

## Supporting Information

### Preparation of Graphene Supported Nickel Nanoparticles and Their Application to Methanol Electrooxidation in Alkaline Medium

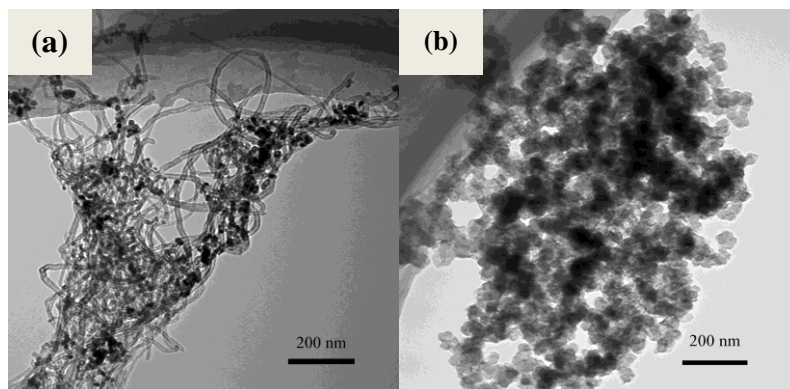
Ling-Rong Zhang, Jin Zhao, Meng Li, Hai-Tao Ni, Jin-Lei Zhang, Xiao-Miao Feng,  
Yan-Wen Ma,\* Qu-Li Fan, Xi-Zhang Wang, Zheng Hu, Wei Huang\*

#### SI 1. Experimental procedure for preparation of Ni/CNT and Ni/CB catalysts

CNTs were treated in concentrated HNO<sub>3</sub> solution at 110°C for 6 h to generate –COOH and –OH groups and then collected by filtration, washing and drying. 120 mg acid-oxidized CNTs were dispersed into 120 mL ethanol by sonication for 1 h to form 1 mg/mL CNT suspension. Then 3.4 mL of 0.1 mol/L NiCl<sub>2</sub>/ethanol solution was dropped into the solution and magnetically stirred for 12 hour at room temperature. Next, under vigorous stirring, 2 mL of hydrazine was added into the mixture at ~60 °C for 4 h. The generated black power was separated by filtration and thoroughly washed with ethanol and deionized water several times, and finally vacuum dried at room temperature. Then the dried power was placed in a quartz tube furnace and then heated under Ar protection from room temperature to 500 °C respectively at a rate of 1 °C/min and kept there for 2 h. The black powder was collected after the furnace was cooled down to room temperature, denoted as Ni/CNT-500. Carbon black (CB) was also used as support to prepare Ni/CB-500 by the same procedure.

#### SI 2. TEM images of Ni/CNT and Ni/CB catalysts

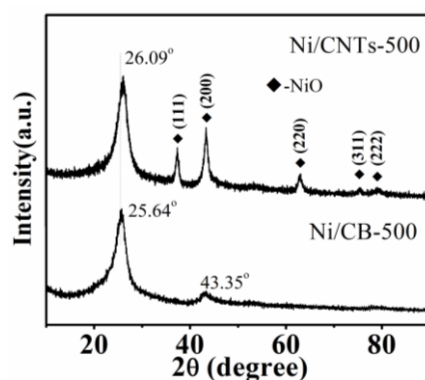
The typical TEM images of Ni/CNT-500 and Ni/CB-500 catalysts are shown in Figure S1. It is seen that Ni-based nanoparticles could not be efficiently immobilized by the acid-oxidized CNTs (Figure S1a) and no distinct Ni-based nanoparticles could be observed in the carbon black (Figure S1b). Compared with the large planar sheet owned by graphene, the narrow tubular structures (5~20 nm) of CNTs or the small spheres (20~80 nm) of carbon black are not beneficial for the immobilization of metal nanoparticles. In addition, a large amount of oxygen-containing groups on the precursor of graphene (i.e., graphene oxide) is also the advantage for metal species anchoring.



**Figure S1** Typical TEM images of (a) Ni/CNT-500 and (b) Ni/CB-500 catalysts.

### SI 3. XRD curves of Ni/CNT and Ni/CB catalysts

Figure S2 presents the XRD curves for Ni/CNT-500 and Ni/CB-500 catalysts. There is no Ni signal in the XRD curves for Ni/CB-500 catalyst, well supports the TEM observation. The peaks in the curve for Ni/CNT-500 catalyst should come from the diffraction of NiO [JCPDS, No.73-1519], indicating that the formation of Ni-based nanoparticles on CNTs is different from that on graphene. It is revealed in the text that graphene support has participated in the reduction of nickel oxide at elevated temperature ( $> 500\text{ }^{\circ}\text{C}$ ), so metal Ni nanoparticles were obtained for Ni/G-500 and Ni/G-700 catalysts. But for CNTs, they did not show the reductive characteristic at  $500\text{ }^{\circ}\text{C}$  due to their high stability, so only NiO nanoparticles were formed on CNTs.

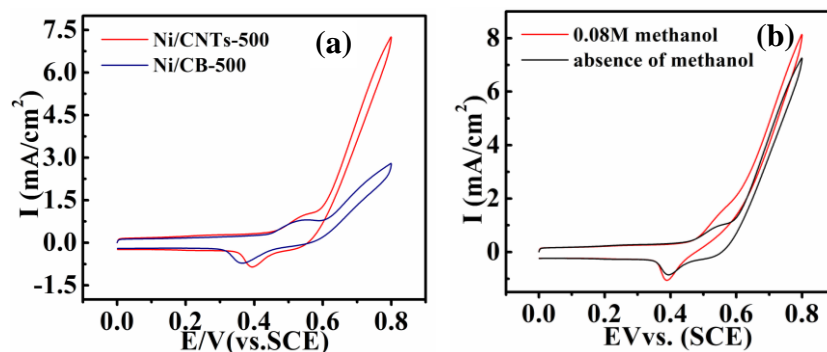


**Figure S2** XRD curves of (a) Ni/CNT-500 and (b) Ni/CB-500 catalysts.

### SI 4. Electrochemical properties of Ni/CNT and Ni/CB catalysts

The CV curves for Ni/CNT-500 and Ni/CB-500 catalysts were measured in 0.1 M NaOH solution are shown in Figure S3a. Both catalysts have the  $\text{Ni}^{2+}/\text{Ni}^{3+}$  transition in CV with high potential differences ( $>120\text{ mV}$ ). The small redox peak intensity in the CV curves suggest that the two catalyst do not own enough active Ni species, i.e.  $\text{Ni}(\text{OH})_2$  or/and  $\text{NiOOH}$ . This is in accordance with the XRD results. In methanol solution, the current density for Ni/CNT-500

catalyst gives a slight increase, indicating that NiO nanoparticles on CNTs are not an efficient catalyst for methanol oxidation.



**Figure S3** (a) CV curves of Ni/CNT-500 and Ni/CB-500 catalysts in 0.1 M NaOH solution at a scan rate of 100 mV/s; (b) CV curves of Ni/CNT-500 catalyst in 0.1 M NaOH solution at a scan rate of 100 mV/s in presence of 0.08 M methanol, the CV curve in absence of methanol is also incorporated for comparison.

### SI 5. Current density of methanol oxidation for some Ni-based catalysts

Table S1 lists the current density of some carbon black (CB) and glass carbon (GC) supported Ni catalysts. In a moderate methanol concentration of 0.3~1.0 M, the current density varies in the range of 15 to 150 mA/cm<sup>2</sup> for different catalysts.

In order to compare the catalytic activity of Ni/G-500 catalyst with that of other reported Ni catalysts in Table S1, we also carried out CV experiments for Ni/G-500 catalyst using comparable testing parameters (10 mV/s in 1.0 M NaOH containing 0.5 M methanol) as shown in Figure S4. The current density is 77 mA/cm<sup>2</sup> at a scan rate of 10 mV/s, which is higher than the activity of carbon black supported Ni catalysts<sup>1-4</sup>.

**Table S1** A comparison of current density of some Ni-based catalysts for methanol oxidation in alkaline medium

catalysts	current density (mA/cm <sup>2</sup> )	testing conditions				references
		scan rate (mV/s)	electrolyte	methanol concentration	reference electrode	
Ni/GC	150	50	1.0 M KOH	0.5 M	Hg/HgO	Ref. 23*
Ni/GC	40	10	1.0 M NaOH	0.3 M	Ag/AgCl	Ref. 24*
Ni/GC	40	10	1.0 M NaOH	0.3 M	Ag/AgCl	1
Ni/CB	75	10	1.0 M NaOH	0.5 M	Ag/AgCl	2
Ni-P/C	15	10	0.1 M KOH	0.5 M	Hg/HgO	3
Ni/CB	50	50	1.0 M NaOH	1.0 M	Hg/HgO	4

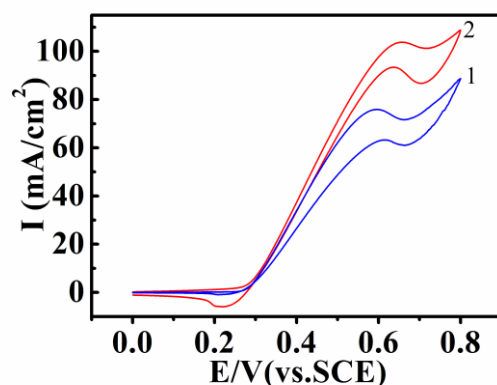
Note: Refs 23 and 24 are given in text.

1 I. Danaee, M. Jafarian, F. Forouzandeh, F. Gobal and M. G. Mahjani, *Int. J. Hydrogen Energy*, 2009, **34**, 859

2 I. Danaee, M. Jafariana, A. Mirzapoor, F. Gobal and M. G. Mahjani, *Electrochimica Acta*, 2010, **55**, 2093.

3 R. M. Abdel Hameed and K. M. El-Khatib, *Int. J. Hydrogen Energy*, 2010, **35**, 2517.

4 Q. Jiang, L. H. Jiang, H. Y. Hou, J. Qi, S. L. Wang and G. Q. Sun, *J. Phys. Chem. C*, 2010, **114**, 19714.



**Figure S4** CV curves of Ni/G-500 catalysts in 1 M NaOH solution containing 0.5 M methanol at a scan rate of 10 mV/s (1), 100 mV/s (2).

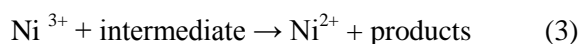
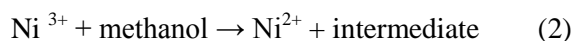
#### SI 6. CV curves of Ni/G-500 catalyst in methanol of different concentration

The current density of Ni/G-500 catalyst changed with methanol concentration is shown in Figure S5. With increasing methanol concentration, the anodic peak current density increases significantly, while the cathodic current density suffers slight reduction. The cathodic current decrease could be attributed to the consumption of NiOOH species during the methanol oxidation on the positive-going sweep (Ref. 24). The opposite trend between the oxidation and reduction peak current related to methanol concentration is indicative of a catalytic mechanism for the Ni<sup>3+</sup> active species proposed by Fleischmann and Virtes et al (Refs. 36-38). The involved reactions taken from these papers are shown as follows (Refs. 24, 36 & 37):

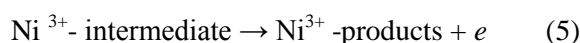
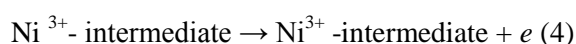
The redox transition of nickel species on the surface of catalyst is:

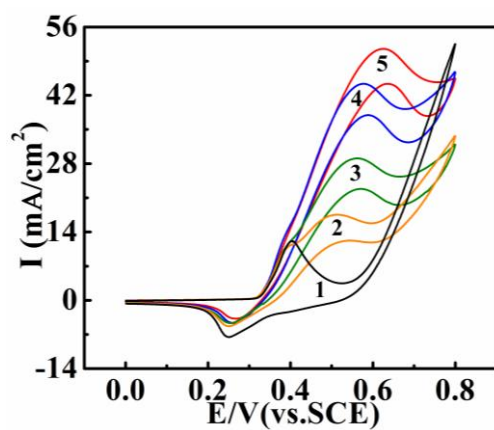


and methanol is oxidized on the surface via the following reaction (Refs. 36 & 37):



Where Ni<sup>3+</sup> sites are regenerated by the power source and then direct electrooxidation reactions take place on the Ni<sup>3+</sup> oxide surface (Ref. 38):





**Figure S5.** CV curves of the catalysts in 0.1M NaOH solution in (1) 0, (2) 0.08, (3) 0.2, (3) 0.3 and (4) 0.45 M methanol.