Electronic Supplementary Information for :

Multi-walled carbon nanotubes supported Pd nanocubes with enhanced electrocatalytic activity

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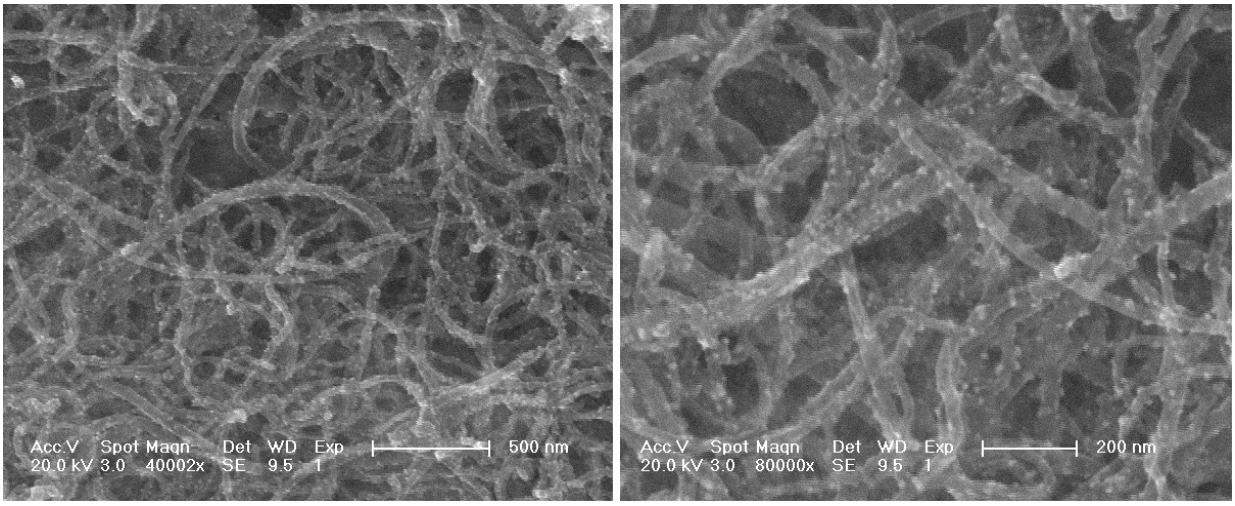

Fig. S1. Representative SEM images of the as-prepared MWCNTs/Pd NCs with different magnifications.

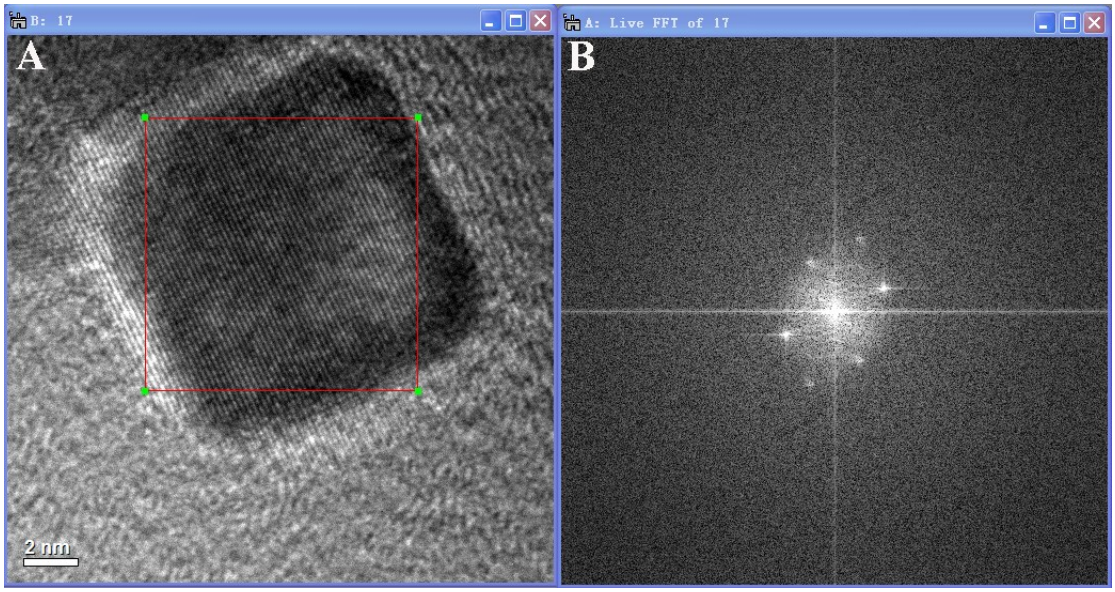

Fig. S2. (A) HRTEM of a single Pd nanocubes. **(B)** The corresponding FFT of the region marked by the red square, the rings in the FFT demonstrate the single-crystalline feature of the Pd nanocubes.

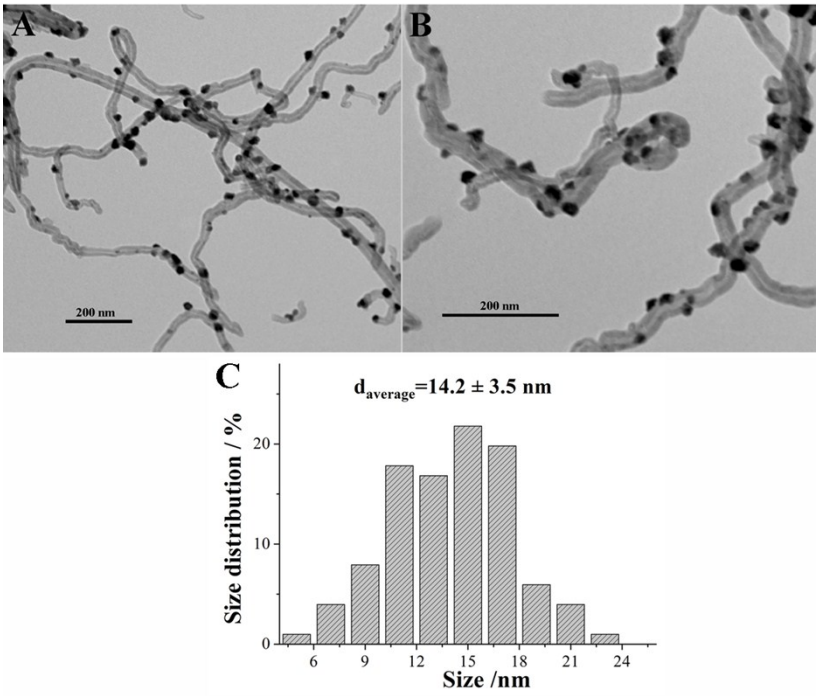

Fig. S3. (A, B) Representative TEM images of the as-prepared MWCNTs/Pd NPs with different magnifications. **(C)** The size distribution of Pd nanoparticles, the total statistic number of the Pd NPs is 135.

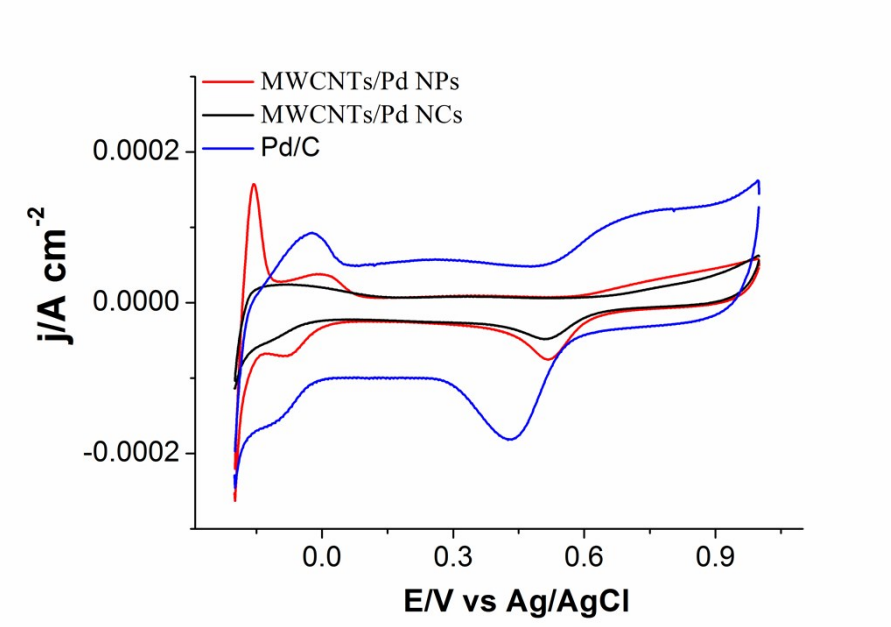

Fig. S4. CV characteristic of the prepared MWCNTs/Pd NCs and MWNCTs/Pd NPs in 0.5 mol L^{-1} H_2SO_4 aqueous solution.

Based on the reported methods,[1, 2] the active surface area of MWCNTs/Pd NCs, MWNCTs/Pd NPs and Pd/C is measured to 57, 88 and 470 cm^2 mg^{-1}, respectively. Note: the current density is the original current obtained on the CHI instrument without normalized, and the Pd loading mass for these two catalysts was 28.2 μg cm^{-2}. The lower active surface area of MWCNTs/Pd NCs than that of MWNCTs/Pd NPs exclude that the higher electrocatalytic activity of MWCNTs/Pd NCs is simply caused by their higher active surface area.

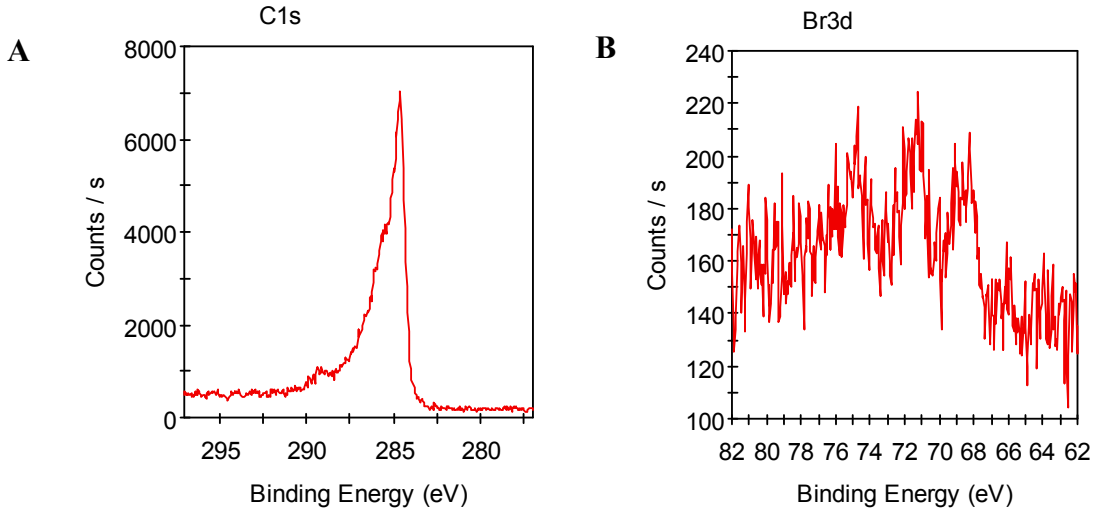

Fig. S5. XPS of MWCNTs/Pd NCs, (A) C1s, (B) Br 3d.

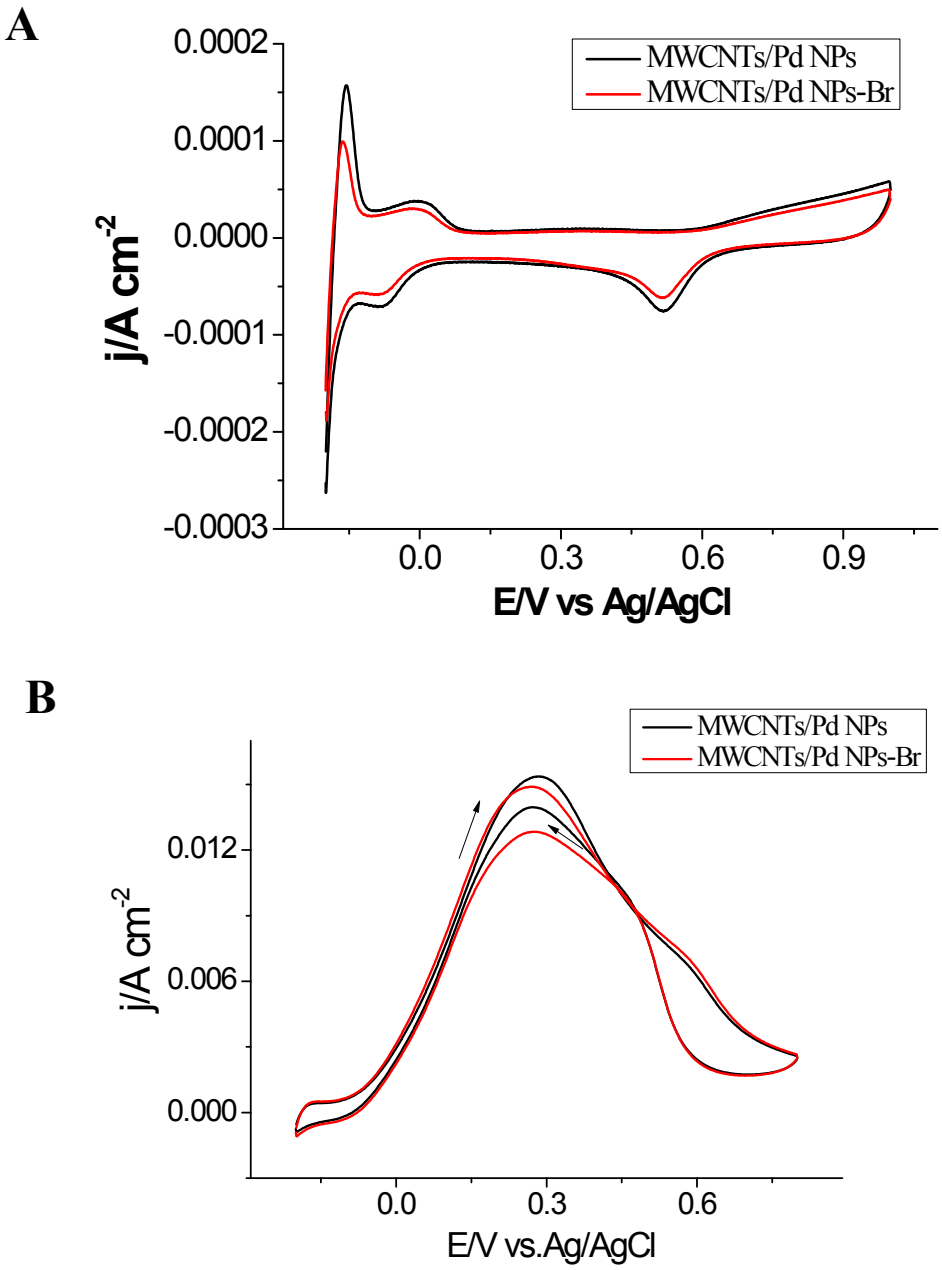

Fig. S6. (A) CV characteristic of the prepared MWCNTs/Pd NCs and MWNCTs/Pd NPs that adsorbed bromide ions (denoted as: MWCNs/Pd NPs-Br) in 0.5 mol L^{-1} H_2SO_4 aqueous solution. Similar to the Fig. S4, the active surface area of MWNCTs/Pd NPs and MWCNTs/Pd NPs-Br is measured to 88 and 78 cm^2 mg^{-1}, respectively. **(B)** CV curves for formic acid electrooxidation in a solution containing 0.5 mol L^{-1} formic acid + 0.5 mol L^{-1} sulfuric acid, scan rate: 50 mV s^{-1}. Synthesis of MWCNs/Pd NPs-Br: The synthetic process is similar to the synthesis of MWCNTs/Pd NPs. After reacted for 3.5 hours, the solution was cooled to room

temperature and added 0.5 mL of KBr (0.2 mol L^{-1}), then stirred for another 3.5 hours. Finally, then the product was collected with centrifugation and washed with water several times. The above results demonstrated that the absorption of bromide ions will lead to a slight decrease of active surface area and catalytic activity.

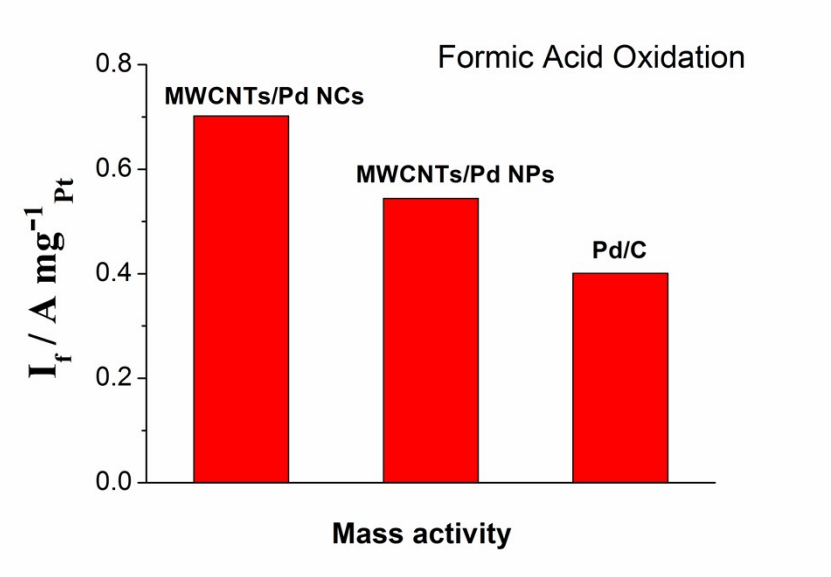

Fig. S7. Mass activity of different catalysts toward formic acid electrooxidation.

Reference

1. W. Hong, J. Wang, E. Wang, *ACS Appl. Mater. Interfaces,* 2014*,* **6***,* 9481-9487.

2. L. Xiao, L. Zhuang, Y. Liu, J. Lu, H. c. D. Abruña, *J. Am. Chem. Soc.,* 2008, **131**, 602-608.