Supplementary Information for

Deposition of Fe-Ni Nanoparticles on Polyethyleneimine Decorated Graphene Oxide and Application in Catalytic Dehydrogenation of Ammonia Borane

Xiaohui Zhou,[‡] Zhongxin Chen,[‡] Danhua Yan, Hongbin Lu*

State Key Laboratory of Molecular Engineering of Polymers, and Department of Macromolecular Science, Fudan University, 220 Handan

Road, Shanghai 200433, China

[‡]These authors contributed equally to this work.

*To whom correspondence should be addressed: hongbinlu@fudan.edu.cn.

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1. Raman and UV-vis evidence of covalent grafting of PEI chains on GO sheets



Figure S1. Raman and UV-Vis spectra of GO and PEI-GO_{1to2}; Inset: digital photo of PEI-GO_{1to2} (left) and GO (right) aqueous solution.

PEI chains can be absorbed or covalent linked to GO. The covalent bonding between PEI chains and GO is further confirmed by Raman spectra, which can be reflected by the comparing integrity of graphene (GNs). Two primary characteristic bands, 1580 cm⁻¹ (G band) and 1325 cm⁻¹ (D band), correspond to sp² carbon atoms from the aromatic structure and sp³ carbon atoms of the defect structure, respectively. As shown in **Figure S1a**, the intensity ratio of D to

G bands (I_D/I_G) of PEI-GO_{1to2} is 1.36, which is largely enhanced relative to that of the raw graphite (not shown, ~0.3 for our samples), indicating the formation of covalent bonds between PEI chains and GNs. Although GO also reveals an enlarged I_D/I_G ratio (1.15), it was reported that GO can be reduced by PEI or other amine-containing molecules, leading to partial recovery of the graphitic region and a decreased I_D/I_G ratio.¹ The size of crystal domains in GNs (L_a) is estimated according to the previous method, that is, L_a (nm) = 2.4 × 10⁻¹⁰ × $\lambda_{laser}^4 \times (I_D/I_G)^{-1}$, where λ_{laser} is the laser excitation wavelength (631 nm). For the raw graphite, a crystallite size of 131.2 nm is obtained. By comparision, GO (33.1 nm) and PEI-GO_{1to2} (28.9 nm) reveal smaller crystallite sizes, indicating the covalent bonding. During the reaction between PEI and GO, the color of the mixture turns black gradually. As shown in **Figure S1b**, GO has a characteristic absorption peak at 231 nm, while the characteristic absorption peak of PEI-GO_{1to2} red-shifts to 259 nm with decreasing intensity. This suggests the reduction of GO and the recovery of conjugate structures and is consistent with the FTIR and Raman results.



2. TEM observation of the morphology of GO and PEI-GO composites



To investigate the morphology of GO and PEI-GO composites, transmission electron microscopic (TEM) images were taken by depositing GO and PEI-GO aqueous solution (~0.1 mg/ml, roughly) on holey copper grids. As shown in **Figure S2a**, many corrugations with the width 10-30 nm and the length 300-600 nm can be discernible in the overlap-stacked GO sheets, due to the presence of oxygen functional groups and the reduced strain energy. Similar corrugations can be also found in PEI-GO composites, however, the number of corrugations decreases with increasing ratios of PEI to GO. It may result from the coverage of PEI chains to GO, electrostatic interactions and covalent bonding between PEI chains and GO. In our previous work, it was found that grafting PAA chains favor to flatten the

corrugation of reduced GO sheets.² The corrugations in PEI-GO may be due to lower grafting densities of PEI chains and weaker binding between PEI and GO (a combination of physically absorbed and covalent binding). Moreover, with the increasing ratios of PEI to GO, the color of PEI-GO composites becomes darker in TEM images, indicating more PEI chains being attached on GO. This agrees well with our TGA results.



3. Mean Roughness (R_a) of AFM micrographs of GO and PEI-GO composites

Figure S3. Mean Roughness (R_a) of AFM micrographs of GO and PEI-GO composites. (a-d): GO, PEI-GO_{1to2}, PEI-GO_{2to1} and PEI-GO_{10to1}, respectively.

In order to investigate the effect of PEI chains on the morphology of GO, the software, *Nanoscope 5.30r1*, is employed to estimate the mean roughness of AFM micrographs. Some modifications, *e.g.* flatten, are carried out for all AFM micrographs before roughness analysis. The flatten order is chosen to be 1 since a higher flatten order may bring some disturbance to AFM micrographs and thus it's not advised. The mean roughnesses of GO and PEI-GO composites are estimated from the select area of the AFM micrographs, corresponding to the box in black in **Figure S3**. To minimize the effect of corrugations on the roughness, two stopbands are added in **Figure S3c** where the area in the stopbands is not under consideration. Their mean roughnesses are determined to be 0.084, 0.137, 0.138 and 0.350, respectively.

4. Effect of the electron beam on the crystallization of the NPs

Since the difficulty to distinguish the amorphous Fe-Ni NPs on PEI-GO composites compared to those aggregated particles, these NPs are induced to crystallize by exposing them under electron beam in high-resolution TEM. It is known that electron beams can be used to heat samples, as well as induce structural and chemical defects.³ According to Klimenkov *et al.*⁴, the electron beam in the TEM can induce crystallization of amorphous Ge in SiO₂, depending on the total irradiation dose. Libera found that the thickness of thin film samples is another critical factor, which is practicable for our nanosheets.³ In our tests, a HR-TEM (JEM-2100F) with the accelerating voltage of 200 kV and a magnification of 250,000× is adopted, and the exposure time is recorded. As shown in **Figure S4**, the amorphous NPs begin to crystallize after 2 min, and the nanocrystals become progressively more visible as time goes on. However, GNs start to break even at an exposure time 2 min, and it becomes almost completely fractured at 6 min. To optimize TEM images, we choose an exposure time 4 min for observation.



Figure S4. TEM images of the NPs deposited on PEI-GO_{2to1} with different exposure times: (a) 0, (b) 2, (c) 4 and (d) 6 min, respectively.

5. Investigation on the effect of PEI and GO in the dehydrogenation



Figure S5. Hydrogen generation rates of the AB hydrolysis in the presence of PEI-GO_{10to1}, PEI/Fe-Ni and PEI-GO_{10to1}/Fe-Ni.

To demonstrate that the catalytic activity primarily originates from the Fe-Ni NPs, we carried out a blank experiment in which no Fe or Ni NPs is deposited on the PEI-GO_{10to1}. As shown in **Figure S5**, nearly no released hydrogen can be observed in the case containing the PEI-GO_{10to1} alone. In contrast, both the PEI-GO_{10to1}/Fe-Ni and the PEI/Fe-Ni



Figure S6. Hydrogen generation rates of the AB hydrolysis in the presence of Fe-Ni (5:5) and PEI/Fe-Ni with and without the solid support (GO and AC).

exhibit significant catalytic activity. As a result, it is concluded that the catalytic activity observed essentially originates from the Fe-Ni NPs and the contribution of PEI-GO to the catalysis is nearly negligible, except its control to the size and spatial distribution of NPs.

Activated carbon (AC), a well-known solid support in the catalysis field, is used as a reference to distinguish the effect of GO on the catalytic properties of Fe-Ni NPs. Both AC-supported and PEI-AC-supported catalysts are prepared to demonstrate the control of PEI to the morphology and the size of Fe-Ni NPs on AC. AC is firstly treated by nitric acid solution (2 mol/L) to introduce a large amount of oxygen functional groups as reported by Khelifietal.⁵ PEI decorated acid treated activated carbon (PEI-AC) is then synthesized under similar process for PEI-GO. After the deposition of Fe-Ni (5:5) NPs (AC/Fe-Ni), their catalytic activities for the dehydrogenation reaction of AB are characterized. As shown in Figure S6, although the AC/Fe-Ni catalyst presents an enhanced activity compared to the initial Fe-Ni one. GO appears to be a much better support, where higher catalytic activity and hydrogen generation volume are observed. When PEI is introduced into the AC-supported system, the reaction takes 4.5 min to complete the release of hydrogen from AB (H₂/NH₃BH₃=2.75), much faster than the original one (AC/Fe-Ni). This could be attributed to the smaller particle size and the better spatial particle distribution. The PEI-GO-supported catalyst shows the best catalytic activity in all these samples, which takes only ~ 1 min to release the equivalent hydrogen. Considering the two-dimensional morphology of graphene and abundant oxygen functional groups in GO, it is conjectured that the collapsed pancake-like structure PEI on GO facilitates the metal ions' immobilization and their heterogeneous nucleation. Based on these experimental results, it is concluded that two points are important in catalyzing the dehydrogenation reaction of AB; that is, 1) the existence of GO and PEI is essential for improving the catalytic activity of Fe-Ni NPs, and 2) GO sheets are advantageous as a catalyst support over AC, due to their specific structure features.

6. The effect of the Fe to Ni ratio on the dehydrogenation

In order to investigate the effect of the Fe to Ni ratio on catalytic activities, $Fe_{1-x}Ni_x NPs$ with different x values(x=0, 0.3, 0.5, 0.7, 1) deposited on PEI-GO_{10to1} were synthesized. The results that they catalyze the dehydrogenation reaction of AB are shown in **Figure S7**. It is seen that the activity of the PEI-GO_{10to1}/Fe catalyst is quite low; however, increasing the Ni molar ratio was able to effectively shorten the reaction time. The dehydrogenation reaction took 9.5, 2



Figure S7. Hydrogen generation rates of the AB hydrolysis in the presence of PEI-GO_{10to1}/Fe-Ni composites with different molar ratios of Fe and Ni, as well as the Fe/Ni (5:5) physical mixture.

, 5.5 and 4 min, respectively, to release the equivalent hydrogen (H₂/NH₃BH₃=2.75) when the reaction was catalyzed by the PEI-GO_{10to1}/Fe_{1-x}Ni_x with x=0.3, 0.5, 0.7, 1, respectively. It is evident that the catalyst of PEI-GO_{10to1}/Fe_{0.5}Ni_{0.5} presents the highest activity, even higher than that of pure Ni NPs. This is in accord with the observation by Xu *et al.*⁶ As aforementioned, the influence from adjacent metal atoms, or the synergistic effect, may result in such an enhanced catalytic behavior. This is also supported by the obvious difference between the Fe_{0.5}Ni_{0.5} and the physical mixture.

7. XPS investigation on the chemical composition of PEI-GO/Fe-Ni catalyst

X-ray photoelectron spectra (XPS) was carried out on an AXIS UltraDLD system (Kratos) with monochromatic Al K_{α} radiation (hv=1486.6 eV), to obtain high quality core-level spectra. Survey and high-resolution spectra were collected using 160 eV pass energy, step 1.0 eV and 40 eV pass energy, step 0.1 eV, respectively. All the samples were analyzed at 90° take-off angle. The sample used was prepared separately, considering the negative/harmful effect of sample magnetism on the test system. The deconvolution of peaks was conducted using the XPS Peak processing software version 4.1 (Chemistry, CUHK), along with a Shirley background subtraction.

As shown in **Figure S8a** and **Table S1**, three prominent bandgroups at 285, 400 and 532 eV correspond to the C_{1s} , N_{1s} and O_{1s} , respectively. Three additional weak bandgroups at 104, 712, 855 eV can be assigned to the Si_{2p} , Fe_{2p} and Ni_{2p} , respectively. Contrary to the feed ratio, the peak intensity of Fe_{2p} and Ni_{2p} are quite weak in the survey and nearly undetectable in the core-level spectra without high working power (450 W) and pass energy (40 eV). Moreover, the atom percentage of Fe and Ni are 0.37% and 0.77% in total. This non-equivalence may be due to the different sensitivities of Fe (RSF 2.96) and Ni (RSF 4.04) in XPS or more Ni atoms are placed on the surface of the catalyst. The Si atoms may come from the impurities of graphite and it is not under further consideration.

To further analyze the chemical composition, the C_{1s} core-level spectrum in Figure S8b, is fitted with three Gaussian



Figure S8. XPS spectra of PEI-GO_{10to1}/Fe-Ni catalyst. Survey (a), and corresponding high resolution core-level spectra of C_{1s} (b), N_{1s} (c) and O_{1s} (d), respectively. These spectra were obtained with monochromatic Al K_{α} radiation (hv=1486.6 eV).

Samples	Atom Percentage /%					C _{1s} Core-level /%		
	C_{1s}	O_{1s}	N_{1s}	Fe_{2p}	Ni _{2p}	C-C	C-O/C-N	C(O)NH/COOH
B.E. ¹	285	532	400	712	855	284.8	286.7	289.0
$PEI\text{-}GO_{10tol}/Fe\text{-}Ni^2$	73.39	17.70	7.76	0.37	0.78	70.3	8.4	21.3

Table S1. Surface elemental composition of the PEI-GO $_{10to1}$ /Fe-Ni catalyst.

¹ Binding energy (eV). ² This sample is prepared separately, with a composition of (80 wt% PEI-GO (10to1): 20 wt% Fe-Ni NPs).

peaks at 284.8, 286.7 and 289.0 eV, corresponding to the C-C, C-O/C-N and C(O)NH/COOH species, respectively. According to the literature by Ruoff *et al.*, ⁷ the peak at 289.0 eV is supposed to arise from the COOH species. However, given the relatively low content of COOH species in GO (5.7%, not shown) and the absence of the COOH vibration at 1730 cm⁻¹ in the FTIR spectrum of PEI-GO (Figure 1), this peak (289.0 eV) can be assigned to the amide species. It shifts to a higher energy, which may be caused by the higher working power and pass energy used here.⁸ Clearly, the C-C species is the majority (70.3%) in all species, reflecting the feature of graphene nanosheets. The absence of C=O species (287.8 eV) and relatively low contents of oxygen or nitrogen-containing groups indicate that PEI-GO_{10to1} may be partially reduced by NaBH₄ during the deposition of Fe-Ni NPs. According to the literature, ⁹ the NaBH₄-reduction can effectively remove carbonyl groups while hydroxyl functional groups can be reserved. This is consistent with our C_{1s} spectrum where about 8.4% hydroxyl or amine groups still exist in the catalyst. In addition, the presence of amide bonds (289.0 eV, 21.3%) suggests the presence of covalent bonding between PEI and GO. The N_{1s} core-level spectrum

in **Figure S8c** can be deconvoluted into three subpeaks. The strong peak located at 399.3 eV is assigned to the amide species, other two weak peaks at 400.2 and 402 eV are assigned to amine and N⁺ species, respectively. The O_{1s} core-level spectrum in **Figure S8d** can be fitted to three peaks. The peaks at 531.5 and 532.7 eV are supposed to arise from the amide groups (C(O)NH) and the hydroxyl groups.⁷ The accurate origin of the last at 535.8 eV remains unclear at this time, but it was attributed to the chemisorbed oxygen or adsorbed water in a recent report by Yue *et al.*¹⁰



8. Evidence of the valence state of Fe and Ni in the raw catalyst

Figure S9. Fe_{2p} and Ni_{2p} core-level spectra of PEI-GO_{10to1}/Fe-Ni catalyst before (a, b) and (c, d) after 5 times dehydrogenation. These spectra were obtained with Mg K_{α} radiation (hv=1253.6 eV).

In order to identify the valence state of Fe and Ni in the raw catalyst, we also carried out the XPS examination for the PEI-GO₁₀₀₁/Fe-Ni catalyst before and after 5 times dehydrogenation, on a RBD upgraded PHI-5000C ESCA system (Perkin Elmer) with Mg K_a radiation (hv=1253.6 eV). Fe_{2p} and Ni_{2p} core-level spectra were obtained using 23.5 eV pass energy, step 0.1 eV, and 45° take-off angle. Considering that the effective sampling depth of XPS is usually smaller than 10 nm in polymer matrix or 5 nm in metal/metal oxide, ¹¹ and the diameter of the Fe-Ni NPs is ~3 nm, the analysis volume is assumed to predominantly consist of the surface and thus only a small contribution is from the underlying metal in the photoelectron signal recorded. As shown in **Figure S9a**, we can observe most of Fe atoms in the oxidation state. However, according to Dickinson *et al.*,¹² a weak peak at 706.9 eV likely exists compared to that after 5 recycles, which could probably be assigned to Fe atoms in the zero-valence state. Because of its low proportion, the deconvolution of this peak is not shown in **Figure S9a**. Similarly, we also find that the Ni atoms were partially oxidized. The Ni_{2p} core-level spectrum in **Figure S9b** could be fitted to six subpeaks. The peak at 852.7 eV is assigned to the Ni in the zero-valence state, and the peak at 855.9 eV to the oxidation state. The difference between Fe_{2p} and Ni_{2p} spectra is supposed to come from the relative inertness of Ni atoms, as suggested by Dickinson *et al.*¹²

The PEI-GO_{10to1}/Fe-Ni catalyst after 5 times dehydrogenation was also investigated by XPS. As shown in Figure

S9c,d, it is seen that further oxidation did occur, due to recycling in air. While Fe atoms were suggested to be in oxidation state with the absence of the peak at 706.9 eV, the peak of zero-valent Ni in the Ni_{2p} core-level spectrum was greatly reduced, as opposed to **Figure S9b**. This presents evidence for the opinion that the oxidation of Fe-Ni NPs should be a key factor that affects reusability.

9. Measurement of the magnetism of the Fe-Ni catalyst

Since the Fe-Ni NPs deposited on PEI-GO can be easily attracted by a magnet, we investigated its magnetic property by magnetic hysteresis loops that were measured at 298K with a MPMS (Squid) VSM system (Quantum Design). As shown in **Figure S10**, the profile of the magnetization curves for the Fe-Ni NPs and the composite are characteristic of ferromagnetic material, but the lower coercive force (H_c=200 Oe) and saturation magnetization (M_s=22 emu/g) indicate that the composites are close to superparamagnetic material,¹³ which is ascribed to the contribution of the Fe-Ni NPs with small sizes.



Figure S10. Magnetization curves of PEI-GO_{10to1}/Fe-Ni composites.

10. The phase transition of Fe-Ni NPs after several recycles.

As reported by Xu *et al*, the species of Fe-based catalyst with high activities are mainly composed of amorphous phase rather than crystalline phase.^{14,15} The Fe-Ni NPs deposited on PEI-GO are amorphous, as verified by the XRD result, but it is possible to vary after experiencing several recycles of dehydrogenation. As shown in **Figure S11**, the XRD result of PEI-GO_{10to1}/Fe-Ni after 5 recycles reveals a detectable peak at 44.82°, representative of the (110) Fe-Ni phase. Both low signal intensity and broad peak shape imply the crystalline phase is probably not highly ordered, but such structure is obviously different from that of the original catalyst. Consequently, it is speculated that the reaction-induced crystallization occurred during the dehydrogenation could also be one of reasons that result in a gradually decreased catalytic activity. However, further studies in this regard remain necessary.



Figure S11. X-ray diffraction of the prepared PEI-GO_{10to1}/Fe-Ni composites before (a) and after (b) five recycles of dehydrogenation.

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