



## Full Length Article

# The additive effect of graphene in nickel phosphate/graphene composite and enhanced activity for electrochemical oxidation of methanol



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## ABSTRACT

Graphene doped nickel phosphate/graphene composite (NiPO/G) is prepared by the one-pot hydrothermal synthesis. NiPO/G shows a combined structure of nanospheres and flakes aggregate as well as graphene layered structure. There is strong guest-host interaction between the nickel phosphate (NiPO) and graphene. The change of the charge density of NiPO is revealed by Ni 2p XPS spectra where a down shift is observed on NiPO/G compared with the pure VSB-5. Impressively, the NiPO/G exhibits much higher electro-catalytic activity (12 times compared with VSB-5) and lower over-potential for methanol electro-oxidation than the pure VSB-5 in alkaline medium. The positive correlation between the scan rates and the anodic currents implies a single diffusion-controlled kinetic process. The enhancement of the electro-catalytic activity is due to the synergistic interaction effect between graphene and NiPO.

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## 1. Introduction

The growing environmental problems such as climate change, environmental pollution, and the exhaust of fossil fuels have triggered the worldwide interest in developing sustainable and clean energy technology [1–3]. Due to its high energy conversion efficiency, fuel portability, non-pollution, fuel cell is considered as future energy conversion devices [4]. As a member of fuel cells, Direct methanol fuel cell (DMFC) has attracted considerable interest due to abundant raw materials (methanol), low operating temperature (297 K), high energy density (6100 Wh kg<sup>−1</sup>) as well as low pollution and safely delivered than hydrogen [5]. It is known that high methanol crossover, slow electrode kinetics of methanol oxidation and a high cost of noble metals are the main obstacles inhibiting application of DMFCs [6].

Generally, as to DMFCs, there are two categories according to whether the electrolyte is acidic or alkaline. Alkaline DMFC has also attracted growing attention nowadays. In this field, Pt and Pt-based alloys have been widely studied as anode catalyst due to their high catalytic activity for electro-oxidation methanol. However,

Pt-based catalyst is always poisoned by CO and its intermediates which is owing to the decomposition of methanol. Many researches have been focused on the highly efficient and much cheaper non-noble metals or their complexes for substitution of precious metals [6–13]. Among these materials, transition metal oxides/hydroxides catalysts, such as NiO, Co<sub>3</sub>O<sub>4</sub>, MnO<sub>x</sub>, CoO, Ni(OH)<sub>2</sub> and Co(OH)<sub>2</sub> for DMFC are regarded as good candidates [14–16]. Particularly, nickel based materials are attractive catalysts for direct electro-oxidation of methanol due to their lower cost. However, it is still a key challenge to explore novel transition metal catalysts with catalytic activity, just that the comparatively low electronic conductivity and poor catalytic activity of these metal oxides hinder their further applications. Besides the transition metal oxides/hydroxides, in previous work, we have developed mesoporous nickel phosphates materials series applied in methanol electro-oxidation. Their high surface area, coupled with their high activity and stability, provide potential use as electro-catalysts to overcome the drawbacks of the reported Ni-contained materials [17,18]. In contrast to the precious metals, the redox activity of nickel phosphates materials still need to be further increased. As a kind of main reason for low activity of Ni-contained materials, poor conductivity restrains their application [2]. In order to overcome such disadvantages, the conductive additives can be explored. The most common is carbon materials such as carbon black, graphite, carbon nanotubes and graphene [19–21].

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Graphene, a 2D atomically thin film of carbon atoms, a huge open  $\pi$ -electron system with a combination of armchair and zigzag edges that are analogous to *cis*- and *trans*-polyacetylenes, respectively. Aside from the unique combination of strength, ductility and conductivity, it also has remarkable chemical inertness such as resistance to HF [22,23]. Graphene has been investigated as a support for low-temperature fuel cell catalysts. As conductive support, graphene can highly disperse precious metal and metal oxide catalysts. The proper dispersal of these metal particles by graphene could make low-loading catalysts feasible for fuel cell operation, further lowering the cost of the cell system [24,25]. However, as to transition metal oxides/hydroxides system, the high proportion of the carrier in composites would make active material proportion reduce, which will affect the apparent specific performance. Thus, their amount must be controlled as less as possible to guarantee the energy density, especially volumetrically of the electrode. Moreover, if it is well dispersed, all carbon atoms on graphene can contribute to the formation of the conductive network. With much less amount of conductive additive, the electronic conductivity of electrode can be greatly improved [26,27]. Such graphene additives can even adjust material structure.

In this present work, graphene doped nickel phosphate/graphene composites (NiPO/G) were prepared via a facile hydrothermal method. The physicochemical properties were characterized and further the effect of graphene additive on nickel phosphate structure was investigated in detail. Their electro-catalytic behavior towards methanol oxidation reaction (MOR) was investigated, which exhibited high electro-catalytic activity and good long-term stability.

## 2. Experimental

### 2.1. Preparation of materials

All the reagents in this experiment were the analytical grade and were used without any further purification. As to the synthesis of VSB-5, a large pore nickel phosphate molecular sieve, the experimental details followed the previous methods we have developed [28]: In a typical synthesis method,  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  (4.75 g) was put into a beaker and dissolved in deionized water  $\text{H}_2\text{O}$  (30 mL), then added  $\text{H}_3\text{PO}_4$  (1.15 g, 85%), followed by the dropwise addition of  $\text{NH}_3 \cdot \text{H}_2\text{O}$  (3.1 mL, 28%) and then stirred for 4 h. A starting gel with molar composition 0.5  $\text{H}_3\text{PO}_4$ : 1.0  $\text{NiCl}_2$ : 3.0  $\text{NH}_3$ : 100  $\text{H}_2\text{O}$  was prepared at 333 K. The gel was put into a 50 mL Teflon-lined autoclave at 453 K for 5 days, then the mixture was washed by centrifugation, dried to give VSB-5 raw powder. At last, the VSB-5 was synthesized by calcination the VSB-5 raw powder at 573 K for 4 h with the heating rate  $10\text{ K min}^{-1}$ .

The method of synthesis NiPO/G was the same as that of VSB-5, only with the replacement of the deionized water by different concentrations of graphite oxide (GO) solution. That was to say  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  (4.75 g) was put into a beaker and dissolved in graphite oxide (GO) solution not  $\text{H}_2\text{O}$ . When VSB-5 was synthesized, the GO was also reduced synchronously to graphene. The GO solution containing 60 mg, 80 mg, 100 mg and 200 mg of GO was employed to synthesize NiPO/G-60, NiPO/G-80, NiPO/G-100 and NiPO/G-200 hybrids, and the content of graphene in the hybrid composites is 3.2 wt.%, 4.2 wt.%, 5.3 wt.% and 10.6 wt.%, respectively.

The GO was synthesized by oxidation of purified natural small graphite and graphite flakes according to a modified Hummer's method [29]. Typically, the mixture of graphite (10 g) and sodium nitrate (10 g) was stirred by mechanical agitator in the concentrated sulfuric acid (230 mL) in the ice bath, and then 30 g of potassium permanganate was slowly put into the system within 10 min. After 3 h, the mixture was heated to 308 K for 4 h, and then the deionized

water (460 mL) was added to the mixture slowly ( $<363\text{ K}$ ). After the water was added completely, the temperature of the slurry was increased until 371 K and it was kept at that temperature for 3 h. The batch was poured into a 3 L beaker which filled with 2 L deionized water. Immediately, the hydrogen peroxide (100 mL, 30%) and hydrochloric acid (300 mL, 37%) was added into the mixture. Remove that supernatant twice a day until it did not show any precipitation with  $\text{AgNO}_3$  solution. The mixture was filtered and the cake was put into oven (333 K) for 2 weeks and then carefully powdered to get GO.

### 2.2. Materials characterization

Powder X-ray diffraction (XRD) performing on a RINTD/MAX-2500 X-ray diffractometer using  $\text{Cu-K}\alpha$  radiation ( $\lambda = 1.5406\text{ \AA}$ ) was used for determining the crystal structure of the samples. Raman spectroscopy was obtained using a Horiba HR800 Raman spectroscopy with a 632.8 nm line from He-Ne laser. XPS spectra were obtained using an Axis Ultra spectrometer (Kratos, UK). A mono  $\text{Al-K}\alpha$  (1486.6 eV) X-ray source was used at a power of 225 W (15 kV, 15 mA). To compensate for surface charge effects, binding energies were calibrated using the C 1s hydrocarbon peak at 284.8 eV. UV-visible spectroscopy (Cary Varian 50) with a 1 cm quartz cell was used. FTIR spectra of the samples were measured on a Bruker Tensor spectrometer with KBr as the solid dispersant.

### 2.3. Preparation of nickel electrodes and electrochemical measurements

Electrochemical measurements were conducted using CHI760D electrochemical workstation (CHI, Shang Hai) with three-electrode setup. Glassy carbon electrode (GCE, 3 mm diameter, Tian Jin Aida, Inc.) acted as the working electrode, with  $\text{Ag/AgCl}$  as the reference electrode, and platinum wire as the counter. Glassy carbon electrode (GCE) was polished with 70 nm  $\text{Al}_2\text{O}_3$  power, rinsed by deionized water, ethanol and deionized water, and dried at room temperature. 5 mg material was dispersed in 1 mL of 0.1 wt.% nafion solution. 10  $\mu\text{L}$  of well-dispersed catalysts suspension was dropped on the surface of glassy carbon to fabricate the modified GCE electrode. The solvent was evaporated under an infra-red lamp. The electrocatalytic performances of NiPO/G electrodes were examined by cyclic voltammetry (CV) and chronoamperometry (CA) tests. The electrolytes for MOR tests were 0.1 M NaOH and all the tests were carried out at room temperature ( $\sim 298\text{ K}$ ).

## 3. Results and discussion

Fig. 1 shows the X-ray diffraction (XRD) patterns of the as-prepared products. All peaks of VSB-5 can be readily indexed as those of typical VSB-5 phase reported previously [30]. The diffraction peaks of the NiPO/G-60 composites resemble that of the pure VSB-5, indicating that the structure of the host is preserved during the synthetic processes. Intensity of some peaks decrease and shift to small angle for the NiPO/G-60 compared with that of the as-synthesized VSB-5. As to NiPO/G-80, this phenomenon is more serious. The assembly of graphene in the channels and surface of VSB-5 will decrease the scattering ratios between the walls of the VSB-5 channels and graphene, which may result in the intensity decrease of some diffraction peaks, such as (100), (110) and (200). These three diffraction peaks of NiPO/G-100 and NiPO/G-200 are even disappeared. That is, the graphene can regulate the structure of VSB-5 material. As to GO additive, there are lots of hydroxyl and epoxy groups in the plane surface of GO besides a small amount of carboxyl in the edge. We know that hydroxyl, epoxy and carboxyl groups are all hydrophilic but the graphite domain skeleton of GO is hydrophobic. The  $\text{PO}_4^{3-}$  is easy to combine with the hydrophilic

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