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Hydrogen Assisted Synthesis of Branched Nickel Nanostructures: A Combined Theoretical and Experimental Study

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Supporting Information

Chemical Potential Calculation Method of Atomic H

In present work, the chemical potential of atomic H were calculated according the following equation, which was referenced from Res. S1

$$\begin{aligned}\mu_H(T,p^o) &= \mu_H^{H-rich}(0K,p^0)+1/2\Delta G(T,p^0,H_2)\\ &=1/2[H(T,p^0,H_2)-H(0K,p^0,H_2)]\\ &-1/2T[S(T,p^0,H_2)-S(0K,p^0,H_2)]\end{aligned} \tag{1}$$

where H was enthalpy; S was entropy of H_2 molecule at standard pressure p^0 and temperature of T. The thermodynamic data of H_2 were got from JANAF Thermochemical Table.[S2]

Based on the calculated $\mu_H(T,p^o)$ at standard pressure of 1 atm, it can also further calculated the H chemical potential at and pressure of p, according to the Eq. 2:

$$\mu_H(T,p)=\mu_H(T,p^o)+1/2kT\ln(p/p^0) \tag{2}$$

where k represent the Boltzmann constant. The calculated chemical potential of atomic H at T = 100-1200 K and P = 6 and 14 bar were listed in Table S1 and Table S2, respectively.

(S1) Reuter, K.; Scheffler, M. Composition, Structure, and Stability of RuO_2(110) as a function of oxygen pressure. Phys. Rev. B, 65, 035406.

(S2) Stull, D. R.; Prophet, H. JANAF Thermochemical Tables, 2nd ed. (U.S. National Bureau of Standards, Washington, DC, 1971).

Table S1. Various k-point grids used in bulk and surface slab structure calculations.

Model	*k*-point grid
Ni Bulk	10 x 10 x 10
Ni(111)-p(2x2)	4x4x1
Ni(100)-p(2x2)	3x4x1
Ni(111)-p(2x2)	4x4x1

Table S2. Adsorption energy (ΔE_{ads}) and magnetic moments data of atomic H adsorption on Ni(111), Ni(100), and Ni(110)

Ni facet	H site	H coverage / ML	Adsorption energy(ΔE_{ads}) / eV	Magnetic moment per Nickle / eV
Ni(111)	Fcc	0.25	-0.65	0.56
Ni(111)	Fcc	0.5	-1.22	0.53
Ni(111)	Fcc	0.75	-1.80	0.48
Ni(111)	Fcc	1	-2.37	0.45
Ni(111)	Fcc+Hcp	1.5	-1.58	0.21
Ni(100)	4F[a]	0.25	-0.59	0.59
Ni(100)	4F[a]	0.5	-1.19	0.56
Ni(100)	4F[a]	0.75	-1.79	0.51
Ni(100)	4F[a]	1	-2.39	0.48
Ni(100)	Br[b]	1.5	-1.68	0.47
Ni(100)	Br[b]	1.75	-1.61	0.44
Ni(100)	Br[b]	2.0	-1.46	0.49
Ni(110)	3F[c]	0.25	-0.46	0.65
Ni(110)	3F[c]	0.5	-0.970	0.63
Ni(110)	3F[c]	0.75	-1.37	0.64
Ni(110)	3F[c]	1	-1.84	0.61
Ni(110)	SB[d]	1.5	-2.67	0.55
Ni(110)	SB[d]	1.75	-2.98	0.50
Ni(110)	SB[d]	2.0	-3.43	0.48

[a] four fold site

[b] bridge site

[c] three fold site

[d] short bridge site

Table S3. Chemical potential of atomic H at P = 6 bar and T = 100-1200 K

T / K	$\mu_H(T,p)$ /eV	T / K	$\mu_H(T,p)$ / eV
100	-0.03	700	-0.41
200	-0.08	800	-0.48
300	-0.14	900	-0.56
400	-0.2	1000	-0.63
500	-0.26	1100	-0.71
600	-0.33	1200	-0.79

Table S4. Chemical potential of atomic H at P = 14 bar and T = 100-1200 K

T / K	$\mu_H(T,p)$ /eV	T / K	$\mu_H(T,p)$ / eV
100	-0.03	700	-0.38
200	-0.07	800	-0.45
300	-0.13	900	-0.52
400	-0.18	1000	-0.60
500	-0.25	1100	-0.67
600	-0.31	1200	-0.75

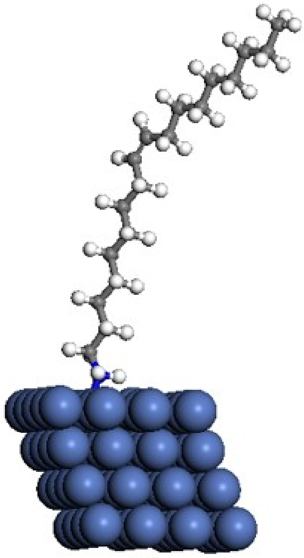
Table S5. The crystalline size of Ni samples estimated by Debye-Scherrer equation using Ni (111) diffractions

Sample	Crystalline Size[a] (nm)	Relative Crystallinity[b]
Ni-NP	59	96
Ni-SB	49	90
Ni-MP	60	93

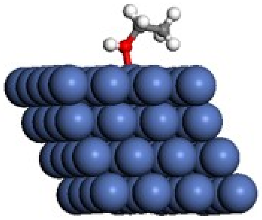
[a] measured by Debye-Scherrer equation

[b] with respect to (111) diffraction of standard Ni (PDF #01-0850)

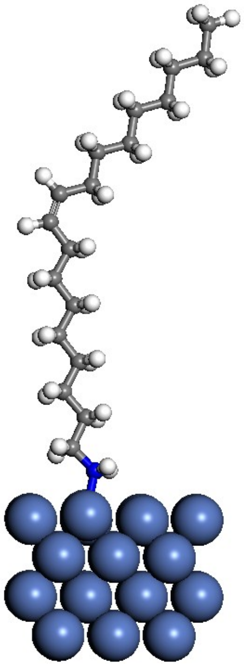
The crystalline size of Ni-MP and Ni-SB were calculated based on Ni (111) diffractions according to Debye-Scherrer equation. The calculation results were listed in table S4.



(a)



(b)



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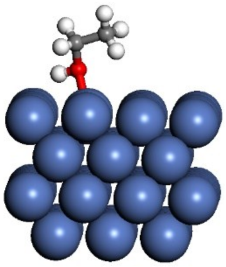
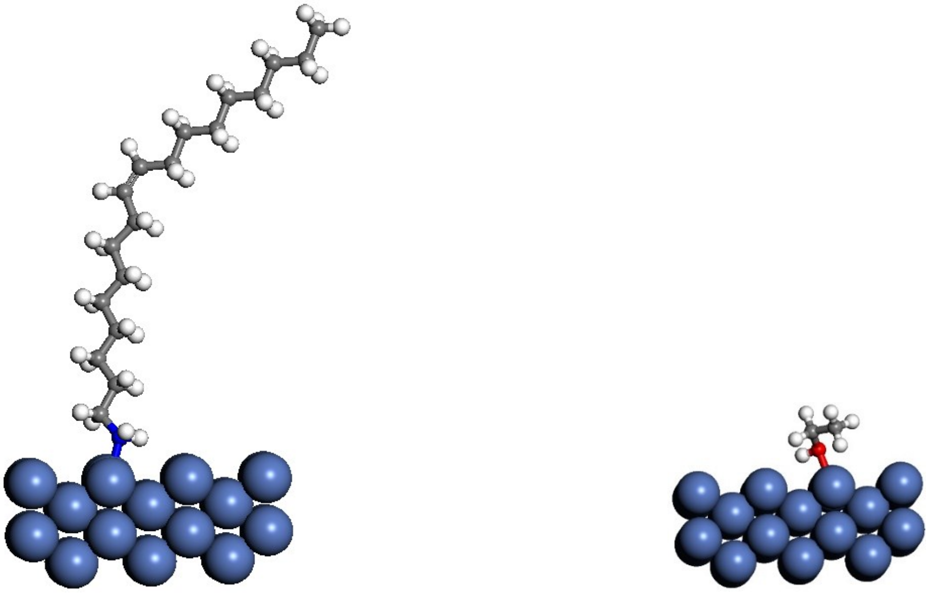
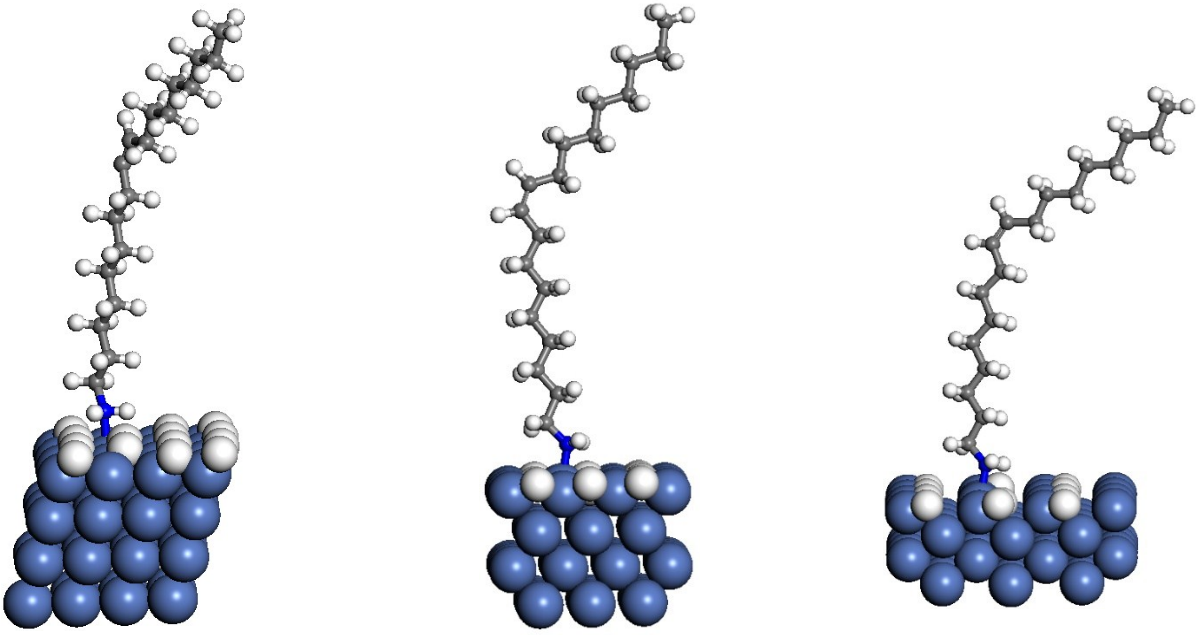


(d)



(e) (f)

Fig. S1 Optimized adsorption models of oleylamine and ethanol on Ni(111) (a, b), Ni(100) (c, d), and Ni(110) (e, f).



(a) (b) (c)

Fig. S2 Optimized adsorption models of oleylamine and atomic H coadsorption on Ni(111) (a), Ni(100) (b), and Ni(110) (c).

The total adsorption energies was respectively calculated to be -1.02 (Ni111), -0.61 (Ni100), and -0.95 eV (Ni110).

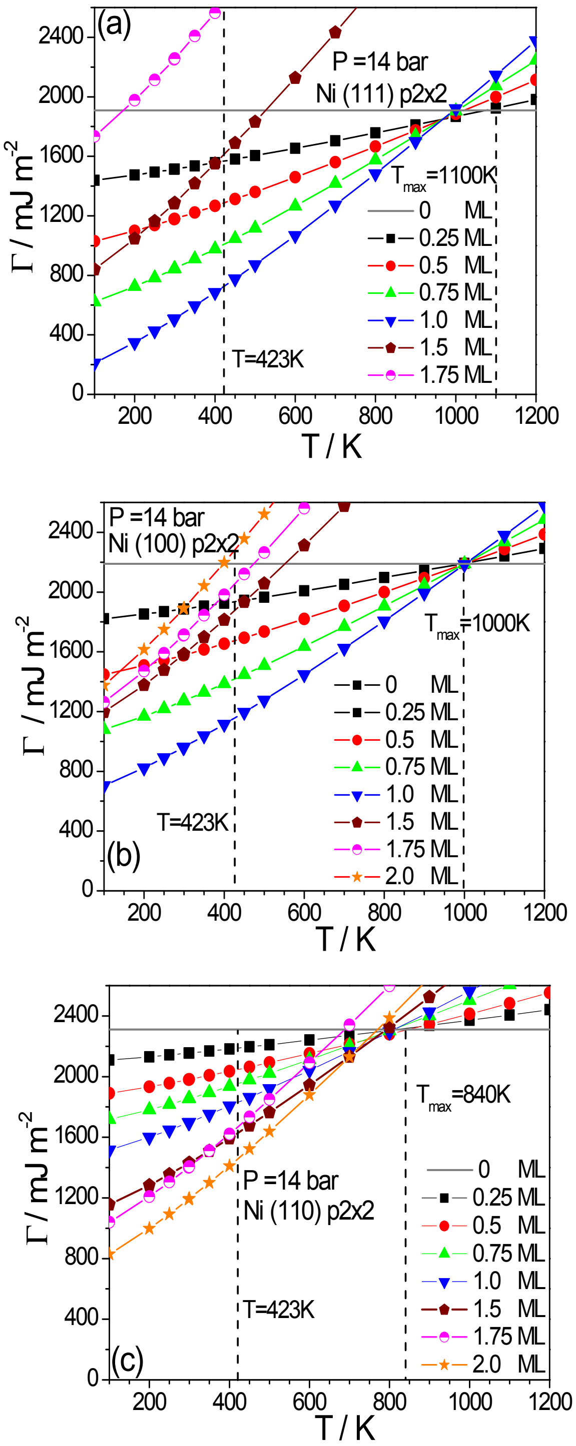


Fig. S3. Surface free energy of (a) Ni(111), (b) Ni(100), and (c) Ni(111)as a function of temperature for different H coverages (0, 0.25, 0.5, 0.75, 1.0, 1.5, 1.75, 2.0 ML) at P = 14 bar.

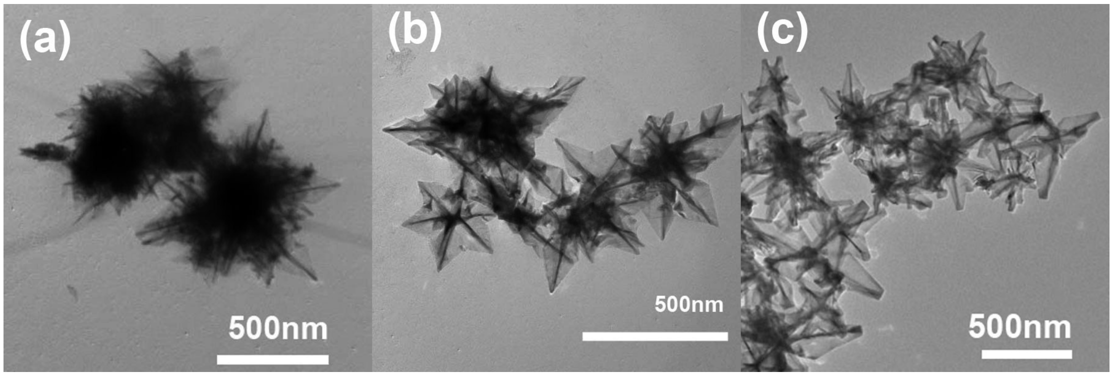


Fig. S4 TEM images of the intermediates of Ni-SB synthesized using different times: (a) 40 min; (b) 1.5 h; (c) 2.5 h

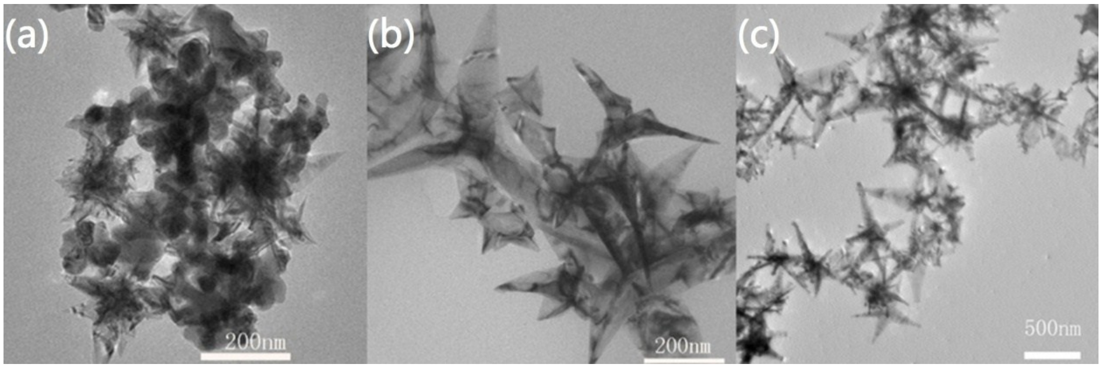


Fig. S5 TEM images of the intermediates of Ni-MP synthesized using different times: (a) 40 min; (b) 1.5 h; (c) 2.5 h

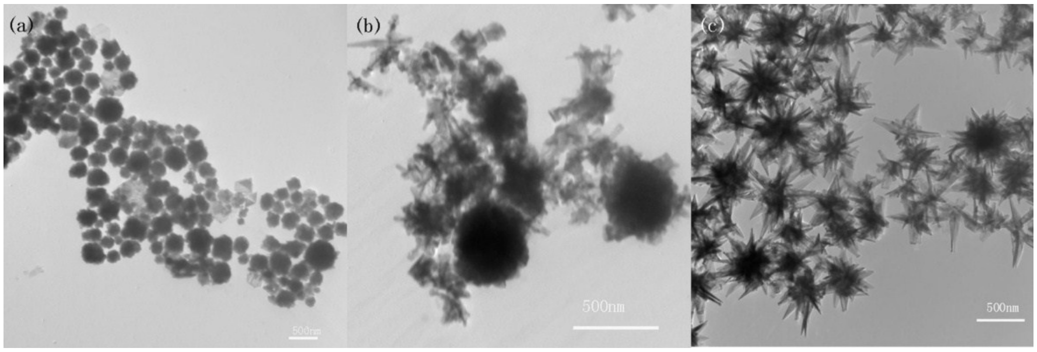


Fig. S6 Influencing of the magnetic stirring rate on the morphologies of the Ni-MP: (a) r=0 r/min (b) r = 200 r/min (c) r=400 r/min

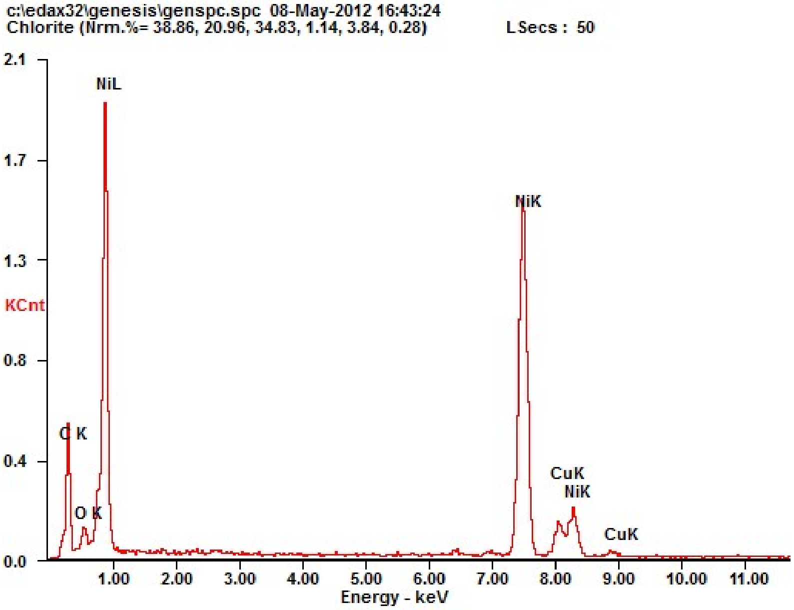


Fig. S7. EDS spectrum of Ni nanoparticles.

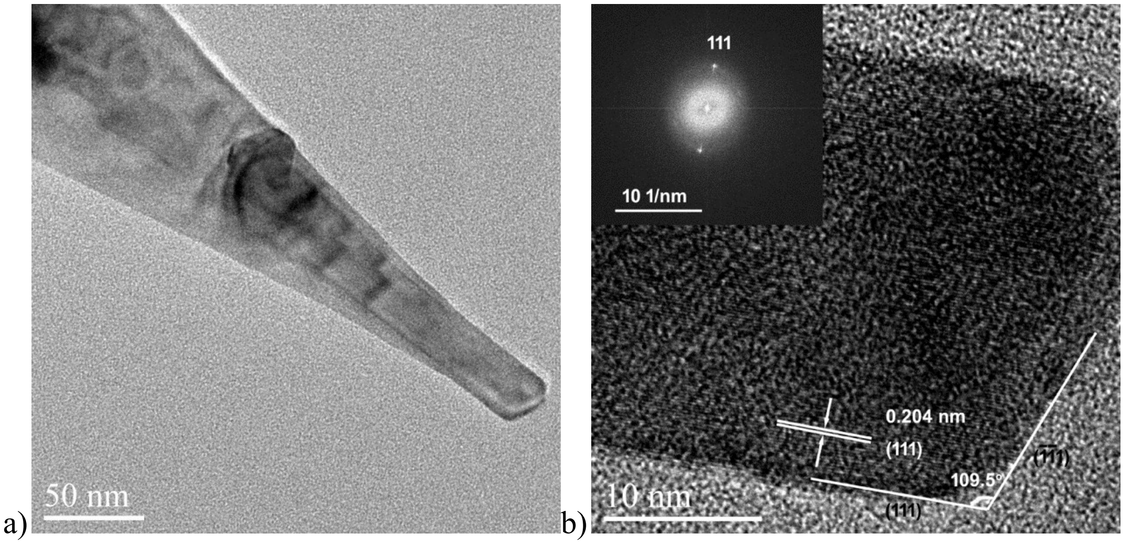


Fig. S8 a) TEM image of the pod of Ni-MP, b) HRTEM image of the pod of Ni-MP, the insert is corresponding FFT transferred pattern.

Figure S5b shows the crystal fringes with a d spacing 0.204 nm, corresponding to the (111) crystal planes of fcc Ni. Careful observations reveal that the angle between the end plane and the (111) crystal plane is 109.5°. For cubic lattice system, the angle between two crystal planes, such as planes ($h_1k_1l_1$) and ($h_2k_2l_2$), follows the following formula:

$$cos\emptyset = \frac{h_1h_2 + k_1k_2 + l_1l_2}{\sqrt{\left(h_1^2 + k_1^2 + l_1^2\right) + (h_2^2 + k_2^2 + l_2^2)}}$$

According to the formula, the angle between (111) and (-1-11) crystal planes is 109.5°. So it can be inferred that the end plane of the pod is (-1-11) crystal plane. The HRTEM supported that the growth directions of the pod is <111> directions.

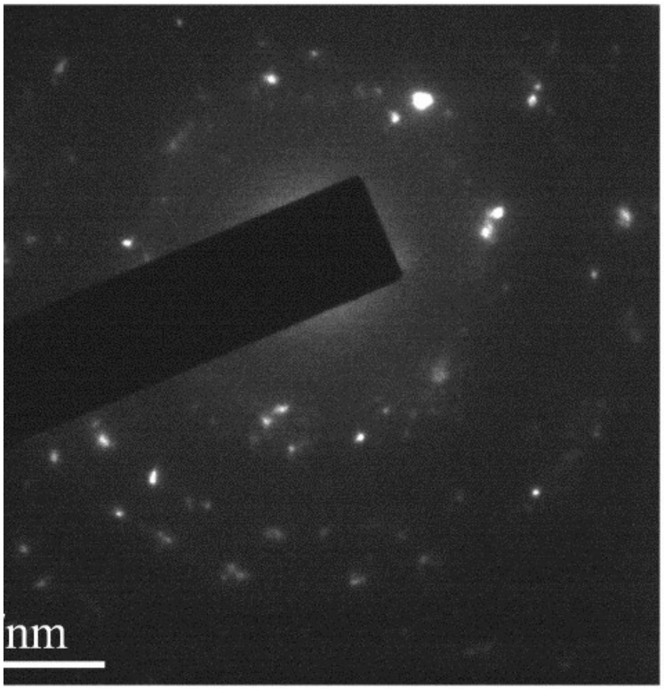


Fig. S9 SAED image of Ni-SB.