

## Supplementary information

### X-ray Chemical Imaging and Electronic Structure of a Single Nanoplatelet Ni/Graphene Composite

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#### 1 Experimental

##### 1.1 Precursor synthesis

The precursor of Ni/Graphene composite was synthesized by the pressurized multiplex reduction<sup>1</sup> of graphene oxide and metal compounds with hydrazine hydrate. Briefly, graphite oxide (2 g) was dispersed in deionized water (50 ml) in beaker Teflon reactor (80 ml). With magnetic stirring, nickel acetate hydrate (200 mg) was added. 10min later, hydrazine hydrate (2.5 ml) was added dropwise into the blend. Then the autoclave with the beaker Teflon reactor was tightly covered, fastened, and placed in oven. The pressurized multiplex reduction was carried out at 110 °C for 1 h. Subsequently, the mixture was repeatedly washed with hydrochloric acid and deionized water, coupled with vacuum filtration to remove residual impurities. The precursor of Ni/Graphene composite was finally obtained from the filtrate through freeze-drying for 12 h.

##### 1.2 Thermal treatment

Thermal treatment was designed to synthesize Ni/Graphene composite from its precursor. The schematic of the reactor part of the furnace is shown in Fig. S 1. Prior to the thermal processing, the instrument was tested to be leakage free with liquid leak detector for 10 min. The quartz tube was then purged with argon (99.99%, purity) at 50 mL min<sup>-1</sup> to remove impurities in the tube<sup>2</sup>. 10 min later, the system was heated to 800°C for the exfoliation of graphite oxide and decomposition of Ni(OAc)<sub>2</sub>·xH<sub>2</sub>O in argon atmosphere<sup>3,4</sup>. When the temperature reached 800°C, the temperature control was further switched to 500°C and remains at this temperature for 1 h. Meanwhile, the gas input was switched from argon to hydrogen (99.99%, purity) with flow at 50

mL min<sup>-1</sup>. Hydrogen here served as a reducing agent converting NiO to Ni particles, which deposit on graphene nanoplatelets.

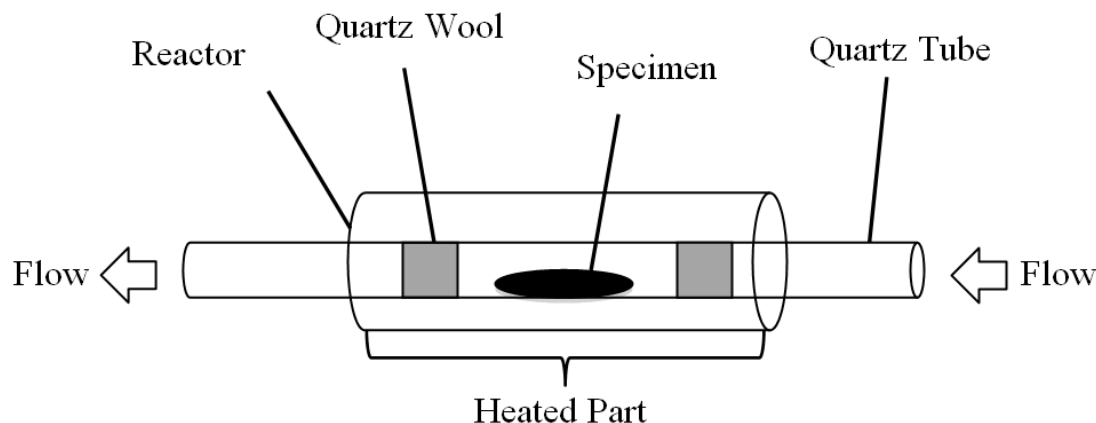
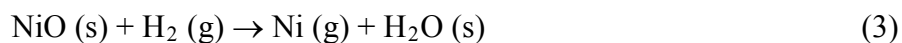
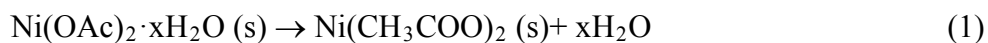


Fig. S1 Schematic diagram of the reactor part for the thermal treatment.

The thermal treatment involved a series of reactions, including the decomposition and reduction of  $\text{Ni}(\text{OAc})_2 \cdot x\text{H}_2\text{O}$ , as well as exfoliation and reduction of graphite oxide. In particular,  $\text{Ni}(\text{OAc})_2 \cdot x\text{H}_2\text{O}$  underwent dehydration at 160 °C, further decomposed at 500 °C, converting to Ni and NiO<sup>5</sup>. Meanwhile, graphite oxide powder was thermally exfoliated to graphene oxide nanoplatelets. The oxygen-containing groups on the nanoplatelets were then thermally removed, resulting in reduced graphene oxide. After hydrogen was purged to the system, NiO was reduced and transferred into Ni particles which were attached to the graphene nanoplatelets. The Ni/Graphene composite material was accordingly obtained in powder. The following chemical equations depict the process of decomposition and hydrogen reduction of  $\text{Ni}(\text{OAc})_2 \cdot x\text{H}_2\text{O}$ . The reaction phases occur at 160 °C, 363 °C and 500 °C, respectively<sup>5</sup>.



## 2 Characterization

X-ray diffractometer (XRD, Bruker D8) equipped with a Cu K $\alpha$  tube ( $\lambda=0.1542$  nm) was used to determine the crystal structures and composition of samples, including as-purchased Ni(OAc) $_2 \cdot xH_2O$ , Ni obtained from the thermal treatment of Ni(OAc) $_2 \cdot xH_2O$  (500 °C in H $_2$  for 1 h), Ni/Graphene precursor and as-obtained Ni/Graphene composite from the thermal treatment of precursor (RT to 800 °C in Ar, 500 °C in H $_2$  for 1 h). The XRD result is shown in Fig. S2. The XRD patterns displayed in Fig. S2a shows that all peaks in the spectrum of as-purchased Ni(OAc) $_2 \cdot xH_2O$  disappeared after its thermal processing at 500 °C in H $_2$  atmosphere for 1 h. It clearly demonstrates that the as-purchased Ni(OAc) $_2 \cdot xH_2O$  was successfully converted to Ni particles through the thermal processing. The XRD pattern in Fig. S2b illustrates that Ni/Graphene composite was obtained from the thermal processing of its precursor. Compared to the spectrum of pure Ni in Fig. S2a, an additional weak peak of the carbon (002) plane appeared in Fig. S2b, confirming the existence of graphite-like structure.

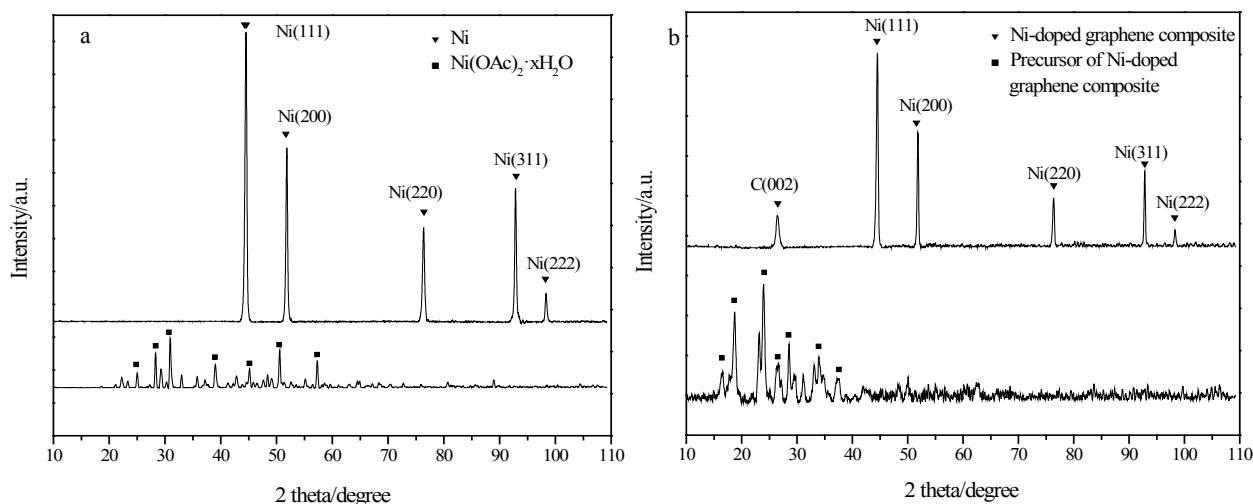


Fig. S2 XRD patterns of samples before and after thermal processing: (a) as-purchased Ni(OAc) $_2 \cdot xH_2O$  and Ni; (b) Ni/Graphene precursor and Ni/Graphene from thermal processing (RT to 800 °C in Ar, 500 °C in H $_2$  for 1 h).

Scanning Electron Microscopy (SEM, FEI XL30) was performed to characterize the modification of graphene by Ni. The morphology of graphene, Ni(OAc) $_2 \cdot xH_2O$  and Ni, and Ni/Graphene composite is shown in Fig. S3. After thermal treatment of the as-purchased Ni(OAc) $_2 \cdot xH_2O$  in hydrogen at 500°C for 1 h, Ni was obtained with severely decreased particle

size of  $\text{Ni(OAc)}_2 \cdot x\text{H}_2\text{O}$  (Fig. S3b and  $\text{Ni(OAc)}_2 \cdot x\text{H}_2\text{O}$ , insert). Compared to pure graphene sheet in Fig. S3a, Ni particles are homogeneously distributed on graphene nanoplatelets, as shown in Fig. S3c. It is also observed that the modified graphene system still remains structurally stable, which facilitates a high specific surface area of the composite and sufficient anchoring sites for Ni particles. A higher magnification image, Fig. S3d, further displays that nanosized Ni particles are uniformly distributed on graphene. This nanostructured composite can accommodate active sites for both atomic and molecular hydrogen, which directly correlates with the enhancement of hydrogen uptake.

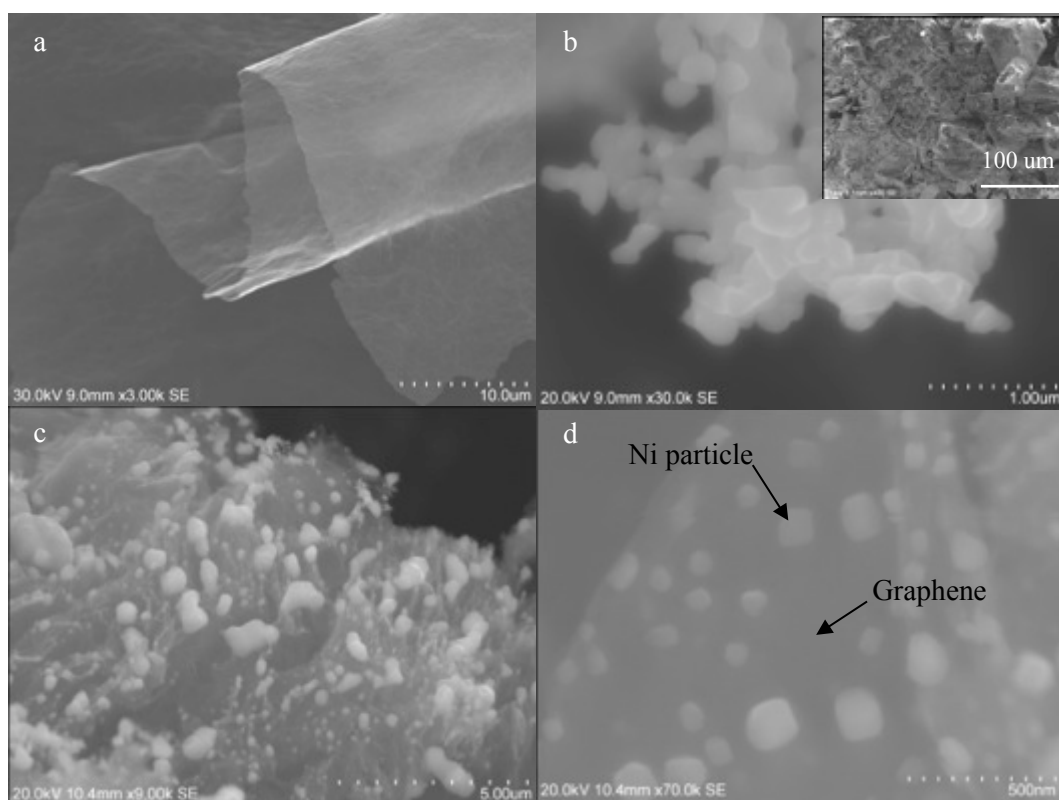


Fig. S3 SEM images of graphene oxide, Ni and Ni/Graphene composite: (a) graphene; (b) Ni (insert,  $\text{Ni(OAc)}_2 \cdot x\text{H}_2\text{O}$ ); (c) and (d) low and high magnification of Ni/Graphene composite from thermal processing (RT to 800 °C in Ar, 500 °C in  $\text{H}_2$  for 1 h), respectively.

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