



Probing the electronic structure of M-graphene oxide (M = Ni, Co, NiCo) catalysts for hydrolytic dehydrogenation of ammonia borane

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ABSTRACT

Various metal elements (M = Ni, Co, NiCo) were dispersed on graphene oxide (GO) to form the M-GO hybrids by a facile way. The hybrids showed good catalytic activities in the hydrolytic dehydrogenation of ammonia borane (AB, NH_3BH_3), which were significantly enhanced when compared to the metal nanoparticles or GO alone. The electronic structure of the hybrids has been probed by scanning transmission X-ray microscopy (STXM). The distribution of metal elements was clearly imaged with identical electronic structure. Moreover, an interfacial interaction between metal and GO was observed with the peak intensity proportional to the catalytic performance in the hydrolysis of AB. The results provide new insight into the enhanced performance of the M-GO hybrids and may help for the design of advanced catalysts.

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1. Introduction

Ammonia borane (AB) has been regarded as a promising candidate for chemical hydrogen storage due to its high hydrogen content of 19.6 wt% [1–9]. In the hydrogen release process from AB, noble metals (such as Pt) are typically used to achieve high efficiency. However, noble metals are high-cost with low element abundance thus their applications are highly limited [1,3,6]. Alternative catalysts with low-cost such as non-noble metal based catalysts are then required and widely studied [5,6,8,9]. For example, monodisperse Ni nanoparticles (NPs) were reported to have a good total turnover frequency (TOF) value of 8.8 (H_2) mol/(Cat-Ni)mol min [5]. A high TOF value of 30.7 (H_2) mol/(Cat-Ni)mol min was also achieved by surfactant-free Ni NPs deposited into porous carbon [2]. Recently, a catalyst with binary Cu–Ni oxides was reported to show a high TOF value of about 60 (H_2) mol/(Cat-metal)mol min in the hydrolysis of AB [8].

To improve the performance of metal based catalysts, various supporting materials have been widely used and graphene has been considered to be a good material due to its high surface area and large density of free electrons [10–14]. Actually, the

hybrids of graphene and non-noble metal NPs were widely used for the hydrolysis of AB to achieve enhanced performance when compared to the metal or graphene alone [15–19]. Although the performance of the hybrids have been widely studied, there are only few studies on the electronic structure of the hybrids and the synergetic effects in the hybrids for enhanced catalytic activity are still unclear [15–19]. Understanding the relationship between the electronic structure and the enhanced performance is thus important for the design of advanced catalysts. Here we show a facile way to prepare the hybrids of metal (M = Ni, Co, NiCo) and graphene oxide (GO) by mixing GO and $\text{M}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ solution together. The hybrids show good catalytic properties in the hydrolysis of AB and their electronic structures have been probed by scanning transmission X-ray microscopy (STXM). The presence of metal on graphene has been imaged and an interfacial interaction between metal and graphene has been detected, which might be related to the enhanced performance of the hybrids.

STXM is a synchrotron radiation based technique and it is very effective to detect the electronic structure of nanomaterials [20–24]. It combines both X-ray absorption near-edge structure (XANES) spectroscopy and microscopy [20–24]. XANES is sensitive to various chemical states by revealing the electronic structure of complicated nanomaterials [23–26]. For example, the electronic structure of the NP-graphene hybrids was recently investigated by STXM, revealing that an interfacial interaction might be a key issue for the enhanced performance in catalyzing the oxidation of

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cyclohexanol [23]. Here we use STXM to study the electronic structure of the M-GO hybrids and try to reveal the relationship between the electronic structure and the performance in the hydrolysis of AB.

2. Experimental

2.1. Materials preparation

Graphene oxide (GO) was prepared from natural graphite by a modified Hummers' method. To decorate GO with various metal elements (M = Ni, Co), GO was first immersed in an ethanol solution (15 ml) under ultrasonication for 30 min and then an ethylene glycol solution (50 ml) of $M(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ (5 mmol) was added under ultrasonication for 30 min, followed by stirring for 12 h [27]. Centrifugal separation was then used several times and the samples were washed by ethanol to remove ethylene glycol. The products were finally dried at 60 °C overnight and labeled as M-GO (M = Ni, Co). For the preparation of NiCo-GO sample, an mixed ethylene glycol solution (50 ml) of $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ (2.5 mmol) and $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ (5 mmol) was used instead of pure $M(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ solution in the same treatment. To prepare reduced sample (NiCo-G), NiCo-GO sample was heated to 300 °C in H_2 (100 sccm) at the rate of 8 °C min^{-1} and held at 300 °C for 2 h to achieve the final reduced product.

2.2. Structural characterization

The samples were measured by transmission electron microscope (TEM) (FEI Tecnai G2 F20 S-TIWN). The metal contents were measured by an inductively coupled plasma (ICP) spectrometer (VISTA-MPX (CCD Simultaneous ICP-OES), Varian). STXM experiments were performed on the SM beamline at the Canadian Light Source (CLS). The X-ray beam was perpendicular to the sample surface. The focused X-ray beam has a size of about 30 nm with the photon flux of about 2×10^7 photons/s. The software to analyze the STXM data is *aXis2000* [20–24].

2.3. Catalytic activity measurement

An one-neck round-bottom flask (25 ml) was used for the hydrolysis of AB. Briefly, 5 ml of AB (5 mg/ml, Aldrich) was added into the flask. The neck was sealed and connected to a gas-collection tube [22,28]. Then 10 mg M-GO (M = Ni, Co, NiCo) samples were mixed with 2 ml deionized water, and the suspension liquid was quickly injected into the flask with an airtight syringe. The experiment was performed under room temperature and ambient atmosphere. The reaction time was recorded when observing the first bubble. The hydrolysis process can be described by the formula: $\text{NH}_3\text{BH}_3 + 2\text{H}_2\text{O} = \text{NH}_4^+ + \text{BO}_2^- + 3\text{H}_2$ [22,28,29].

3. Results and discussion

The M-GO samples were prepared by simply mixing GO and $M(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ solutions. The surface functional groups on GO would strongly anchor the metal in the solution according to the reference [27]. After centrifugal separation, washing and drying, the final products were prepared and labeled as M-GO samples. Typically the metal was considered to be reduced by AB in the hydrolysis process and small NPs on graphene could be observed [15–19]. However, here we mainly probe the electronic structure of the initial M-GO samples before the exposure to AB. From the TEM images, no obvious NPs larger than 1 nm on GO can be observed for all the M-GO samples.

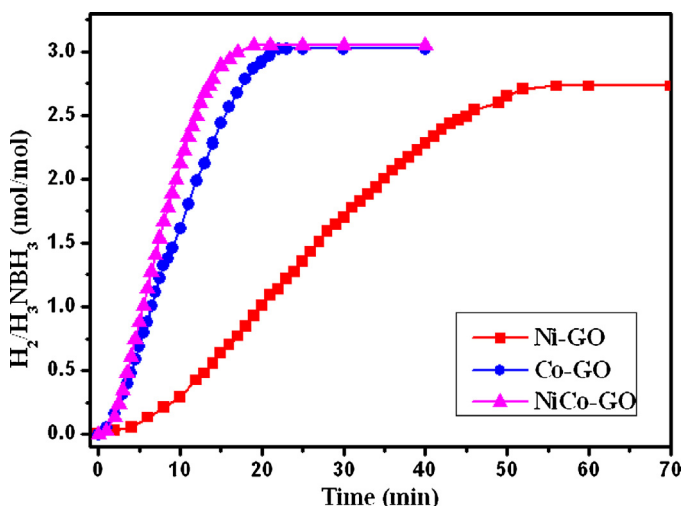


Fig. 1. Hydrogen evolution curves of hydrolysis of AB aqueous solution catalyzed by the M-GO samples.

Table 1

M contents and TOF values of the samples.

Samples	M-loading (wt%)	TOF (H_2) (mol)/(Cat-M) (mol min)
Ni-GO	12.4	2.07
Co-GO	12.2	5.63
NiCo-GO	12.3	6.78
Ni particles	–	0.30
NiO nanoparticles	–	0.29
Co nanoparticles	–	0.04
CoO nanoparticles	–	0.1
GO	–	0

In Fig. 1 we show the catalytic performance of the M-GO (M = Ni, Co, NiCo) hybrids for the hydrolysis of AB aqueous solution. In Table 1 we also show the metal loading and TOF values of all the samples with a comparison to that of pure GO, pure metal or metal oxides. Actually, the literatures also reported that pure metal or metal oxides without supporting materials showed very low performance [15–19]. The M-GO samples have a similar M loading of about 12 wt% according to the ICP measurement. All the M-GO samples show enhanced TOF values compared to pure GO or pure metals alone, suggesting the synergetic effects by the combination of GO and metals. In Table 1 Ni-GO shows a TOF value of 2.07 (H_2) mol/(Cat-M)mol min, while Co-GO shows a much higher performance with a TOF value of 5.63 (H_2) mol/(Cat-M)mol min. Moreover, when a bimetallic oxide is used in the NiCo-GO sample, the performance can be further improved with a TOF value of 6.78 (H_2) mol/(Cat-M)mol min, which is comparable to some recent reports for the NP-graphene hybrids [15,19]. Although the performances of these M-GO samples are not as high as the optimized values in recent reports [2,8], the hybrids really show enhanced catalytic properties compared to the pure materials alone and exhibit increased TOF values from Ni-GO to Co-GO and NiCo-GO, which can be used as a good model to study the relationship between the performance and the electronic structure.

Figs. 2–4 show the TEM images and STXM results of the M-GO samples. In Fig. 2a the TEM image shows some GO pieces in Ni-GO sample, which are selected for the STXM experiments. Fig. 2b is the corresponding STXM map measured at the C K-edge. The STXM map is in good agreement with the TEM image. Actually, we use the same sample on the TEM grid for both TEM and STXM experiments, thus the contribution from impurities such as aggregated amorphous carbon can be excluded. In both TEM image and the STXM map at

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