magnifications.



Figure S5. The ultra-high resolution TEM image (a), element mapping images of Ni@SNG-800 etched for 6 h in 1.0 M HCl (b-e), and the selected area electron diffraction of Ni (f).



Figure S6. Element mapping images of Ni@SNG-800 (a-d) and contents of Ni, C and N in the in the yellow square area (e).



Figure S7. Raman spectra of Ni@SNG-800, Ni@SNG-700, Ni@SNG-600, and Ni@SG-800.



Figure S8. High-resolution Ni 2p XPS spectra of (a) Ni@SNG-800, (b) Ni@SNG-700, (c) Ni@SNG-600 and (d) Ni@SG-800.

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Figure S9. HER polarization curves of Ni@SG and Ni@SNG samples with baseline correction.



Figure S10. High-resolution TEM image of Ni@SNG-800 after 1000 CV cycles.

 Table S1. Resistances in the EIS equivalent circuit (see Fig. 5) analyzed through Zview software (Scribner Associates Inc.).

Samples	Rs (Ω)	R1(Ω)	R2(Ω)
Ni@SNG-800//Ni foil (M)	0.62	8.60	0.82
Ni@SNG-800//Ni foil (Nafion)	0.57	9.49	5.49



Figure S11. The HER performances of Ni@SNG-800, Ni@SNG-800 treated with 1.0 M HCl for 6 h and Ni@SG-800.



Figure S12. (a) Electronic interaction on graphene/nickel interface, (b) Differential charge density distribution shows dipolar layer model of graphene/nickel interface. Green and grey represents Ni and C atoms, respectively; Blue and yellow colors represent lose and gain of charge, respectively.

DFT computational details

All the density functional theory (DFT) calculations were performed by Vienna Ab-initio Simulation Package (VASP),^{1,2} employing the Projected Augmented Wave(PAW) method.³ The revised Perdew-Burke-Ernzerhof (RPBE) functional was used to describe the exchange and correlation effects.⁴⁻⁶ The van der Waals interactions were described using the empirical correction in Grimme's scheme. The surface models were constructed by using a 3×3 supercell, with single layer graphene or nitrogen-doped graphene on the (111) surface of Ni. For all the geometry optimizations, the cutoff energy was set to be 500 eV. A $3\times3\times1$ Monkhorst-Pack grid was used to carry out the surface calculations on all the models.⁷ At least a 20 Å vacuum layer was applied in *z*-direction of the slab models, preventing the vertical interactions between slabs. The convergence criterions of energy and force calculations were set to 10^{-5} eV/atom and 0.01 eV Å⁻¹, respectively. For charge density difference calculation of graphene/Ni(111) interface, the lattice constants of the Ni (111) unit cell are much closed to those of graphene, so the graphene/Ni (111) interface model was directly built without any operation of expanding supercell. The calculated Ni-C bond length of the graphene/Ni (111) interface system is 2.14 Å, which is fully consistent with the previous result of 2.13 Å.⁸

The computational hydrogen electrode (CHE) model was used to calculate the free energies of HER,⁹ and the free energy of an adsorbed species is defined as

$$\Delta \mathbf{G}_{ads} = \Delta \mathbf{E}_{ads} + \Delta \mathbf{E}_{ZPE} - \mathbf{T} \Delta \mathbf{S}_{ads}$$

where ΔE_{ads} is the binding energy for H*, OH* and H* + OH* species, ΔE_{ZPE} is the zero-point energy difference between adsorbed and gaseous species, and $T\Delta S_{ads}$ is the corresponding entropy difference between these two states.

The H* binding energy was calculated by $\Delta E_{H*} = E_{slab+H*} - E_{slab} - 1/2E_{H2}$ The OH* binding energy was calculated by $\Delta E_{OH*} = E_{slab+OH*} - E_{slab} - E_{H2O} + 1/2E_{H2}$ The (H*+OH*) binding energy was calculated by $\Delta E_{H*+OH*} = E_{slab+H*+OH*} - E_{slab} - E_{H2O}$ where $E_{slab+H^*+OH^*}$, E_{slab+H^*} , $E_{slab+OH^*}$, E_{slab} , E_{H2} , E_{H2O} , is the total energy of slab with adsorbed H and OH radicals, the total energy of slab with an adsorbed H atom, the total energy of slab with an adsorbed OH radical, energy of slab, energy of a gas H₂ molecule, energy of an isolated water molecule, respectively.

Species	ZPE(eV)	TS(eV)
*Н	0.16	0.01
*OH	0.31	0.01
H ₂ O	0.56	0.67
H ₂	0.27	0.41

Table S2. The correction of zero-point energy and entropy of the adsorbed and gaseous species.

References

- (1)Kresse, G.; Furthmüller, J. Efficient Iterative Schemes for Ab Initio Total-Energy Calculations Using a Plane-Wave Basis Set. *Phys. Rev.* B1996, 54, 11169–11186.
- (2)Kresse, G.; Hafner, J. Ab Initio Molecular-Dynamics Simulation of the Liquid-Metal-Amorphous-Semiconductor Transition in Germanium. *Phys. Rev.* **B1994**, *49*, 14251–14269.
- (3)Blöchl, P. E. Projector Augmented-Wave Method. Phys. Rev. B1994, 50, 17953–17979.
- (4)Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.***1996**, *77*, 3865–3868.
- (5)Zhang,Y.; Yang,W. Comment on "Generalized Gradient Approximation Made Simple". *Phys. Rev. Lett.***1998**, *80*, 890.
- (6)Hammer, B.; Hansen, L. B.; Nørskov, J. K. Improved Adsorption Energetics within Density-Functional Theory Using Revised Perdew-Burke-Ernzerhoffunctionals. *Phys. Rev.* B1999, 59, 7413–7421.
- (7)Monkhorst, H. J.; Pack, J. D. Special Points for Brillouin-Zone Integrations. *Phys. Rev. B* 1976, 13, 5188–5192...
- (8)Bertoni, G.; Calmels, L.; Altibelli, A.; Serin, V. First-Principles Calculation of the Electronic Structure and EELS Spectra at the Graphene/Ni(111) Interface. *Phy. Rev.* B2005, 71, 075402.
- (9)Nørskov, J. K.; Rossmeisl, J.; Logadottir, A.; Lindqvist, L.; Kitchin, J. R.; Bligaard, T.; Jónsson, H. Origin of the Overpotential for Oxygen Reduction at a Fuel-Cell Cathode. J. Phys. Chem. B2004, 108, 17886–17892.