

## Supporting information

### High-efficiency activation of C-H bond to synthesize the *p*-methoxy benzaldehyde over MnO<sub>2</sub>/CNTs/Gr catalyst

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# 1. Experimental

## 1.1 Materials

Carbon nanotubes (CNTs) and graphene (Gr) were purchased from Suzhou TanFeng Technology Co., Ltd. Nitric acid (HNO<sub>3</sub>), polyethylene glycol (M=6000), sulfuric acid (H<sub>2</sub>SO<sub>4</sub>), KMnO<sub>4</sub> and ethanol were purchased from Beijing Chemical Works. All experimental reagents were in analytical grades, and deionized water was utilized in all the experiments.

## 1.2 Preparation of catalysts

MnO<sub>2</sub>/CNTs/Gr catalyst was prepared by hydrothermal technique. The CNTs were firstly surface-oxidized and purified in 60% nitric acid for 4 h. It was shown in Fig. S2 that hydrophilic groups are successfully modified on the surface. The good dispersibility creates favorable conditions for subsequent loading of MnO<sub>2</sub>. After 20 min ultrasonic treatment, 0.09 g modified CNTs stably dispersed in 100 mL deionized water. 30 mL Gr solution was then added into the CNTs solution under sonication condition. When the mixture dissolved, the solution was standing for more than 12 h. CNTs/Gr catalyst was obtained after drying and grinding. Subsequently, the substrates (CNTs or CNTs/Gr) were immersed in 100 mL mixture solution consisting of 0.1 g polyethylene glycol (M=6000) and 0.09 g KMnO<sub>4</sub>. After treating by ultrasonic dispersion for 2h, the pH of the solution was adjusted to 3 using 0.5 M H<sub>2</sub>SO<sub>4</sub>. The temperature was increased to 70°C and kept stirring for 3 h. After that, the catalysts were washed with ethanol and deionized water for 3 times. The as-made samples were dried at 100°C for 24 h to get the final products (MnO<sub>2</sub>/CNTs or MnO<sub>2</sub>/CNTs/Gr).

## 1.3 Characterization

The phase purity and crystal structure of the samples were evaluated using X-ray diffraction (XRD, Ultima IV, Rigaku Corporation, Japan) with Cu K $\alpha$  ( $\lambda = 0.1541$  nm) radiation at a scan rate of 3 min<sup>-1</sup> from 5° to 90°. The morphology and microstructure of the CNTs and as-prepared composites were characterized by scanning electron microscope equipped with an energy-dispersive X-ray spectroscopy (SEM-EDS, SU8000, Hitachi Limited, Japan), and transmission electron microscope (TEM, Talso 200, FEI company, USA). The surface elements and electronic states of the composites were investigated by an Escalab 250Xi X-ray photoelectron spectroscopy (XPS, Escalab 250Xi, Thermo Fisher Scientific, USA).

## 1.4 Electrochemical measurement

Electrochemical studies were performed in three-electrode testing system at room temperature. All tests were carried out on CHI 660E electrochemical workstation (CH Instruments, Inc., Shanghai) with Pt foil as counter electrode and saturated calomel electrode (SCE) as reference electrode. Modified graphite electrode was used as work electrode. Typically, the bath solution was prepared as follows: 5.0 mg of the catalysts was dispersed in

1 mL of isopropanol and 60  $\mu$ L Nafion solution (5% wt). The solution was then sonicated to get a uniform mixture. After ultrasonic homogenization, 20  $\mu$ L of the dispersed catalyst was drop-casted on graphite electrode, and dried in the oven for 15 min at 70°C.

Cyclic Voltammetry (CV) was performed by sweeping the potential range of 0-2.2 V at scan rates of 5 mV/s in 1.5 M sulfuric acid including 30% acetone (acetonitrile, isopropanol, DMF), tetraethylammonium chloride (tetrabutylammonium hexafluorophosphate, 1-butyl-3-methylimidazolium tetrafluoroborate) and 5 mM *p*-MT solution. The electrolysis process is conducted in an H-cell separated by a piece of anion exchange membrane (AEM).

### 1.5 Product quantification

After reaction, the electrolyte was purified by extracting with 10 mL ethyl acetate for three times. The combined ethyl acetate phase was further diluted to 100 mL. 100  $\mu$ L of the solution was resolved in 5 mL methanol. Once filtered with 0.22  $\mu$ m PTFE membranes, samples were analyzed by high performance liquid chromatography (HPLC, Agilent 1100, Agilent technologies, USA).

The amounts of *p*-MBA in the samples were characterized and quantified by HPLC equipped with an ultraviolet-visible detector and C18 column (25 cm  $\times$  4.6 mm  $\times$  5  $\mu$ m, Shim VP-ODS, Shimadzu Technologies, Japan). Mobile phase is consisted of 30% water and 70% methanol. Flow rate was 0.8 mL/min. The injection volume was 20  $\mu$ L and wavelength used for the detection was 271 nm.

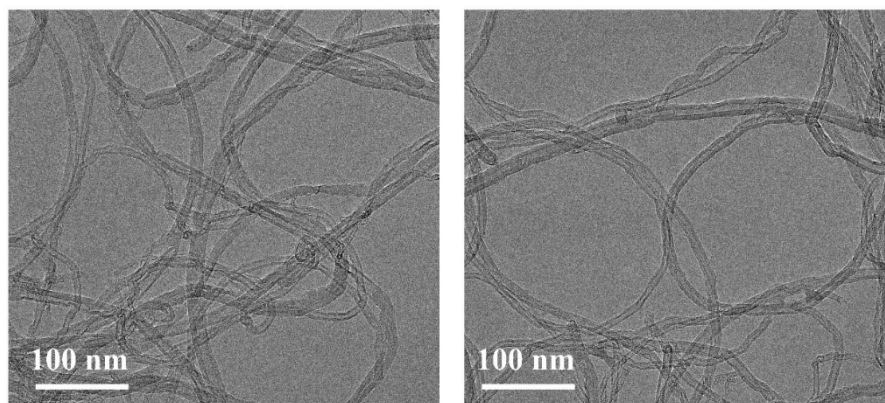


Figure S1. TEM images of CNTs.

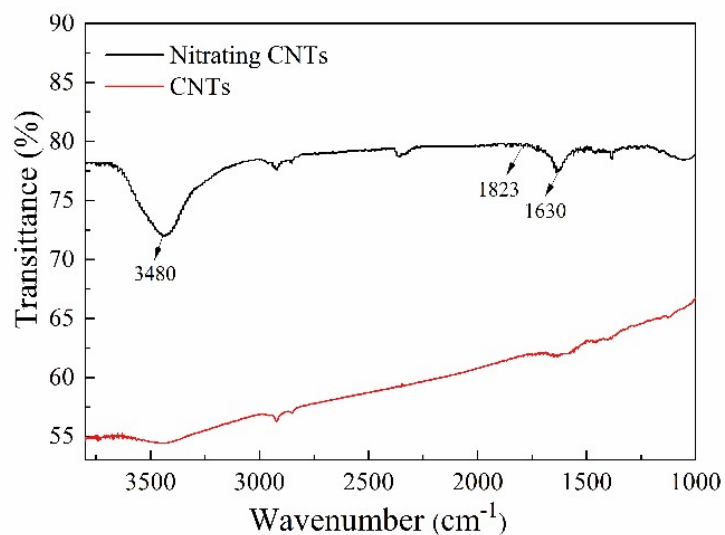


Figure S2. Infrared outer spectrum of CNTs before and after nitrating.

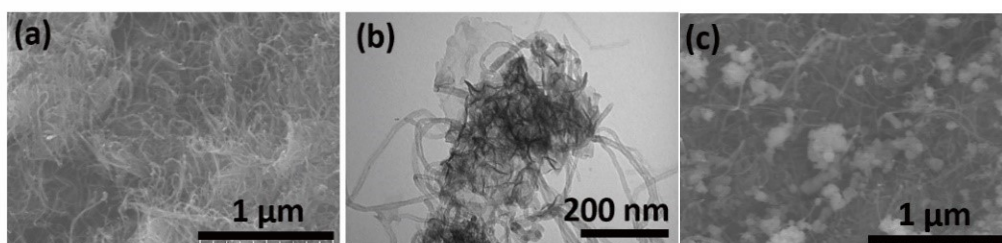


Figure S3. (a) SEM image of CNTs/Gr; (b) TEM image of CNTs/Gr. (c) SEM image of MnO<sub>2</sub>/CNTs/Gr.

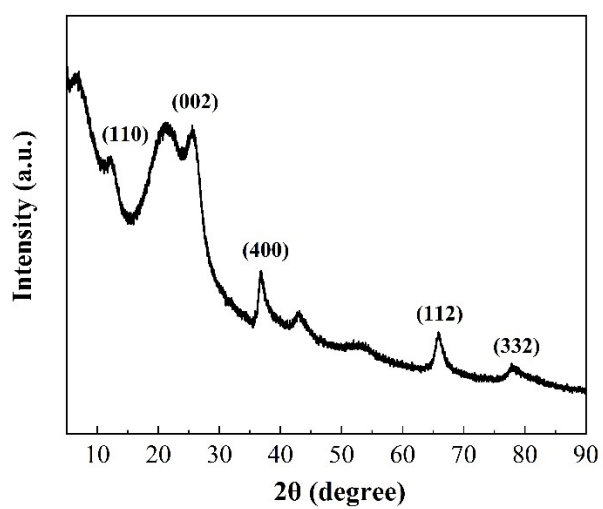


Figure S4. XRD result of MnO<sub>2</sub>/CNTs

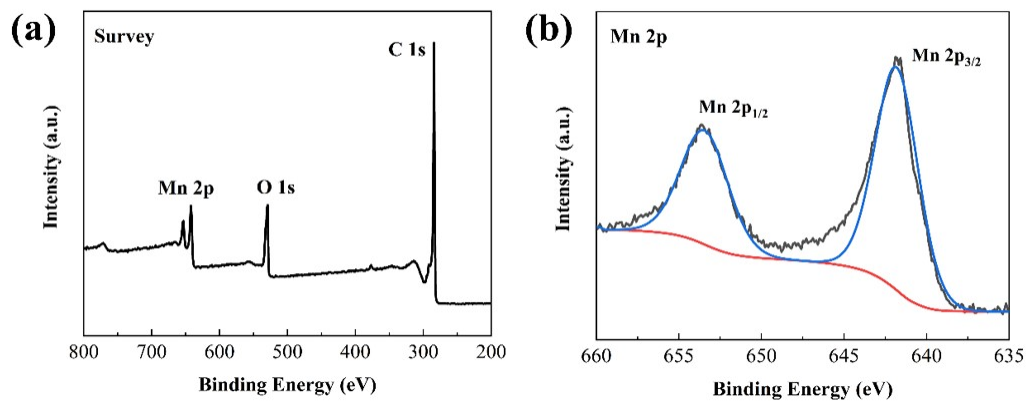


Figure S5. XPS result of MnO<sub>2</sub>/CNTs

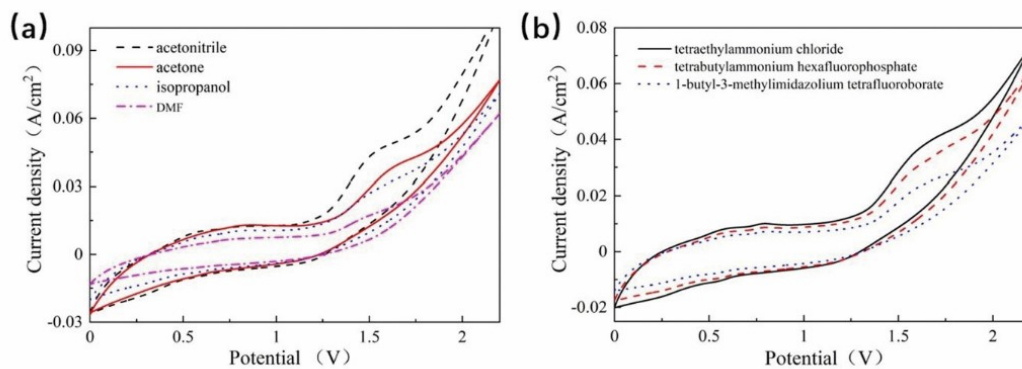


Figure S6. Cyclic voltammetry curves of *p*-MT in different (a) solvents and (b) co-electrolytes.

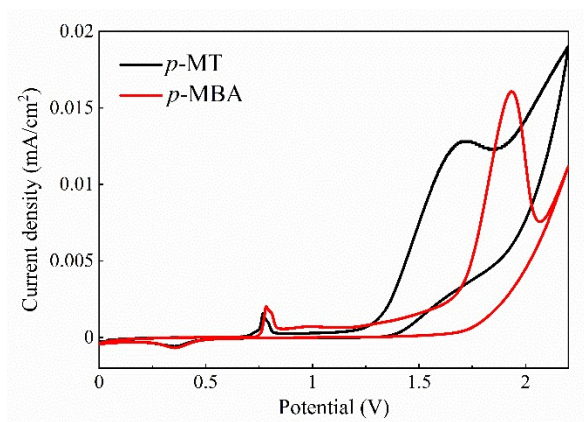


Figure S7. Cyclic voltammetry curves of *p*-MT and *p*-MBA.

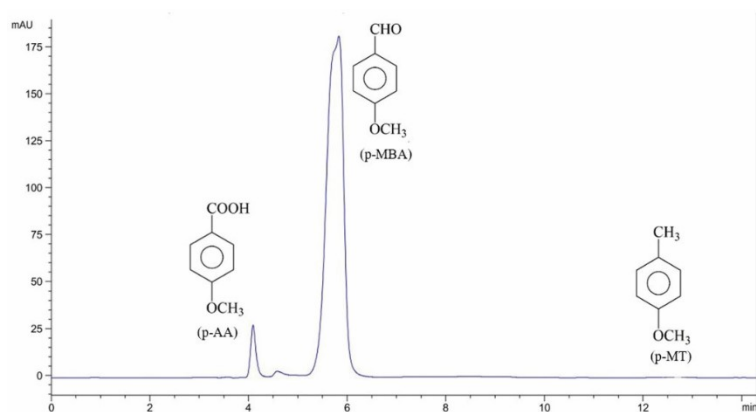


Figure S8. HPLC chromatogram trace of electrochemical oxidation *p*-MT on MnO<sub>2</sub>/CNTs/Gr electrocatalyst.

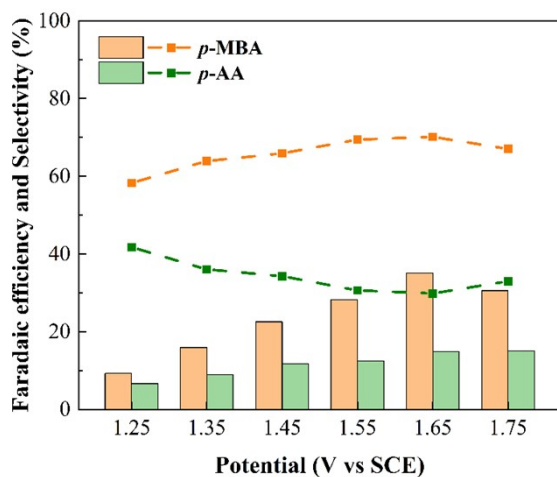


Figure S9. Faradaic efficiency (column) and selectivity (line) of the electrocatalytic oxidation of *p*-MBA on the graphite electrodes loading MnO<sub>2</sub>/CNTs catalyst.