

# Carboxymethyl chitosan-assisted uniformly anchored Pd nanoparticles on carbon nanotubes for methanol electrooxidation in alkaline media

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A carboxymethyl chitosan (CMC)-assisted method is developed for the preparation of a palladium (Pd) nanoparticles (NPs)/carbon nanotubes (CNTs) nanohybrid. The addition of a small amount of CMC to the reaction solution leads to the production of well-crystallised metallic Pd NPs with small diameter and uniformly dispersed on CNTs. The obtained Pd NPs supported on CNTs show enhanced catalytic activity and stability for the electrochemical oxidation of methanol in alkaline media. The as-developed Pd NPs/CNTs nanohybrid is a highly promising catalyst for use in fuel cell technology.

**1. Introduction:** Since carbon nanotubes (CNTs) were reported by Iijima in 1991 [1], they have been intensively studied and suggest great potential application in a wide variety of areas, such as fuel cells, hydrogen storage and chemo/biosensors [2–4]. Especially, because of their high specific surface area, excellent electronic conductivity, outstanding chemical and electrochemical stability and so on, CNTs are widely used as support materials for noble metal nanoparticles (NPs). CNT-supported noble metal NPs may be ascribed to be a kind of hybrid catalysts with unique metal NPs/CNTs interactions, resulting in distinct catalytic behaviour, and they have attracted increasing interest for catalytic applications from fuel/electrochemical cell to heterogeneous catalysts [3, 5–8].

Palladium (Pd) NPs have attracted considerable attention for their applications as catalysts for the oxidation of small organic compounds including glucose and formic acid [9], especially methanol and ethanol [10]. In the application as electrocatalysts, the high dispersion and small particle size of Pd NPs on CNTs are desirable not only because of the extraordinary catalytic activity, but also the low cost. Therefore, Pd NPs are required to be of finely discrete states, where the size and distribution are critical parameters to be controlled. Currently several methodologies have been developed for the preparation of Pd NPs/CNT nanohybrids, including electroless plating [11], electrodeposition [12], microemulsion [13] and supercritical CO<sub>2</sub> [14]. In addition, the covalent or non-covalent functionalisation of CNTs with a wide range of functional groups has also been developed to create preferred sites for the nucleation of metal ions, prior to reduction. These strategies include chemical oxidation at defect sites of CNTs, wrapping with polymer [15, 16], grafting of ionic liquid [6, 17], modification by  $\pi$ -stacking [18, 19] and so on. Although the above strategies are effective to anchor Pd NPs on CNTs, careful examination of them reveals that they involve either a sophisticated synthetic procedure or complex equipment to achieve a high dispersion of Pd NPs on CNTs, and the bulk production is very difficult. Therefore, the development of a simple and effective synthetic route that provides well-dispersed and a small particle size of Pd NPs on CNTs is still a challenge.

In this Letter, we report a carboxymethyl chitosan (CMC)-assisted method for *in-situ* one-pot preparation of Pd NPs highly dispersed on CNTs. The addition of CMC promoted the dispersion of CNTs in solvents and the obtaining of small Pd NPs with an average diameter of 3 nm. To evaluate their catalytic property, the

Pd NPs/CNTs nanohybrids have been used as electrocatalysts for the oxidation of methanol in alkaline media.

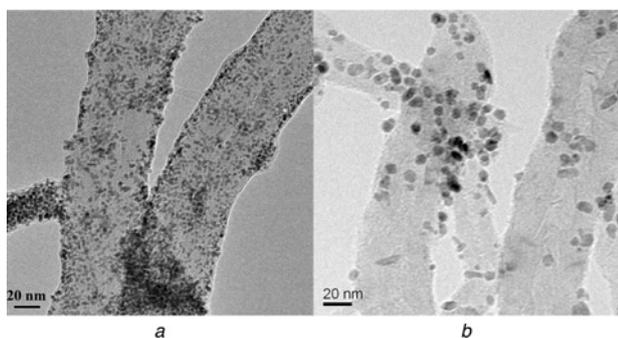
## 2. Experimental

**2.1. Preparation and characterisation of Pd NPs/CNTs nanohybrids:** The synthesis procedure of the Pd NPs/CNTs nanohybrids can be briefly described as follows. First, 100 mg of pristine multi-walled CNTs (diameter 20–60 nm, Shenzhen Nanotech Port Co. Ltd) was added to the mixed solvent of 20 ml of ethylene glycol (EG) and 10 ml of water. The suspension was then sonicated for 5 min after 20 mg of CMC was added. The suspension was sonicated for another 5 min after 940  $\mu$ l of PdCl<sub>2</sub> (50 mM) was added. Then the reaction mixtures were kept at 120°C in oil bath for 4 h. The black precipitates were separated by centrifugation and washed with ethanol and water three times, and then dried in a vacuum oven at 60°C for 12 h to obtain the products. The obtained Pd NPs electrocatalysts supported on the CNTs, are denoted as Pd NPs/CNTs. For comparison, Pd NPs supported on the pristine CNTs without the assistance of CMC, labelled as Pd NPs/CNTs-p, were prepared under the same procedure as described above, except for the addition of CMC.

The surface morphology and crystal structure of the Pd NPs/CNTs and Pd NPs/CNTs-p catalysts were characterised by transmission electron microscopy (TEM, JEM-3010), Fourier transform infrared spectrometry (FTIR) (Nicolet, 6700) and X-ray diffraction (XRD, Bruker AXS X-ray diffractometer), respectively.

**2.2. Electrochemical measurements:** The electrode for electrochemical characterisation was prepared as follows: 5 mg of catalyst was dispersed into 5 ml of water by sonication. For each electrode, 40  $\mu$ l of solutions were cast on a freshly polished glassy carbon (GC, 5 mm diameter) electrode. After drying in air, the electrode was coated with 10  $\mu$ l of 0.05 wt% Nafion ethanol solution to fix the catalyst powder. The mass loading of Pd was 0.04 mg cm<sup>-2</sup>.

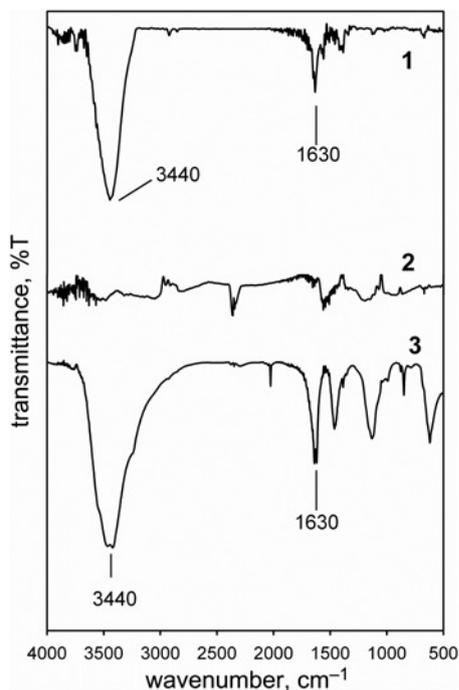
All electrochemical measurements were performed on a CHI660D electrochemical workstation (Chenhua Instrument Company of Shanghai, China). A conventional three-electrode glass cell was used with a platinum wire as the counterelectrode and an Hg/HgO (1.0 M KOH) electrode as the reference electrode.



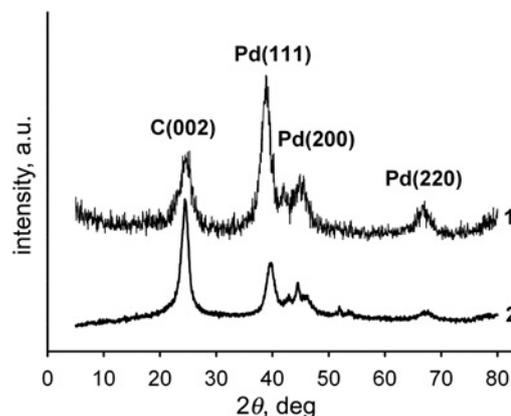
**Figure 1** TEM images  
*a* Pd NPs/CNTs  
*b* Pd NPs/CNTs-p nanohybrids

The electrolyte solution contained 1 M NaOH and a certain amount of methanol.

**3. Results and discussion:** Figs. 1*a* and *b* show the TEM images of the Pd NPs supported on CNTs synthesised with (Fig. 1*a*) and without adding CMC (Fig. 1*b*). As can be observed, CMC addition to the chemical reduction process sharply improved the formation of Pd NPs on CNTs. The uniformly dispersed Pd NPs strongly adhered onto CNTs after adding CMC, and the particle size is estimated to be 3 nm (Fig. 1*a*), which is much reduced compared with 6–8 nm in Fig. 1*b*. It is noteworthy that no NP aggregation was observed on the CNT surface in Fig. 1*a*.



**Figure 2** FTIR spectra of CMC (pattern 1), pristine CNTs (pattern 2) and Pd NPs/CNTs (pattern 3)  
 FTIR spectrum for CMC (pattern 1) shows a typical profile with very broad stretching bands  $\nu(\text{O-H})$  at  $3440\text{ cm}^{-1}$  and  $\nu(\text{C=O})$  at  $1630\text{ cm}^{-1}$  are assigned to the carboxyl groups of CMC. Pristine CNTs show typical absorption peaks of aromatic rings from  $1600\text{ cm}^{-1}$  to  $1450\text{ cm}^{-1}$  (pattern 2). Spectrum of the Pd NPs/CNTs catalysts is very similar to that of CMC and all characteristic peaks of CMC are observed in FTIR of Pd NPs/CNTs catalysts (pattern 3). Results indicate that the CMC has wrapped onto the surface of CNTs during the synthetic process of Pd NPs/CNTs catalysts, which can be ascribed to the excellent solubility and outstanding film-forming ability of CMC.

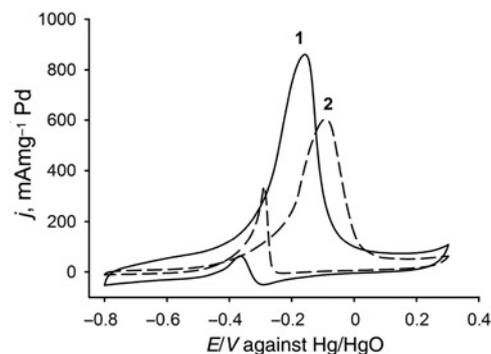


**Figure 3** XRD patterns of Pd NPs/CNTs (1) and Pd NPs/CNTs-p (2) nanohybrids

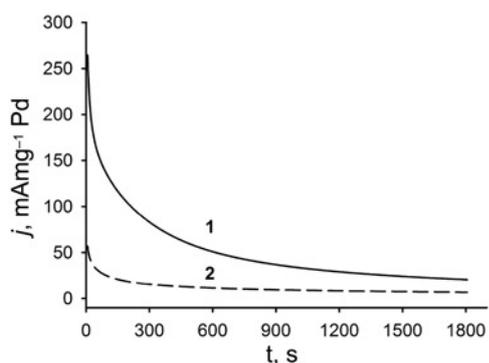
Moreover, the surface chemical properties of the Pd NPs/CNTs were analysed by FTIR and the results show that the CMC has wrapped onto the surface of CNTs in the catalysts (Fig. 2). From the results of TEM and FTIR, it can be deduced that CMC molecular chains have lots of free carboxylic groups which can anchor the  $\text{Pd}^{2+}$  and form small Pd NPs. In addition, CMCs have excellent solubility and an outstanding film-forming ability, which can easily wrap pristine CNTs and act as an ‘interlink’ for the uniform self-assembly of Pd NPs on the CNTs surface.

Fig. 3 shows the XRD patterns of the Pd NPs/CNTs and Pd NPs/CNTs-p catalysts. The diffraction peaks observed on Pd NPs/CNTs catalysts at around  $25^\circ$  correspond to the (002) plane of the hexagonal structure of CNTs. The diffraction peaks at around  $39^\circ$ ,  $46^\circ$  and  $68^\circ$  correspond to the Pd (111), (200) and (220) planes, respectively, which are the characteristic peaks of the face-centred-cubic (fcc) crystalline Pd [20]. The broad peaks of Pd (111) in Pd NPs/CNTs and Pd NPs/CNTs-p catalysts clearly indicate the nanostructure nature of the Pd NPs. The Pd (111) plane characteristic peaks was applied to estimate the average Pd NPs crystallite sizes according to the Scherrer equation  $d = 0.9\lambda K_{\alpha 1} / B_{2\theta} \cos\theta_{\max}$ . The results are 3.63 and 7.9 nm for Pd NPs/CNTs and Pd NPs/CNTs-p catalysts, respectively, which are close to the TEM data.

The electrocatalytic activity of the Pd NPs/CNTs nanohybrids as potential electrocatalysts for methanol electrooxidation was examined. Fig. 4 shows the cyclic voltammograms (CVs) of Pd NPs/CNTs and Pd NPs/CNTs-p nanohybrids measured in a nitrogen-saturated 1 M NaOH + 1 M  $\text{CH}_3\text{OH}$  aqueous solution. Compared with the Pd NPs/CNTs-p catalyst, the significant enhancement of the peak current of methanol oxidation can be observed on the Pd NPs/CNTs catalyst. It is noted that the forward peak current of methanol oxidation on the Pd NPs/CNTs catalyst is  $858\text{ mA mg}^{-1}$ ,



**Figure 4** CVs of Pd NPs/CNTs (1) and Pd NPs/CNTs-p (2) in 1 M NaOH + 1 M  $\text{CH}_3\text{OH}$  aqueous solution at a scan rate of  $50\text{ mV s}^{-1}$



**Figure 5** Amperometric  $i-t$  test of Pd NPs/CNTs (1) and Pd NPs/CNTs-p (2) nanohybrids in 1 M NaOH + 1 M CH<sub>3</sub>OH aqueous solution at  $-0.3$  V

this being 1.4 times higher than that on the Pd NPs/CNTs-p catalyst ( $596 \text{ mA mg}^{-1}$ ). On the other hand, for the catalyst prepared by the CMC-assisted method, the onset potential (forward peak potential) of methanol oxidation shifts by more than 110 mV (70 mV) in the negative direction compared with the Pd NPs/CNTs-p catalyst. The enhancement of the electrocatalytic activity of the Pd NPs/CNTs nanohybrids prepared by the CMC-assisted method may arise from the following two aspects. First, the well-dispersed Pd NPs on the surface of CNTs render more accessible surfaces of Pd NPs for the methanol oxidation reaction, accordingly leading to their higher electrocatalytic activity. Secondly, the smaller size of Pd NPs in the nanohybrids may also contribute to the improvement of the electrocatalytic performance of the nanohybrids towards methanol oxidation reaction.

Fig. 5 shows the chronoamperometric curves for the Pd NPs/CNTs and Pd NPs/CNTs-p catalysts at a potential of  $-0.3$  V in a nitrogen-saturated 1 M NaOH + 1 M CH<sub>3</sub>OH aqueous solution for 30 min. Compared with the Pd NPs/CNTs-p catalysts, the current value of the Pd NPs/CNTs catalysts attenuates at a much slower rate. The steady current values at 1800 s for the Pd NPs/CNTs and Pd NPs/CNTs-p catalysts are  $20.6$  and  $6.7 \text{ mA mg}^{-1}$ , respectively, showing the remarkably improved electrocatalytic stability of the Pd NPs/CNTs nanohybrids prepared in the presence of CMC. The enhanced stability of Pd NPs/CNTs may result from the fact that CMC can effectively stabilise and anchor Pd NPs on the surface of CNTs via the electrostatic and coordinative action.

**4. Conclusion:** In summary, we have successfully developed a CMC-assisted method for the preparation of highly dispersed and small particle size Pd NPs on CNTs. The as-prepared Pd NPs/CNTs composites show enhanced electrocatalytic activity and stability towards methanol oxidation. This provides a facile approach to synthesise CNTs-based nanoelectrocatalysts for high-performance energy conversion devices in the future.

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