

# Journal of Materials Chemistry A

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

*Accepted Manuscripts* are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

# Heterostructured Co<sub>3</sub>O<sub>4</sub>/PEI-CNTs Composite: Fabrication, Characterization and CO Gas Sensors at Room Temperature

Lifang Dang<sup>a</sup>, Guo Zhang<sup>a</sup>, Kan Kan<sup>a,c</sup>, Yufei Lin<sup>a</sup>, Fuquan Bai<sup>d</sup>, Liqiang jing<sup>a</sup>, Peikang Shen<sup>e</sup>, Li Li<sup>\*a,b</sup> and Keying Shi <sup>\*a</sup>

Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

DOI: 10.1039/b000000x

In this paper, a new controllable dispersion of Co<sub>3</sub>O<sub>4</sub> nanoparticles (NPs) on multiwalled carbon nanotubes (CNTs) functionalized with branched polyethylenimine (PEI) had been synthesized by a noncovalent method. In Co<sub>3</sub>O<sub>4</sub>/PEI-CNTs composite, CNTs not only prevent Co<sub>3</sub>O<sub>4</sub> NPs from aggregation, but also provide electron transfer path. The domain sizes of Co<sub>3</sub>O<sub>4</sub> NPs on Co<sub>3</sub>O<sub>4</sub>/PEI-CNTs composite synthesized by hydrothermal time for 5 h at 190 °C (named C-5) is about 4-8 nm. The surface area to volume ratio increase, the overlapped parts of Co<sub>3</sub>O<sub>4</sub> grains contain a high density of defects, which provide a greater number of available active centers for gas/surface reactions. The Co<sub>3</sub>O<sub>4</sub>/PEI-CNTs composite displays the excellent sensitive characteristics to CO even at the level of 5 ppm at room temperature (RT). The C-5 sensor with rapid response property and excellent stability at RT shows highly promising applications in gas sensor.

## 1. Introduction

Carbon monoxide (CO) exposure may cause both acute and chronic health effects. But CO pollutant and harm to human health may be easily missed due to its colorless and odorless. The Occupational Safety and Health Agency recommends a 10 h time-weighted average exposure of 35 ppm, whereas the National Institutes of Occupational Safety and Health recommends an 8 h time-weighted average exposure of 50 ppm.<sup>1</sup> These demonstrate the importance of environmental gas sensor for continuous surveillance, to identify hazardous environments where significant CO levels exist. Thus, it is important to develop CO sensors and detect the CO concentrations in factories, indoor atmospheres, vehicle emissions, natural gas emissions and industrial wastes.

As an important p-type semiconductor, cobalt oxide (Co<sub>3</sub>O<sub>4</sub>) is of special interest due to its potential applications as heterogeneous catalysts, magnetic properties, electrochromic

devices and gas sensors.<sup>2-4</sup> Co<sub>3</sub>O<sub>4</sub> with different morphologies such as nanoplates, well organised cabbage like structures and microspherical composites was reported recently by Cao *et al.*<sup>5</sup> They investigated the CO and alcohol sensing properties of the synthesized nanostructured Co<sub>3</sub>O<sub>4</sub>. The synthesized nanostructured Co<sub>3</sub>O<sub>4</sub> exhibited good sensitivity (> 8-50 ppm), response to alcohol at an operating temperature of 300 °C. It was found to be insensitive to 50 ppm CO at 300 °C but the resistance change was still at a much lower level for 1000 ppm CO.<sup>6</sup> Li *et al.*<sup>7</sup> prepared Co<sub>3</sub>O<sub>4</sub> nanotubes by a thermal decomposition of Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O within an ordered porous alumina templates and investigated the gas sensing characteristics of the nanotubes exposed to H<sub>2</sub> and alcohol. The prepared Co<sub>3</sub>O<sub>4</sub> nanotubes exhibited an excellent sensitivity to hydrogen and alcohol at room temperature. Sun *et al.* synthesized Co<sub>3</sub>O<sub>4</sub> microsphere by solvothermal method. The Co<sub>3</sub>O<sub>4</sub> microsphere show much higher ethanol sensitivity and selectivity at a relatively low temperature (135 °C) compared with those of commercial Co<sub>3</sub>O<sub>4</sub> NPs.<sup>8</sup> Co<sub>3</sub>O<sub>4</sub> semiconductor materials have good development prospects as gas sensors. However, it is difficult for a single oxide based semiconductor gas sensor to satisfy all practical requests: high and fast response, stability, and low energy consumption. To overcome these disadvantages, sensors based on two or more components have been explored for well-designed nanostructures and well-fabricated heterojunction interaction between these components.<sup>9,10</sup> Therefore, in recent years, much effort has been made to develop new methods for the preparation of Co<sub>3</sub>O<sub>4</sub> composited nanomaterials, including thermal deposition, and hydrothermal synthesis *etc.*<sup>11,12</sup> These methods have emerged as attractive and simple routes for the processing of such metal oxide composite.

CNTs are promising building blocks for potential applications in many fields such as nanoelectronic and gas sensors due to their

<sup>a</sup> Key Laboratory of Functional Inorganic Material Chemistry, Ministry of Education. Key Laboratory of Physical Chemistry, School of Chemistry and Material Science, Heilongjiang University, Harbin, 150080, P. R. China

<sup>b</sup> Key Laboratory of Chemical Engineering Process & Technology for High-efficiency Conversion, School of Chemistry and Material Science, Heilongjiang University, Harbin 150080, P. R. China

<sup>c</sup> Daqing Branch, Heilongjiang Academy of Sciences, Daqing 163319, P. R. China.

<sup>d</sup> State Key Laboratory of Theoretical and Computational Chemistry, Institute of Theoretical Chemistry, Jilin University, Changchun 130023, China.

<sup>e</sup> Department of Physics and Engineering Sun Yat-sen University Guangzhou, 510275, P. R. China

E-mail: shikeying2008@163.com; llwji@sohu.com; Fax: +86 4518667 3647; Tel: +86 451 8660 9141

unique structure-dependent physical and chemical properties. CNTs have the potential to provide unique properties leading to advanced catalytic systems, and very sensitive photo/chemical sensors.<sup>13-17</sup> In particular, CNTs are ideal templates for the decoration of functional NPs. Surface functionalization and hybridization of CNTs currently attracts significant research interest.<sup>18</sup> So, CNTs were introduced into the gas sensitive materials to reducing the corresponding temperature.<sup>19, 20</sup> Wu *et al.* doped 0.1% CNT into Co<sub>3</sub>O<sub>4</sub>-SnO<sub>2</sub> compositions. It was found that the sensor response varied under CO concentrations ranging from 20-1000 ppm at 25 °C. The response time was 21 s when the CO concentrations was 600ppm. But the formation process of gas sensor compositions have not been further investigated.<sup>21</sup>

Herein, we present a simple noncovalent assembly of CNTs functionalized by PEI for density controllably and uniformly assembling the CNTs with Co<sub>3</sub>O<sub>4</sub> nanoparticles (Co<sub>3</sub>O<sub>4</sub>/PEI-CNTs composite). The approach provided high density homogeneous functional groups on the CNTs' sidewalls for binding Co<sup>2+</sup> ions or/and Co<sub>3</sub>O<sub>4</sub> NPs. The Co<sub>3</sub>O<sub>4</sub> NPs are dispersed on conducting scaffold of PEI-CNTs. The beneficial aspects of the PEI-CNTs in improving the gas sensing performance of the Co<sub>3</sub>O<sub>4</sub>/PEI-CNTs composites are presented. The CNT-based hybrid composites are becoming the subject of increasing interest in exploiting large-area, low-cost, flexible electronic and gas sensor.

## 2. Experimental

### 2.1 Synthesis

All chemicals were purchased with analytical grade and used without further purification. CNTs are from Shenzhen Nanotech Port Co. Ltd, with a diameter of 30-80 nm and lengths ranging of 5-30 μm. The purity is higher than 99%. 2.4 mg CNTs functionalized by the acid solution (HNO<sub>3</sub>:H<sub>2</sub>SO<sub>4</sub> in 1:3 (v/v) ratio) and 4 mg PEI (branched PEI, M<sub>w</sub>= 600, Aldrich) were dissolved and dispersed in 100 mL distilled water under magnetic stirring, the pH was adjusted to be about 9.0 and kept about 1h. Then, 20 mL Co(NO<sub>3</sub>)<sub>2</sub> solution of the concentration about 2 mg/mL was added dropwise to the mixed solution. The pH was kept below 9.0 during the mixing process. Then, 90 mg/mL NaOH solution was slowly added to the solution, and the pH was adjusted to be about 12.0. At the same time, the air flow was set to the solution with 50 mL/min for 2 h. Then, the mixed solution/precursor was placed for 24 h at RT. The precipitate was filtrated and washed by deionized water. The obtained precipitate was dispersed in deionized water and transferred to a Teflon-lined stainless steel autoclave. Hydrothermal synthesis was conducted at 190 °C for 1, 3, 5 and 7 h, respectively. The obtained Co<sub>3</sub>O<sub>4</sub>/PEI-CNTs composite were named as C-1, C-3, C-5 and C-7 respectively.

### 2.2 Material characterizations

The structures and compositions of the as-prepared products were characterized by X-ray powder diffraction (XRD, D/max-III B-40 kV, Japan, Cu-K<sub>α</sub> radiation, λ=1.5406 Å). The structures of the synthesized samples were studied by TEM (JEOL-JEM-2100, 200 kV). The Fourier transform infrared (FT-IR) spectra were carried out with FT-IR Spectrometer (Perkin Elmer Spectrometer, KBr pellet

technique). Thermo gravimetric (TG-DTA) analysis of the samples was performed using a TA-SDTQ600. The air flow rate was maintained at 60 mL/min, and the temperature of the reactor was increased at the rate of 8 °C/min. Electrochemical impedance spectroscopy (EIS) and Mott-Schottky (MS) plot measurements were carried out by using an electrochemical working station (CHI660C, Shanghai, China) in a half-cell setup configuration at RT. In EIS measurement the range of frequency was 0.01 Hz~100 kHz and the excitation amplitude was 5 mV.

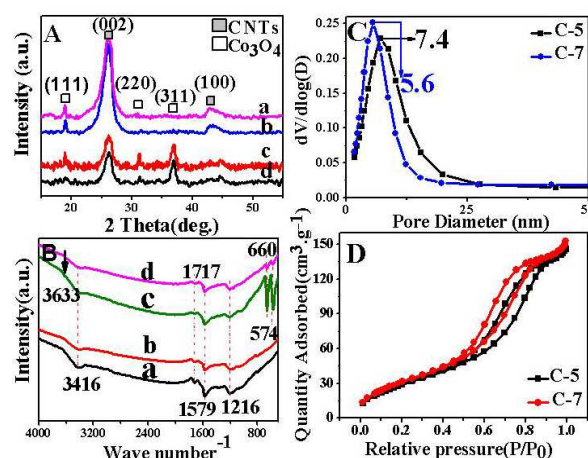
### 2.3 Gas sensing tests

An alumina substrate (99.6% 7×5×0.38 mm) with two interdigitated Au electrodes on its top surface was used. Each Au electrode contained 100 fingers which interleaved each other, and the distance between two fingers was 20 μm (Fig.S1). The Au electrodes were cleaned by diluted HCl, distilled water and acetone. A certain amount of Co<sub>3</sub>O<sub>4</sub>/PEI-CNTs composite was dispersed in ethanol to form suspension. Sensors were fabricated by a simple drop-casting method and dried at 70 °C for 5 h. The sensor was installed into a test chamber with an inlet and an outlet. The electrical resistance measurements of the sensor are carried out at RT and a relative humidity (RH) around 26%. CO gas concentration was controlled by injecting volume of the gas and the chamber was purged with air to recover the sensor resistance. The sensor response<sup>22</sup> was defined as the ratio (R<sub>C</sub>-R<sub>0</sub>)/R<sub>0</sub>%, where R<sub>0</sub> is the sensor resistance in air, and R<sub>C</sub> is the resistance that in CO gas.

## 3. Results and discussion

### 3.1. Structure Characterizations

Fig.1 shows the XRD patterns and FT-IR spectra of Co<sub>3</sub>O<sub>4</sub>/PEI-CNTs composite C-1, C-3, C-5 and C-7. The diffraction peaks around 19.0°, 31.3° and 36.8° can be indexed as (111), (220) and (311) planes of face centered cubic phase of Co<sub>3</sub>O<sub>4</sub>.<sup>23</sup> The *d* spacing are 4.67, 2.86 and 2.44 Å, respectively, and the lattice



**Fig. 1** (A) XRD diffraction patterns; (B) FT-IR spectra of Co<sub>3</sub>O<sub>4</sub>/PEI-CNTs composites synthesized by hydrothermal method at 190 °C for different time (a) C-1, (b) C-3, (c) C-5, (d) C-7; (C) The pore-size distribution curve and (D) N<sub>2</sub> adsorption-desorption isotherm of C-5 and C-7.

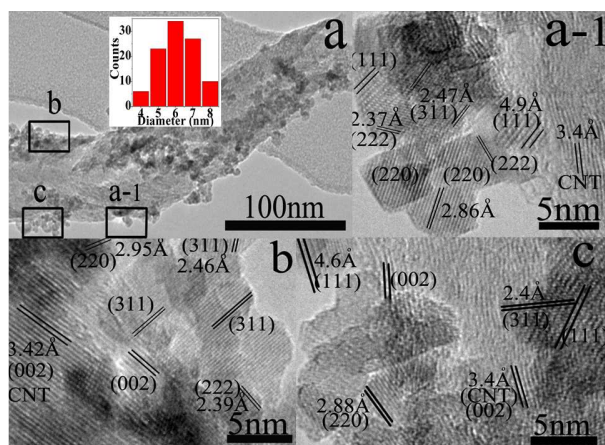
parameters of  $a = b = c = 8.09 \text{ \AA}$  (JCPDS No. 78-1970). In addition, the XRD patterns of Fig. 1A exhibit two main well-resolved Bragg peaks of CNTs, corresponding to the  $2\theta$  of  $26.2^\circ$  and  $41.4^\circ$  ( $d$  spacing of 3.39, and 2.14  $\text{\AA}$ ). These two main peaks can be indexed as the (002) and (100) planes (JCPDS No. 75-1621). The width of the main peak of the CNTs at half-maximum height had been broadened obviously, which indicate the walls of the CNTs were eroded during oxidation and the existence of defect sites.

Furthermore, the (220) and (311) peaks of C-5 and C-7 are wider obviously. The average crystallite size calculated from the XRD data is 8.83 nm. This implies that the existence of small  $\text{Co}_3\text{O}_4$  NPs, when hydrothermal time was conducted at  $190^\circ\text{C}$  for 5 or 7 h. There is no obvious (220) and (311) peaks exist in the C-1 and C-3. This indicates that  $\text{Co}_3\text{O}_4$  crystalline phase of the  $\text{Co}_3\text{O}_4/\text{PEI-CNTs}$  composite can be controlled by changing hydrothermal time. In addition, no obvious characteristic peaks of impurity phases (such as CoO and CoOOH) are present in samples, indicating the high purity of the final products.

The FT-IR spectra of the  $\text{Co}_3\text{O}_4/\text{PEI-CNTs}$  composites are shown in Fig. 1B. The broad peak dominated at about  $3416 (3633) \text{ cm}^{-1}$  corresponded to the N-H stretch of secondary amines and primary amines.<sup>24</sup> There are two weak absorption peaks at about  $1579$  and  $1717 \text{ cm}^{-1}$ , which is attributed to the carbonyl stretching vibration in the -COOH groups.<sup>25</sup> In the region from  $1100$  to  $1500 \text{ cm}^{-1}$ , these absorption peaks correspond to several types of modes of PEI.<sup>26</sup> The sharp absorptions at  $574$  and  $660 \text{ cm}^{-1}$  correspond to Co(III)-O and Co(II)-O stretching vibrations of  $\text{Co}_3\text{O}_4$ .<sup>27</sup> From Fig. 1B, it can be seen that C-5 sample Co (III)-O and Co (II)-O stretching vibrations of  $\text{Co}_3\text{O}_4$  is relatively stronger.

Fig. 1(C, D) shows the  $\text{N}_2$  adsorption-desorption isotherms and BET pore size distribution plots of C-5 and C-7. The isotherm curve demonstrates type IV isotherms in the BET classification. The BET specific surface area and pore size of C-5 and C-7 are about  $112, 96.9 \text{ m}^2 \text{ g}^{-1}$  and  $7.4, 5.6 \text{ nm}$  respectively. The BET specific surface area and pore size of C-5 are larger than that of C-7.

The growth of  $\text{Co}_3\text{O}_4$  nanocrystals on PEI-CNTs was confirmed by TEM and high-resolution transmission electron



**Fig. 2** TEM images of  $\text{Co}_3\text{O}_4/\text{PEI-CNTs}$  composite (C-5); (a) Low magnification TEM image of C-5, the inset shows the diameter

distribution of (a); (a-1), (b) and (c) HRTEM images of (a).

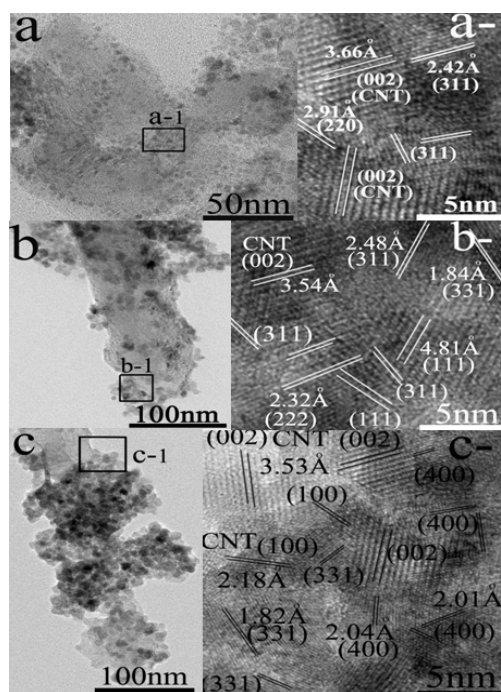
microscopy (HRTEM). The TEM/HRTEM images of C-1, C-3, C-5 and C-7 are shown in Fig.2 and Fig.3. Fig. 2a show that the  $\text{Co}_3\text{O}_4$  NPs dispersed on the surface of PEI-CNTs and formed the composited structure. The sizes of  $\text{Co}_3\text{O}_4$  NPs is about 4-8 nm.

Fig. 2(a-1, b, c) is the HRTEM images of the C-5. The adjacent lattice fringes is around 4.6 ( $\sim 4.9$ ), 2.86 ( $\sim 2.95$ ), 2.4 ( $\sim 2.47$ ) and 2.37 ( $\sim 2.39$ )  $\text{\AA}$ , corresponding to the  $d$  spacing of the (111), (220), (311) and (222) planes of  $\text{Co}_3\text{O}_4$ , respectively. In addition, the (002) plane of CNTs can be observed, and the lattice spacing of 3.4 ( $\sim 3.42$ )  $\text{\AA}$  was got. Moreover, Fig. 2(b, c) shows the defects at the branching locations (interface) of  $\text{Co}_3\text{O}_4$  NPs and CNTs, attributing to the linear and planar defects, which might be formed by the oxide defects caused by PEI.

Fig. 3(a, a-1), Fig.(b, b-1) and Fig. (c, c-1) are the TEM images of the C-1, C-3 and C-7 samples, respectively. The average distance between the adjacent lattice fringes is around 4.81, 2.91, 2.42 ( $\sim 2.48$ ), 2.01 ( $\sim 2.04$ ) and 1.82 ( $\sim 1.84$ )  $\text{\AA}$ , corresponding to the  $d$  spacing of the (111), (220), (311), (400) and (331) planes of  $\text{Co}_3\text{O}_4$ , respectively. Furthermore, the lattice fringes is 3.53 ( $\sim 3.66$ ) and 2.18  $\text{\AA}$ , corresponding to the  $d$  spacing of the (002) and (100) planes of CNTs. Fig. 3c appears to possess the loosely packed structure. The sizes of  $\text{Co}_3\text{O}_4$  particles is 5-10 nm.

Similar with C-5, many defects existed in the samples between  $\text{Co}_3\text{O}_4$  NPs and CNTs as shown in Fig. 3(a-1), (b-1), (c-1). These have the irregular lattice, such as the fringes with the spacing of 2.42-2.48  $\text{\AA}$  corresponding to the (311) plane of  $\text{Co}_3\text{O}_4$ ; the spacing of 1.82-1.84  $\text{\AA}$  corresponding to the (331) plane and the spacing of 2.01-2.04  $\text{\AA}$  corresponding to the (400) plane.

From all the above, it can be found that the  $\text{Co}_3\text{O}_4/\text{PEI-CNTs}$  composite materials with highly dispersed  $\text{Co}_3\text{O}_4$  NPs on PEI-CNTs were prepared by a noncovalent method. The  $\text{Co}_3\text{O}_4$  grains



80

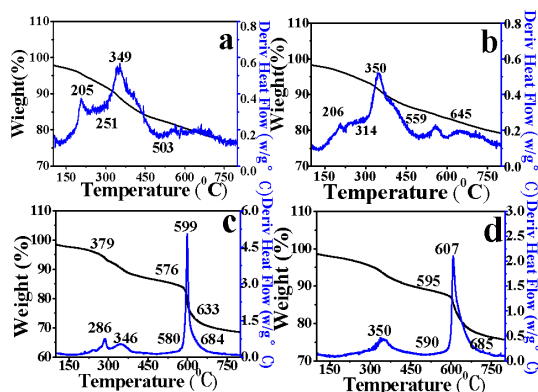
**Fig. 3** TEM/HRTEM images of Co<sub>3</sub>O<sub>4</sub>/PEI-CNTs composites (a), (a-1) TEM/HRTEM images of the C-1; (b), (b-1) TEM/HRTEM images of the C-3; (c), (c-1) TEM/HRTEM image of the C-7.

mostly anchor on defect and functionalization of CNTs or/and PEI-CNTs surface. The dispersion and particle size of Co<sub>3</sub>O<sub>4</sub> on Co<sub>3</sub>O<sub>4</sub>/PEI-CNTs composite were controlled by changing the hydrothermal time. This could be confirmed by the results of TG-DTA and TEM.

Fig.4 shows the TG-DTA results of Co<sub>3</sub>O<sub>4</sub>/PEI-CNTs composites under N<sub>2</sub>. As shown in Fig.4a, there are two main exothermic peaks/oxidation peaks before 800 °C in C-1 and C-3, the temperatures of oxidation are 205 (206) and 349(350) °C, respectively. The strongest peak at 349 (350) °C might be attributed to the oxidation peak of PEI. As for C-5 and C-7, the strongest peaks at 599 (or 607) °C might be attributed to the oxidation peak of CNTs due to the existence of Co<sub>3</sub>O<sub>4</sub>, which can be regarded as an oxygen reservoir under N<sub>2</sub>. CNTs were oxidized by using Co<sub>3</sub>O<sub>4</sub> as the oxidant. Therefore, the exothermic peaks/oxidation peaks between 500 and 800 °C are attributed to the dissociation and oxidation of CNTs.<sup>28</sup>

The PEI content of the Co<sub>3</sub>O<sub>4</sub>/CNTs composites are calculated with 200-400 °C temperatures range. The calculated PEI content of the C-1, C-3, C-5 and C-7 samples are 10.7, 10.9, 8.02 and 6.39 mass % respectively. For all the samples, the synthesis condition of PEI-CNTs is the same; hence, the PEI content of the five samples should be also the same. However, the results of TG are quite different. These indicate that the interaction of PEI with Co<sub>3</sub>O<sub>4</sub> NPs increases with Co<sub>3</sub>O<sub>4</sub> content and hydrothermal time increasing. That is, in the assembling process of the Co<sub>3</sub>O<sub>4</sub>/PEI-CNTs composite, the PEI might interact strongly with the CNTs via n-p stacking interaction, and providing a fixation point for Co<sub>3</sub>O<sub>4</sub> NPs on the CNTs. The calculated Co<sub>3</sub>O<sub>4</sub> content of the C-1, C-3, C-5 and C-7 samples are 6.98, 21.84, 45.1 and 32.5 mass % (see Table S1) (the Co<sub>3</sub>O<sub>4</sub> content of the C-190 synthesized by hydrothermal time for 4 h at 190 °C is 41.7 mass %, as described in our previous work<sup>29</sup>) respectively. For the C-1 and C-3 samples, the amount of Co<sub>3</sub>O<sub>4</sub> is relative lower. At the same time, accompanied with the Co<sub>3</sub>O<sub>4</sub> amount of C-5 and C-7 samples increase, the oxidation peaks of CNTs widen and shift to high temperature.

To study the electrical characteristics of Co<sub>3</sub>O<sub>4</sub>/PEI-CNTs composite, MS and EIS measurements were carried out. Fig. 5 and Fig.S2 show the MS plots of electrodes based on samples synthesized by different hydrothermal time. The negative slopes



**Fig. 4** TG-DTA curves of the samples synthesized by different hydrothermal time with a temperature ramp of 8 °C/min under pure N<sub>2</sub> (a) C-1, (b) C-3, (c) C-5 and (d) C-7.

of MS plots of all the samples show the p-types semi-conducting behavior. The carrier density can be calculated from the slope of MS plots using the equation 1 (eq 1):

$$N_a = (-2/e_0 \epsilon \epsilon_0) [d(1/C^2)/dV]^{-1} \quad (1)$$

where  $e_0$  is the fundamental charge constant,  $\epsilon_0$  is the permittivity of vacuum,  $\epsilon$  is the relative permittivity of Co<sub>3</sub>O<sub>4</sub> ( $\epsilon=12.9$ ).<sup>30</sup> The carrier density of Co<sub>3</sub>O<sub>4</sub> NPs, C-1, C-3, C-5 and C-7 were then calculated to be  $3.50 \times 10^{17}$ ,  $2.23 \times 10^{17}$ ,  $1.33 \times 10^{17}$ ,  $5.40 \times 10^{17}$  and  $2.30 \times 10^{17} \text{ cm}^{-3}$  at frequency of 10 kHz, respectively.  $\epsilon$  is the relative permittivity of CNTs ( $\epsilon = 10$ ).<sup>31</sup> The carrier density of CNTs and PEI-CNTs were  $8.16 \times 10^{18}$  and  $1.96 \times 10^{18} \text{ cm}^{-3}$ . MS studies showed that the CNTs sample has much higher carrier densities than the PEI-CNTs sample. PEI is relatively stable n-type doping effects<sup>32</sup> and CNTs is p-type semiconductor, so the carrier density of PEI-CNTs is relatively low (Fig.S2(a, b)). Similarly, the carrier density of the pure Co<sub>3</sub>O<sub>4</sub> NPs ( $\sim 3.50 \times 10^{17}$ ) is lower than that of the CNTs. Compared with other Co<sub>3</sub>O<sub>4</sub>/PEI-CNTs composite, the carrier density of C-5 is the biggest.

Generally, particle size effects could positively influence the catalytic activity and sensing performance. The sensing performance is in particularly related to the space-charge layer (or Debye length), which can be calculated from the eq 2:

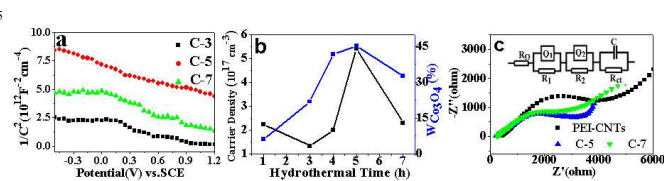
$$L_a = \sqrt{\epsilon \epsilon_0 k T (N_a (e_0)^2)^{-1}} \quad (2)$$

where T is the experimental temperate, k is Boltzmann constant ( $k = 1.38 \times 10^{-23}$ ),  $N_a$  is the carrier density, and  $L_a$  is the thickness of the space-charge layer (or Debye length). Here, if  $N_a = 5.40 \times 10^{17}$ , we estimated  $L_a = 5.84 \text{ nm}$ .

Fig.5b shows the relationship of the Co<sub>3</sub>O<sub>4</sub> content, carrier density change and hydrothermal time. To the best of our knowledge, the resistance of materials in the air plays a key role in gas sensing responses. Better electron transportation in air induces faster response. Thus, the electron transportation ability of samples was studied, as shown in Fig.5c and Fig.S2(c, d).

To perform a quantitative analysis, an appropriate equivalent circuit,<sup>33</sup> as shown in Fig.5c (inset) and Fig.S2, is proposed to fit the impedance spectra and the fitting results are listed in Table 1. For PEI-CNTs, C-5 and C-7 etc.. The equivalent circuit used to fit the experimental data of the composite (Fig.5c) consists of a resistance  $R_\Omega$  in series with three subcircuits: higher frequencies ( $R_1 Q_1$ ), intermediate frequencies ( $R_2 Q_2$ ), and lower frequencies ( $R_{ct} C$ ).

Here  $R_\Omega$  refers to the resistance composed of solution resistance and electrode resistance  $Q_1$  corresponds to the electrode film interface capacitance  $R_1$  values have been related



**Fig. 5** (a) Mott-Schottky plots of samples (C-3, C-5 and C-7) electrodes in 3 M KOH solution with a frequency of 10 kHz; (b) The relationship between the Co<sub>3</sub>O<sub>4</sub> content, carrier density change and hydrothermal time,

(c) Nyquist plots of different and equivalent circuit model of samples (inset) measured in the frequency range from 0.01Hz to 100 kHz with 0.4V.

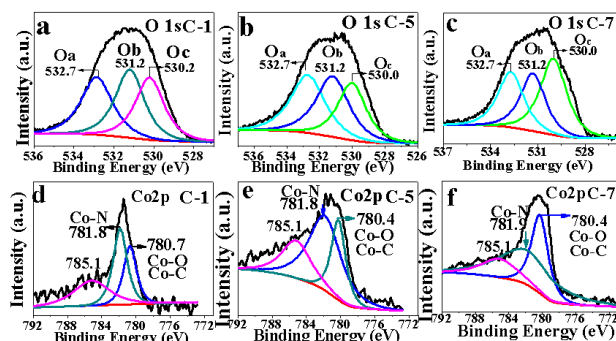
**Table 1** The carrier density and fitted impedance parameters of samples

Samples	CNTs	PEI-CNTs	Co <sub>3</sub> O <sub>4</sub>	C-1	C-3	C-5	C-7
R <sub>Ω</sub> (Ω)	207.9	428.6	1357	340.3	409.4	211.5	244.5
R <sub>ct</sub> (Ω)	3317	4524	2923	6958	5564	1686	4352

to Co<sub>3</sub>O<sub>4</sub> grain boundaries in Co<sub>3</sub>O<sub>4</sub>/PEI-CNTs composite,<sup>33</sup> subcircuit 2 is the response of CNTs. Subcircuit 3 is related to the response of amorphous carbon and impurities in composite. R<sub>ct</sub> is attributed to the charge-transfer resistance at the active material interface. C is the constant phase angle element, involving double layer capacitance.<sup>33, 34</sup> Furthermore, the R<sub>ct</sub> value of C-5 is 1686 Ω, which is the lowest among all the samples (Table 1). C-5 exhibits much higher conductivity than the other samples. Therefore, C-5 can improve the electron transportation, which can be confirmed by the decreasing equivalent series resistance.

In addition, more detailed information on the chemical state of these elements is obtained from the high resolution XPS spectra of the O1s and Co2p peaks in Fig.6 and Fig.S3. For Co<sub>3</sub>O<sub>4</sub>/PEI-CNTs composites, the O<sub>c</sub> peak at 530.0 eV is due to lattice oxygen of the Co<sub>3</sub>O<sub>4</sub> the O<sub>b</sub> peak at about 531.2 generally attributed to oxide defect states<sup>35</sup> and the O<sub>a</sub> peak at 532.7 eV are due to chemisorbed oxygen as shown in Fig.6 (a-c). The values of chemisorbed oxygen contents estimated from XPS measurements yielded as 32.5, 35.2 and 29.1% for the C-1, C-5 and C-7. The calculated oxide defect of the three samples is about 35.2, 36.7 and 29.3%, respectively. The peak area of adsorbed oxygen and oxide defect on C-5 is bigger than the other samples.

In the Co2p range, the XPS spectra gives three main peaks (Fig. 6(d-f)) at 780.4 ± 0.3 eV, 781.8 ± 0.1 eV and 785.1 eV assigned to cobalt oxides (Co-O or Co-C),<sup>36</sup> Co-N<sup>37</sup> and Co salts.<sup>38</sup> The values of Co-N contents are about 39.3%, 51.7%, 48.1% for the C-1, C-5 and C-7, respectively, the calculated Co-O or Co-C of the three samples is about 27.9%, 24.7% and 33.0%. The peak area of Co-N on C-5 is bigger than the other samples. Therefore, the oxide defect on Co<sub>3</sub>O<sub>4</sub>/PEI-CNTs composite might be obtained and showed defects where Co-N (or Co-C) had existed. According to the Serge Palacin's studies, the Co-N structures and N-enriched carbon moieties are keys for a high ORR activity.<sup>36</sup> Hence, Co-N structures and N-enriched carbon moieties are helpful for their good catalytic activity in gas sensors and improve the performance of CO sensors.



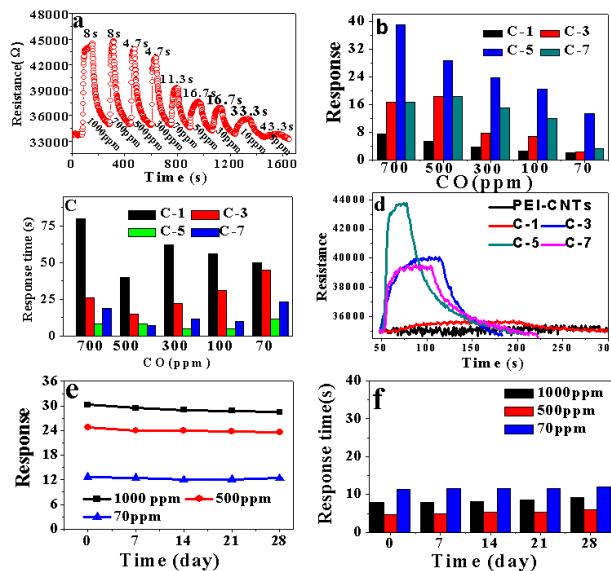
**Fig.6** XPS spectra of the O1s and Co 2p of (a), (d) C-1; (b), (e) C-5; (c), (f) C-7.

### 3.2. Sensing performance

The thin film sensor was fabricated by the Co<sub>3</sub>O<sub>4</sub>/PEI-CNTs composite. The CO gas sensing properties of the Co<sub>3</sub>O<sub>4</sub>/PEI-CNTs composite thin film sensor was investigated at RT.

Fig. 7a depicts representative dynamic gas responses of C-5 thin film sensor on the CO concentrations ranging 1000-5 ppm at RT. It can be seen that, the resistance undergoes a drastic rise upon the injection of CO gas and a decline to its initial value after the sensors were exposed to air for some time to all the samples. The comparison detail results of the response of C-1, C-3 and C-7 were shown in Fig. S4. For 700 ppm CO, the gas response and response time of the C-5 thin film sensor is 27.4% and 8 s. When the concentration of CO is 500 and 300 ppm, the gas response and response time is 24.8%, 23% and 4.7 and 4.7 s, respectively. That is faster than Co<sub>3</sub>O<sub>4</sub>-SnO<sub>2</sub>-CNT,<sup>21</sup> whose response time was 21 s when the CO concentrations was 600 ppm; and also faster than C-190 sensors, as described in our previous work.<sup>29</sup> As can be seen in Fig. 7a, while the lowest detection limit of the thin film sensor is down to 5 ppm CO at RT, its response time is 43.3 s and the gas response is 3.2%. However without oxygen, the gas response of C-5 in pure nitrogen is very low (see Fig.S5)

The thin film sensor fabricated based on a series of Co<sub>3</sub>O<sub>4</sub>/PEI-CNTs composites exhibit different degree of response to CO in the detection range in Fig.7 (b, c). As show in Fig. 7(a, b) and Fig. S4, except C-4 (C-190),<sup>29</sup> the other sensors (C-1, C-3 and C-7) can not reach the lowest level (5ppm). For the C-5, the response time to 1000ppm CO is 8s the maximum response to 1000 ppm CO was 30.3%, which is the highest among all the sensors. In comparison with other samples, the thin film sensor based on C-5 exhibit higher gas response, fast response/recovery time (see Table S2) and lower detection limit than the other samples.



**Fig. 7** (a) Dynamic response-recovery curves of C-5 thin film sensor to CO at RT, (b) Bar graphs represented the sensor response, (c) Response time, (d) The response-recovery curve of the five sensors to 500 ppm CO

at RT in air, (e) and (f) Curves of the stability test of the gas response of for C-5 thin film sensor to 1000, 500 and 70 ppm CO at RT in air (HD: 26%)

Fig. 7d shows the typical response curves of the five sensors to CO (500 ppm) at RT in air for one circle. The response and response time of the C-1, C-3, C-5 and C-7 are 7.4, 11.9, 24.8, 18.3 and 40, 14.7, 4.7, 6.7 s respectively (the response of PEI-CNTs < 5%). The response of C-5 is the 3.4, 2.1 and 1.4 times of C-1, C-3 and C-7, respectively.

The stability of the C-5 thin film sensor is measured at different CO concentrations for 28 days. As shown in Fig. 7(e, f), the response and response time to 1000, 500 and 70 ppm CO show little change after 7 days. To activate the Co<sub>3</sub>O<sub>4</sub>/PEI-CNTs sensor (C-5) with 14 days aging, it was treated in a vacuum oven at 60 °C for 3 h. The response of the sensor was recovered, which conform a good stability of the C-5 sensor. Therefore, the mesoporous 1D structure of C-5 shows the potentials in sensor and related nanodevices.

### 3.3. Discussion of sensing mechanism

From all the above, in Co<sub>3</sub>O<sub>4</sub>/PEI-CNTs composite, when CNTs architecture was employed as conducting scaffolds in Co<sub>3</sub>O<sub>4</sub> semiconductor based sensor not only prevent Co<sub>3</sub>O<sub>4</sub> nanoparticles from aggregation, but also can boost the electron transfer efficiency. PEI provided high density homogeneous functional groups on the CNTs' sidewalls for binding Co<sub>3</sub>O<sub>4</sub> NPs. Meanwhile PEI is helpful for high density dispersion Co<sub>3</sub>O<sub>4</sub> grains, and enhance the interaction between Co<sub>3</sub>O<sub>4</sub> grains and CNTs. Co<sub>3</sub>O<sub>4</sub> NPs whose the domain sizes of Co<sub>3</sub>O<sub>4</sub> NPs on C-5 are between  $L_a$  (the thickness of the space-charge layer (or Debye length) of 5.84 nm) and  $2L_a$  were dispersed on PEI-CNTs to improve the transport of carriers to the surface.

The sensing mechanism of the Co<sub>3</sub>O<sub>4</sub>/PEI-CNTs composites to CO was analyzed based on its structure and composition. The discussion on the sensing mechanism consists of two points: i) The synergetic effect on gas sensing characteristic between one-dimensional (1D) Co<sub>3</sub>O<sub>4</sub>/PEI-CNTs composited structure and Co<sub>3</sub>O<sub>4</sub> or PEI. ii) The effects of structure and composition of Co<sub>3</sub>O<sub>4</sub>/PEI-CNTs composite on gas sensing performance, such as: Co<sub>3</sub>O<sub>4</sub> NPs size, n-p or p-p heterostructure, carrier density, chemisorbed oxygen (O<sub>2</sub><sup>-</sup>), defects *etc.*

In generally, a high surface area provides an efficient space for gas adsorption sensing. C-5 possess higher BET specific surface area of 112 m<sup>2</sup>/g and mesopores of 7.4 nm (Fig. 1), which are greatly advantageous for gas adsorption-desorption, diffusion and surface contact reaction. So, CO gas molecules diffused more easily inside the large mesopores 1D hollow composited structures of C-5. This can be in favour of the response to CO at RT.

For porous 1D nature of Co<sub>3</sub>O<sub>4</sub>/PEI-CNTs composite, the role of added CNT is a conducting wire and increase the electric conductivity of the sensing materials.<sup>23, 39</sup> Therefore, the graphitized parts in CNTs offer a fluent electrical pathway,<sup>40</sup> resulting in fast migrating of electrons and response (see Scheme 1). As a result, C-5 sensor shows fast response to the CO concentrations ranging of 1000-5 ppm detection at RT.

The small size and appropriate electrical conductivity are crucial improving gas sensing performance of the materials. In our work, the domain sizes of Co<sub>3</sub>O<sub>4</sub> NPs on C-5 is about 6 nm,

which is between ( $L_a=5.84$  nm) and  $2L_a$  (see Fig. 2 and Fig. 3). As Co<sub>3</sub>O<sub>4</sub> NPs become smaller, the surface area to volume ratio increase, this would provide a greater number of available sites for gas/surface reactions to occur. Moreover, as Co<sub>3</sub>O<sub>4</sub> NPs size decreases, the interparticle connection sizes or "nanoparticle necks" become smaller and more numerous. The overlapped parts of Co<sub>3</sub>O<sub>4</sub> grains contain a high density of defects. As a result, little Co<sub>3</sub>O<sub>4</sub> NPs with high density of defects form large amount of sensing activity sites, which provide the fast adsorption-desorption channels and the accessibility of active centers for target gases.

Furthermore, Co<sub>3</sub>O<sub>4</sub>/PEI-CNTs composite, particularly C-5, the interaction of PEI with Co<sub>3</sub>O<sub>4</sub> NPs enhances with Co<sub>3</sub>O<sub>4</sub> content increasing. C-5 sample with the most dense attachment of the Co<sub>3</sub>O<sub>4</sub> NPs (of 45.1 mass %) and carrier densities (of  $5.40 \times 10^{17}$ ) has the lowest charge-transfer resistance  $R_{ct}$  of 1686 Ω among all the samples. These can make electrons transport easily, and allow carriers to diffuse freely. This benefits to gas detection.

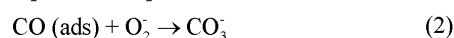
In the Co<sub>3</sub>O<sub>4</sub>/PEI-CNTs composite, the PEI-CNTs contained chemisorbed oxygen. Co<sub>3</sub>O<sub>4</sub> NPs contained oxide defect states and chemisorbed oxygen also. These are suggested to act as an electron donor or shallow energy level. This demonstrates that the n-p heterostructure might be formed between the interface of the PEI and CNTs or PEI and Co<sub>3</sub>O<sub>4</sub>. The oxide defects caused impurity bands in the bandgap of CNTs or Co<sub>3</sub>O<sub>4</sub>. Meanwhile, p-p homotype heterostructure might be formed at the interface of Co<sub>3</sub>O<sub>4</sub> and CNTs. Also, the defects between CNTs and Co<sub>3</sub>O<sub>4</sub> NPs cause impurity bands in the bandgap of Co<sub>3</sub>O<sub>4</sub>/PEI-CNTs. There are a lot of Co-N or Co-C, chemisorbed oxygen and oxygen defects existed in n-p or p-p heterostructure of Co<sub>3</sub>O<sub>4</sub>/PEI-CNTs composite.

The model is introduced to explain the sensing mechanism in Scheme 1. The electronic transport and the CO gas response in the C-5 are as followed:

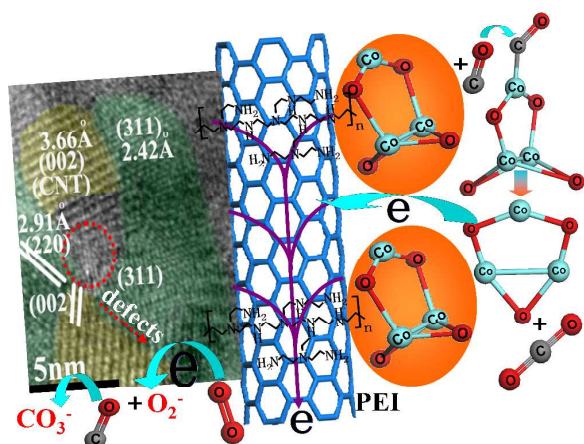
Firstly, sensor is exposed to air. Then, oxygen molecules tend to trap and react with the electrons from Co<sub>3</sub>O<sub>4</sub>/PEI-CNTs composite conduction band. The produced negative oxygen species (O<sub>2</sub><sup>-</sup>) causes the depletion layer (see the reaction 1 (R1)).

Secondly, when the sensor film is exposed to reducing gas CO, CO molecule react with O<sub>2</sub><sup>-</sup> to form CO<sub>3</sub><sup>-</sup> (R2). Then CO<sub>3</sub><sup>-</sup> molecule reacts with CO to form CO<sub>2</sub> (R3). At this stage, the electrons are released back to the Co<sub>3</sub>O<sub>4</sub>/PEI-CNTs composite which lead the thickness of space-charge layer become thinner. This process decreases the holes density and the rapid increasing of the resistances (Fig.7a).

Thirdly, CO molecule is favorable to adsorb on the Co<sup>3+</sup> ions in the octahedral coordination of the Co<sub>3</sub>O<sub>4</sub>. The oxidation of adsorbed CO occurs by abstracting the surface oxygen that might be coordinated with three Co<sup>3+</sup> cations.<sup>41</sup> The electron transfer from adsorbates CO to the Co<sup>3+</sup> of Co<sub>3</sub>O<sub>4</sub> NPs, and the CO molecules are activated and formed CO<sub>2</sub> (R4).<sup>42</sup>



Finally, the partially reduced cobalt site, which might be a  $\text{Co}^{2+}$  cation, is re-oxidized by a gas-phase neighbouring oxygen molecule to be active  $\text{Co}^{3+}$  sites.



**Scheme 1** Electronic transport characteristics and model of  $\text{Co}_3\text{O}_4/\text{PEI}$ -CNTs composite. The left is HRTEM image of  $\text{Co}_3\text{O}_4/\text{PEI}$ -CNTs composite, containing the linear and planar defects, which might provide electrons to  $\text{O}_2$  and occur R 1-3; CO adsorbs on  $\text{Co}_3\text{O}_4$  NPs and occur R 4.

#### 4. Conclusion

A simple and efficient noncovalent chemical approach is developed for elaborately hybridizing the PEI-CNTs with the  $\text{Co}_3\text{O}_4$  nanoparticles. The as-prepared  $\text{Co}_3\text{O}_4/\text{PEI}$ -CNTs composite synthesized by hydrothermal method at  $190^\circ\text{C}$  for 5 h. The sensor exhibit excellent sensing properties at RT to CO detection: When the concentration of CO is 1000 ppm, the gas response is 39%, the response time is only 8 s, and the detection limit of the sensor is down to 5 ppm CO at RT.

The enhanced gas sensing could be ascribed to the synergistic effects of the mesopores 1D composited structures attached by 4-8 nm  $\text{Co}_3\text{O}_4$  nanoparticles and the role of the PEI on the sensor characteristic. The unique 1D structure of  $\text{Co}_3\text{O}_4/\text{PEI}$ -CNTs with high surface-to-volume ratio can act as channels for gas adsorption-desorption and diffusion. That provides more approachable active sites for the reaction of CO with surface-adsorbed oxygen ions, which resulting the favorable response to CO at room temperature. Also,  $\text{Co}_3\text{O}_4$  to PEI-CNTs might significantly increase the carrier densities, chemisorbed oxygen and defects; The PEI might enhance the interaction between CNTs and  $\text{Co}_3\text{O}_4$  NPs, thus allow carriers to diffuse freely, which benefit to improving the performance of CO sensors.

The assembly method can be easily adapted to controllably produce various nanoparticles and PEI-CNT hybrid materials. This facile approach represents a potential and simple chemical route to control nanoparticles density and dispersity to form heterogeneous nanostructures on CNTs by utilizing PEI noncovalent assembly.

#### Acknowledgement

This work was supported by the Union Funds of the National Natural Science Foundation of China (No. U1034003), Key

Projects of the Natural Science Foundation of Heilongjiang Province (No. ZD201002), Scientific Research Fund of Heilongjiang Provincial Education Department (Nos. 12521421, RC2012XK018005) and the Program for Innovative Research Team in Heilongjiang University (Hdtd201 0-02).

#### References

- B. L. Risavi, R. J. Wadas Jr, C. Thomas and D. F. Kupas, *The Journal of Emergency Medicine*, 2013, 44, 637-640.
- L. Hu, Q. Peng and Y. Li, *Journal of the American Chemical Society*, 2008, 130, 16136-16137.
- L. Hu, Q. Peng and Y. Li, *ChemCatChem*, 2011, 3, 868-874.
- Y. Sun, P. Lv, J.-Y. Yang, L. He, J.-C. Nie, X. Liu and Y. Li, *Chemical Communications*, 2011, 47, 11279-11281.
- A.-M. Cao, J.-S. Hu, H.-P. Liang, W.-G. Song, L.-J. Wan, X.-L. He, X.-G. Gao and S.-H. Xia, *The Journal of Physical Chemistry B*, 2006, 110, 15858-15863.
- D. Patil, P. Patil, V. Subramanian, P. A. Joy and H. S. Potdar, *Talanta*, 2010, 81, 37-43.
- W.-Y. Li, L.-N. Xu and J. Chen, *Advanced Functional Materials*, 2005, 15, 851-857.
- C. Sun, S. Rajasekhara, Y. Chen and J. B. Goodenough, *Chemical Communications*, 2011, 47, 12852-12854.
- C. Zhao, G. Zhang, W. Han, J. Fu, Y. He, Z. Zhang and E. Xie, *CrystEngComm*, 2013.
- H. Yang, S. Wang and Y. Yang, *CrystEngComm*, 2012, 14, 1135-1142.
- J. R. Sietsma, J. D. Meeldijk, J. P. den Breejen, M. Versluijs - Helder, A. J. van Dillen, P. E. de Jongh and K. P. de Jong, *Angewandte Chemie*, 2007, 119, 4631-4633.
- S. K. Meher and G. R. Rao, *The Journal of Physical Chemistry C*, 2011, 115, 15646-15654.
- Z. Wen, Q. Wang, Q. Zhang and J. Li, *Advanced Functional Materials*, 2007, 17, 2772-2778.
- G. G. Wildgoose, C. E. Banks and R. G. Compton, *Small*, 2006, 2, 182-193.
- V. Georgakilas, D. Gourmis, V. Tzitzios, L. Pasquato, D. M. Guldi and M. Prato, *Journal of Materials Chemistry*, 2007, 17, 2679-2694.
- B. Wu, D. Hu, Y. Kuang, B. Liu, X. Zhang and J. Chen, *Angewandte Chemie International Edition*, 2009, 48, 4751-4754.
- S. Liu, J. Li, Q. Shen, Y. Cao, X. Guo, G. Zhang, C. Feng, J. Zhang, Z. Liu and M. L. Steigerwald, *Angewandte Chemie*, 2009, 121, 4853-4856.
- Z. Tan, H. Abe, M. Naito and S. Ohara, *Chem. Commun.*, 2010, 46, 4363-4365.
- W. Li, H. Jung, N. D. Hoa, D. Kim, S.-K. Hong and H. Kim, *Sensors and Actuators B: Chemical*, 2010, 150, 160-166.
- J. Yang, W.-d. Zhang and S. Gunasekaran, *Electrochimica Acta*, 2011, 56, 5538-5544.
- R.-J. Wu, J.-G. Wu, M.-R. Yu, T.-K. Tsai and C.-T. Yeh, *Sensors and Actuators B: Chemical*, 2008, 131, 306-312.
- A. D'Amico and C. Di Natale, *IEEE Sensors Journal*, 2001, 1, 183-190.
- S. K. Meher and G. R. Rao, *The Journal of Physical*



- Chemistry C*, 2011, 115, 25543-25556.
24. N. M. Rocher and R. Frech, *Macromolecules*, 2005, 38, 10561-10565.
25. K. Kan, T. Xia, L. Li, H. Bi, H. Fu and K. Shi, *Nanotechnology*, 2009, 20, 185502.
26. S. S. York, S. E. Boesch, R. A. Wheeler and R. Frech, *Macromolecules*, 2003, 36, 7348-7351.
27. C. Nethravathi, S. Sen, N. Ravishankar, M. Rajamathi, C. Pietzonka and B. Harbrecht, *The Journal of Physical Chemistry B*, 2005, 109, 11468-11472.
28. W. Yan, J. Tang, Z. Bian, J. Hu and H. Liu, *Industrial & Engineering Chemistry Research*, 2012, 51, 3653-3662.
29. G. Zhang, L. Dang, L. Li, R. Wang, H. Fu and K. Shi, *CrystEngComm*, 2013, 15, 4730-4738.
30. S. Thota, A. Kumar and J. Kumar, *Materials Science and Engineering: B*, 2009, 164, 30-37.
31. W. Lu, D. Wang and L. Chen, *Nano letters*, 2007, 7, 2729-2733.
32. S. M. Kim, J. H. Jang, K. K. Kim, H. K. Park, J. J. Bae, W. J. Yu, I. H. Lee, G. Kim, D. D. Loc and U. J. Kim, *Journal of the American Chemical Society*, 2008, 131, 327-331.
33. D. Cai, P. Lian, X. Zhu, S. Liang, W. Yang and H. Wang, *Electrochimica Acta*, 2012, 74, 65-72.
34. Q. Wang, D. Wang and B. Wang, *Int. J. Electrochem. Sci*, 2012, 7, 8753-8760.
35. S. C. Petitto, E. M. Marsh, G. A. Carson and M. A. Langell, *Journal of Molecular Catalysis A: Chemical*, 2008, 281, 49-58.
36. A. Morozan, P. Jégou, B. Jusselme and S. Palacin, *Physical Chemistry Chemical Physics*, 2011, 13, 21600-21607.
37. K. Niu, B. Yang, J. Cui, J. Jin, X. Fu, Q. Zhao and J. Zhang, *Journal of Power Sources*, 2013.
38. K. Artyushkova, S. Levendosky, P. Atanassov and J. Fulghum, *Topics in Catalysis*, 2007, 46, 263-275.
39. W.-D. Zhang, B. Xu and L.-C. Jiang, *Journal of Materials Chemistry*, 2010, 20, 6383-6391.
40. Y. Wang, H. J. Zhang, L. Lu, L. P. Stubbs, C. C. Wong and J. Lin, *Acs Nano*, 2010, 4, 4753-4761.
41. B. Mehrabi Matin, Y. Mortazavi, A. A. Khodadadi, A. Abbasi and A. Anaraki Firooz, *Sensors and Actuators B: Chemical*, 2010, 151, 140-145.
42. Y. Xie, F. Dong, S. Heinbuch, J. J. Rocca and E. R. Bernstein, *Physical Chemistry Chemical Physics*, 2010, 12, 947-959.

45