Supporting Information

Amorphous NiB/Carbon Nanohybrids: Synthesis and Catalytic Enhancement Induced by Electron Transfer

Weikai Liu,[a] Ruifen Chen,[a] Lijun Liu,*[a] Shuangzhi Li,[a] Zhiyong Xue*[a] and Chiyang He[a]

[a] College of Chemistry and Chemical Engineering, Wuhan Textile University, Wuhan 430073,

People's Republic of China

* To whom correspondence should be addressed.

Lijun Liu: E-mail: eduliu@163.com; Tel: +86-27-59367685

Zhiyong Xue: E-mail: xuezhiyong@wtu.edu.cn; Tel: +86-27-59367685

Discussion of FTIR results

In this work, we have observed the so-called strong metal-support interaction (SMSI) effect in the NiB/C catalyst, which is manifested by the charge transfer between metal and carbon support. It is suggested oxygen-containing surface groups on carbon supports (e.g., carbon nanotube, graphene) could induce the charge transfer between metal and support.[1] As a result, we have carefully investigated the change of these surface groups on the carbon by FTIR.

The FTIR spectra show the adsorption band of carboxylic C=O group on the carbon is positively shifted after coupling with NiB alloy.

Generally, the vibration frequency of a chemical bond is determined as follows:

$$\nu = \frac{1}{2\pi c}\sqrt{\frac{\kappa}{\mu}}$$

(eq. 1)

where ν is the vibration frequency, κ is the force constant, and μ is the reduced mass, $\mu = m_1 m_2 /(m_1 + m_2)$, where m_1 and m_2 are the component masses for the chemical bond.

The vibration frequency will positively shift when the force constant (κ) of a chemical bond is increased. Therefore, the positive shift of ν(C=O) indicates an enhancement of C=O bond strength, which could be caused by the electron transfer from Ni species to oxygen-containing groups due to the electronegative difference between Ni and O element. Such electron transfer can increase the electron density of C=O bonds and lead to a positive shift of ν(C=O) as shown in Fig. 4 (see Manuscript). Thus, we believe this could be another fact to prove the strong interaction between NiB and C support.
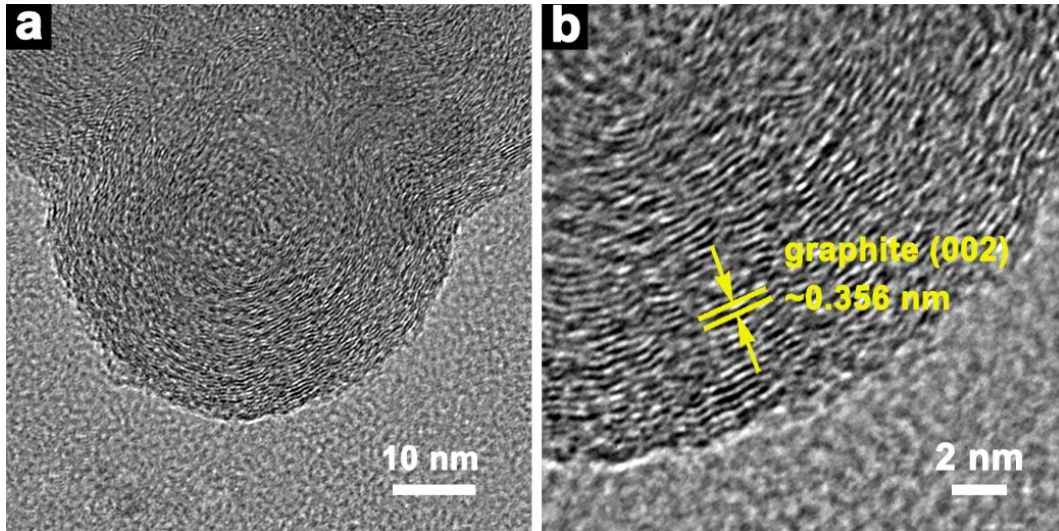
Fig. S1. (a) TEM and (B) HRTEM images of the graphite carbon NP. The image clearly shows

the slightly-distorted lattice fringes with an interplanar distance of 0.356 nm corresponding to the
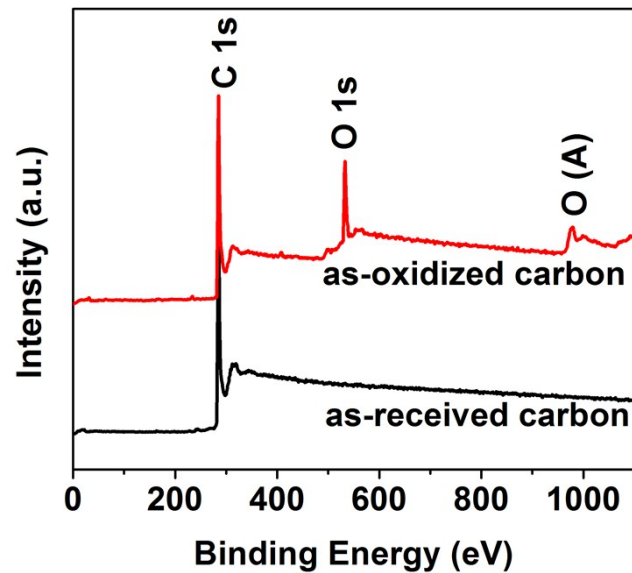
(002) facets of graphite carbon.

Fig. S2. The survey XPS spectra of as-received and as-oxidized carbon NPs. Both samples contain carbon and oxygen elements with a carbon/oxygen atomic ratio of 0.9/0.1 for as-received carbon and 0.7/0.3 for as-oxidized carbon, respectively.
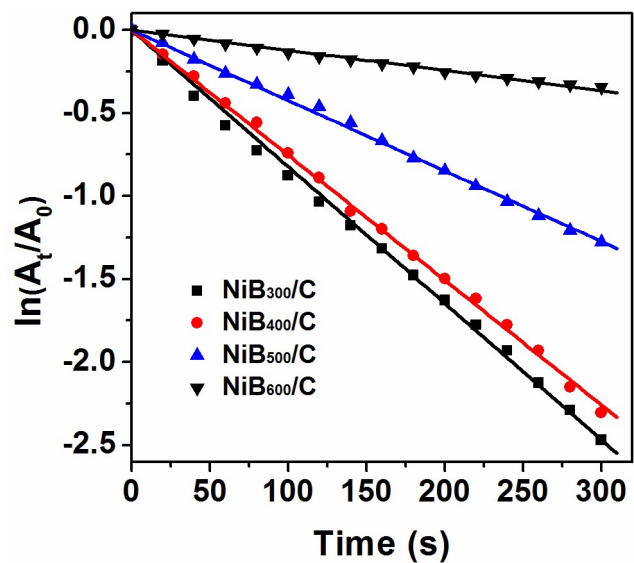
Fig. S3. The plots of $\ln(A_t/A_0)$ *versus* reaction time for the 4-NP reduction over the crystalline

NiB/C catalysts obtained by calcining the amorphous NiB/C at various temperatures.
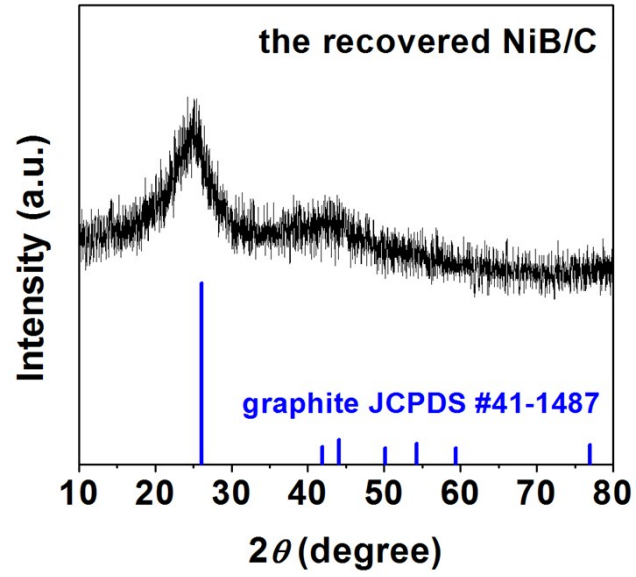
Fig. S4. The XRD pattern of NiB/C after five times of cycling uses, which shows that the NiB/C still shows diffractions belonging to graphite carbon. No phase change is observed after cycling uses.

Table S1 Comparison of the normalized rate constants ($k_n = k / m_{metal}$) of NiB/C with the prior catalysts reported for the 4-NP reduction with $NaBH_4$.

catalysts		$k_n{}^a$	references
active metals	supports	$(s^{-1} \cdot mg^{-1})$	
Raney® Ni	–	0.0370	[2]
NiPt NPs	–	0.5735	[2]
crystalline Ni NPs	CB	0.0452	[3]
crystalline Ni NPs	SiO_2	0.0910	[4]
crystalline Ni NPs	rGO	0.6093	[5]
Au NPs	GO/CNT	0.1136	[6]
Au shell	C nanofibers (core)	0.2390	[7]
Pd NPs	rGO	2.350	[8]
amorphous NiB	CB	3.640	this work

^{a} k_n is the normalized reaction rate constant, $k_n = k / m_{metal}$.

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