

## Intermix of metal nanoparticles-single wall carbon nanotubes

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### Experimental

#### 1. Purification of single wall nanotube tubes (SWNTs)

Raw Chemical Vapour Deposition (CVD) SWNTs were kindly offered by Thomas Swan & Co Ltd. SWNTs were purified in Argon steam at 900 °C for 4 h to oxidize the amorphous carbon and graphite particles. Following the reflux in 6 M HCl over night to dissolve the Fe metal particles, the SWNTs were filtered using plenty of distilled water and dried at 80 °C under vacuum overnight.

#### 2. Material Preparation

100 mg of SWNTs were ultrasonically dispersed in 50 mL of ethylene glycol for 1h, then 5 mL of 0.07M (NH<sub>4</sub>)<sub>2</sub>PtCl<sub>4</sub> or 0.07M (NH<sub>4</sub>)<sub>2</sub>PdCl<sub>6</sub> aqueous solution was added. The pH value of the solution was adjusted to 13 with 1 M NaOH. Refluxed the solution under N<sub>2</sub> at 130 °C for 3 h in an oil bath, followed the filtration with plenty of distilled water and dried under vacuum at ambient temperature overnight, the 20 wt% Pt/SWNTs catalyst was prepared. 20 wt% Pd/SWNTs, 20 wt% Pt/C, 20 wt% Pd/C were prepared using the same method. The carbon support is Vulcan XC-72R (Cabot), used as received.

Different amount of 20 wt% Pt/SWNTs and 20 wt% Pd/SWNTs were mixed, the molar ratios were 7:3, 5:5 and 3:7, recorded as Pd<sub>3</sub>Pt<sub>7</sub>/SWNTs, Pd<sub>5</sub>Pt<sub>5</sub>/SWNTs and Pd<sub>7</sub>Pt<sub>3</sub>/SWNTs. Pt/C and Pd/C were mixed at the molar ratio of 5:5, record as Pd<sub>5</sub>Pt<sub>5</sub>/C. The alloy of PtPd<sup>a</sup>/SWNTs were also synthesised by using equal molar of (NH<sub>4</sub>)<sub>2</sub>PtCl<sub>4</sub> and (NH<sub>4</sub>)<sub>2</sub>PdCl<sub>6</sub>.

### 3. Electrochemical measurements

To prepare the catalyst ink, 6 mg of sample (Pt/SWNTs or carbon) and 100  $\mu\text{L}$  of Perfluorosulfonic acid-PTFE copolymer (5% w/w solution, Alfa Aesar) were ultrasonically dispersed in 1000  $\mu\text{L}$  of 2-propanol for 30min. 6  $\mu\text{L}$  of ink was dropped on the glassy carbon electrode and dried under vacuum at ambient temperature for 30min to prepare the working electrode (WE). the glassy carbon electrode (GC electrode) was pre-polished to a mirror-like finish using ultrafine  $\text{Al}_2\text{O}_3$  powder slurry (<50 nm), the electrode geometric area exposed to the electrolyte was 0.071  $\text{cm}^2$ . All the electrochemical tests were carried out on Ivium CompactStat instrument. Platinum wire was used as counter electrode (CE), saturated calomel electrode (SCE) was used as reference electrode. GC electrode, CE, SCE and  $\text{Al}_2\text{O}_3$  powder were all purchased from BASI. The electrolyte was pre-saturated with ultra-pure Nitrogen for 30 min to expel the air. Each electrode was scanned from 0.0 V to 1.2 V vs. SHE at 50  $\text{mV}\cdot\text{s}^{-1}$  for ten cycles in 0.5 M  $\text{H}_2\text{SO}_4$  before data was recorded.

#### 3.1 Cyclic voltammograms

Cyclic voltammograms (CVs) were carried out in 0.5 M  $\text{H}_2\text{SO}_4$  at 25  $^\circ\text{C}$ . The potential was scanned from 0.0 V to 1.2 V vs. SHE at 50  $\text{mV}\cdot\text{s}^{-1}$  for one cycle.

#### 3.2 CO stripping

The electrodes were immersed in  $\text{N}_2$  pre-saturated electrolyte, kept the potential at 0.02 V while ultra-pure CO was purged through the electrolyte for 30 min. Then  $\text{N}_2$  was purged to expel CO in the electrolyte for another 30 min. The potential was scanned from 0.0 V to 1.2 V vs. SHE at 50  $\text{mV}\cdot\text{s}^{-1}$  for 2 cycles.

#### 3.3 X-ray photoelectron spectroscopy (XPS)

XPS analysis of Pt/SWNTs, Pd/SWNTs and Pt5Pd5/SWNTs was carried out on the VG Excalab MKII. The inks were dried under vacuum at ambient temperature overnight for XPS tests.

### 3.4 Transmission electron microscope (TEM) and energy diffraction X-ray (EDX)

The sample was dispersed in ethanol, the suspension was dropped on the Cu grid and dried in the air. TEM was performed on JEOL JEM1200EXII. Oxford INCA energy X-ray analyser was used for the EDX test.

## 4. Results and discussions

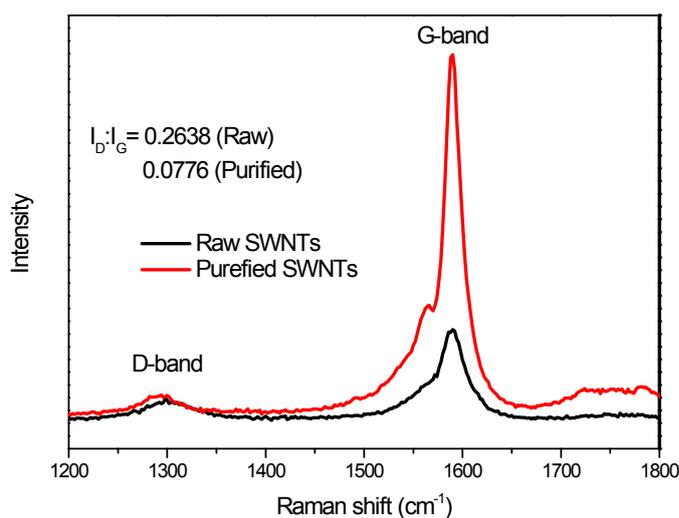


Figure S1 Raman spectrum of SWNTs before and after purification.

Raman spectrum (Fig.S1) shows a decrease of  $I_D:I_G$  from 0.2638 for the raw SWNTs to 0.0776 for the steam purified SWMTs. The ratio of  $I_D:I_G$  demonstrates the comparison of reagent grade graphite and the highly ordered pyrolytic graphite [1]. The ratio decreases as the SWNTs are purified. Two factors are responsible for the decrease: the defects in the wall of SWNTs and the carbon fragments [2]. Hence, the removal of impurities and the efficient oxidation of defective SWNTs during the steam purification are attributed to the decrease of  $I_D:I_G$ .

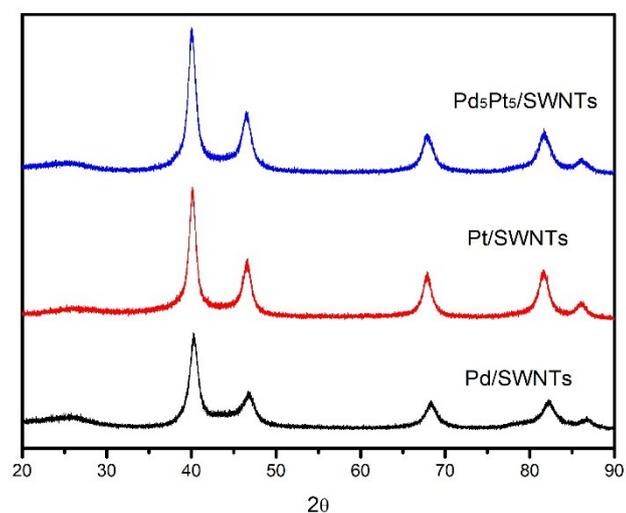


Figure S2 XRD patterns of Pt/SWNTs, Pd/SWNTs, and Pd<sub>5</sub>Pt<sub>5</sub>/SWNTs.

Fig. S2 depicts the XRD patterns of Pt/SWNTs, Pd/SWNTs, and Pt<sub>5</sub>Pd<sub>5</sub>/SWNTs. Typical peaks for (111), (200), (220), and (311) planes, characteristic of the face-centered cubic (FCC) lattice structure of Pt and Pd are also indicated in this figure. These peaks appear at  $2\theta$  values of 39.4, 45.8, 67.3, and 81.1, respectively, for Pt. For Pd, the same reflections appear at similar  $2\theta$  values of 39.7, 46.2, 67.9, and 81.8, respectively. The peaks of Pt and Pd of Pt<sub>5</sub>Pd<sub>5</sub>/SWNTs are found broadened at the similar  $2\theta$  values. There is no clear evidence on the PtPd alloy formation since the broad peaks do not allow their differentiation from those of Pt and Pd.

Pt<sub>5</sub>Pd<sub>5</sub>/SWNTs were studied on TEM (Fig.S3). SWNTs were in bundles, and the size of metal particles are of 5~10 nm. 8 spots were randomly chosen for EDX analysis (Table S1). Pd was detected from 3 spots, and Pt was detected from 5 spots. None of the spots presented both Pt and Pd, which demonstrated that Pt and Pd particles did not create any extensive contact with each other: no alloy, core-shell or modification structure could be formed in the mixed catalysts.

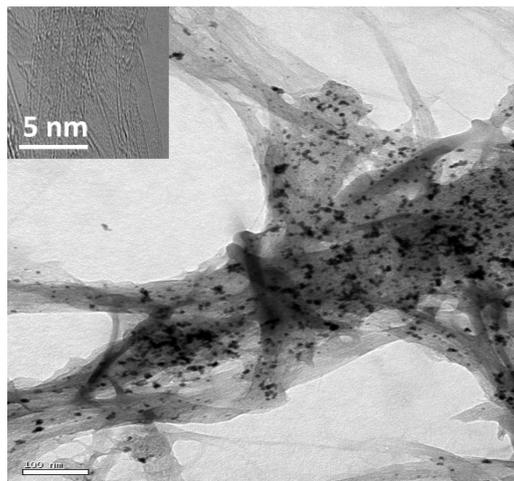


Figure S3 TEM image of Pd<sub>5</sub>Pt<sub>5</sub>/SWNTs (insert: enlarged image).

Table S1 The EDX spectrum of eight spots randomly chosen from Fig. S3.

	C	Pd	Pt	S	Total(%)
Spectrum 1	25.19	\	74.81	\	100
Spectrum 2	\	100	\	\	100
Spectrum 3	\	100	\	\	100
Spectrum 4	73.59	26.41	\	\	100
Spectrum 5	13.08	\	84.67	2.25	100
Spectrum 6	81.03	\	18.97	\	100
Spectrum 7	82.82	\	17.18	\	100
Spectrum 8	78.13	\	21.87	\	100

Fig. S4 shows the XPS spectra of Pt<sub>4f</sub> and Pd<sub>3d</sub> orbital, their binding energies are listed in Tables S2 and S3. The binding energies of Pt<sub>4f</sub> and Pd<sub>3d</sub> orbital stayed identical when the metals were loaded either on SWNTs or C, indicative of the same interactions between the metal and supports. Compared to Pd/SWNTs and Pt/SWNTs, the binding energies of Pt<sub>4f</sub> and Pd<sub>3d</sub> of Pt<sub>5</sub>Pd<sub>5</sub>/SWNTs remained in the same positions, which demonstrate that Pt and Pd did not have extensive interaction with each other as that of corresponding alloys.

Based on the analysis above, we can conclude that the Pt and Pd particles within the mixed catalyst have no direct extensive contact with each other, their electronic structures remain independently.

Table S2 The binding energy of Pd 3d orbital of Pd/SWNTs, Pd<sub>5</sub>Pt<sub>5</sub>/SWNTs, Pd/C, Pd<sub>5</sub>Pt<sub>5</sub>/C.

Sample	Pd 3d <sub>3/2</sub> (eV)	Pd 3d <sub>5/2</sub> (eV)
Pd/SWNTs	341.2	335.9
Pt <sub>5</sub> Pd <sub>5</sub> /SWNTs	341.5	336.1
Pd/C	340.9	335.7
Pt <sub>5</sub> Pd <sub>5</sub> /C	341.2	335.8

Table S3 The binding energy of Pt 4f orbital of Pt/SWNTs, Pd<sub>5</sub>Pt<sub>5</sub>/SWNTs, Pt/C, Pd<sub>5</sub>Pt<sub>5</sub>/C.

Sample	Pt 4f <sub>7/2</sub> (eV)	Pt 4f <sub>5/2</sub> (eV)
Pd/SWNTs	72.1	75.5
Pt <sub>5</sub> Pd <sub>5</sub> /SWNTs	72.6	76.0
Pd/C	72.1	75.6
Pt <sub>5</sub> Pd <sub>5</sub> /C	72.2	75.6

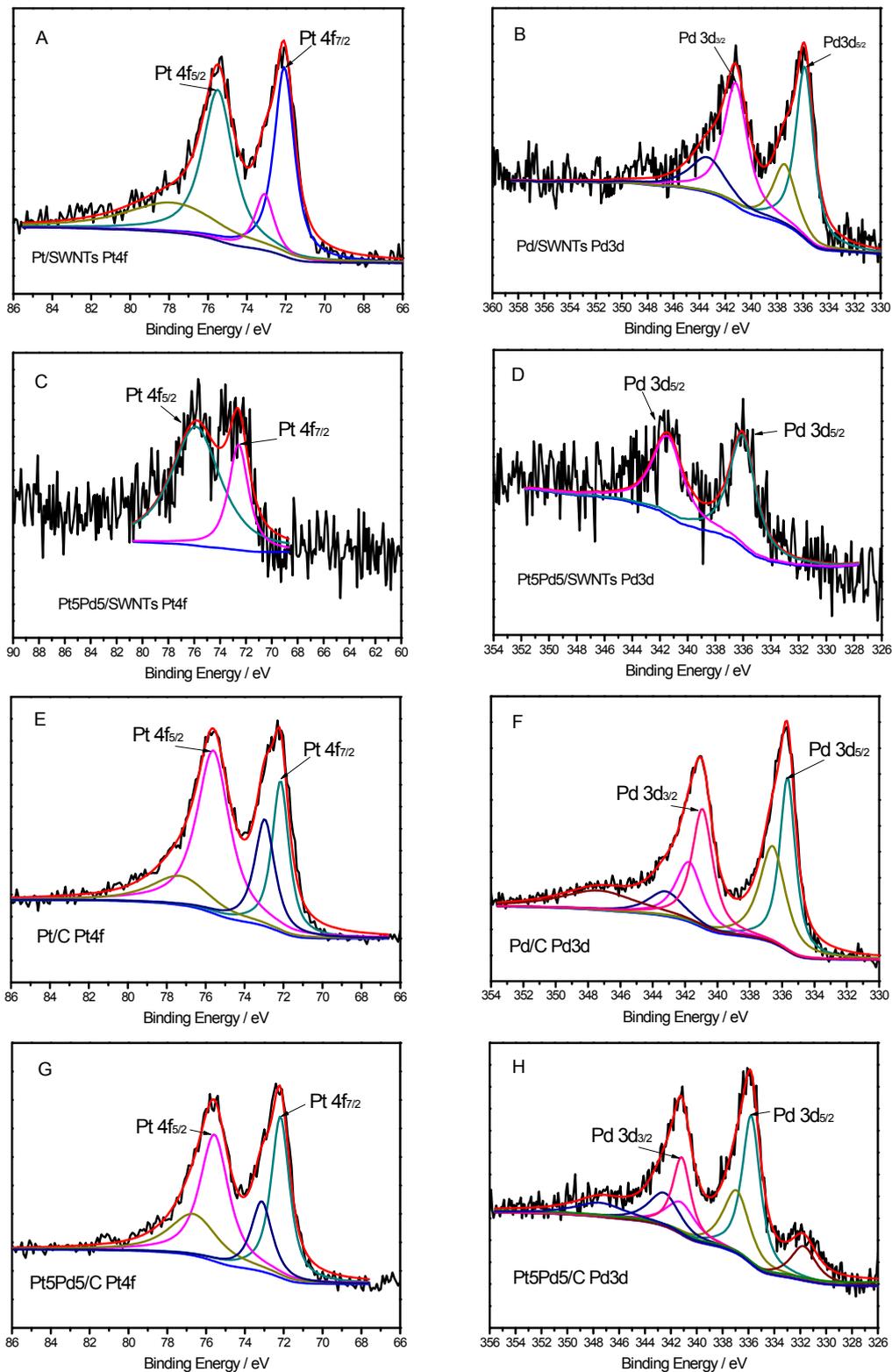


Figure S4 XPS spectra of Pt/SWNTs, Pd/SWNTs, Pd<sub>5</sub>Pt<sub>5</sub>/SWNTs, Pt /C, Pd/C, and Pd<sub>5</sub>Pt<sub>5</sub>/C. A: Pt<sub>4f</sub> orbital of Pt/SWNTs; B: Pd<sub>3d</sub> orbital of Pd/SWNTs; C: Pt<sub>4f</sub> orbital of Pd<sub>5</sub>Pt<sub>5</sub>/SWNTs; D: Pd<sub>3d</sub> orbital of Pd<sub>5</sub>Pt<sub>5</sub>/SWNTs; E: Pt<sub>4f</sub> orbital of Pt/C; F: Pd<sub>3d</sub> orbital of Pd/C; G: Pt<sub>4f</sub> orbital of Pd<sub>5</sub>Pt<sub>5</sub>/C; H: Pd<sub>3d</sub> orbital of Pd<sub>5</sub>Pt<sub>5</sub>/C.

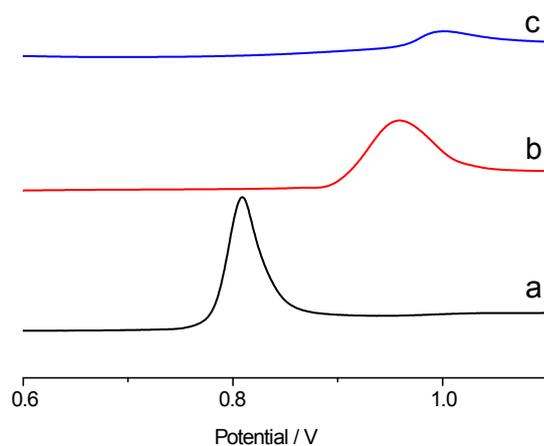


Figure S5 The CO stripping of Pt/SWNTs (a), PtPd<sup>a</sup>/SWNTs (b), and Pd/SWNTs (c) in the potential range of 0.6-1.2 V. PtPd<sup>a</sup>/SWNTs is the PtPd nano-alloy with the Pt:Pd ratio of 1:1, synthesized following the method of Pt/SWNTs but adding (NH<sub>4</sub>)<sub>2</sub>PdCl<sub>6</sub> and (NH<sub>4</sub>)<sub>2</sub>PtCl<sub>4</sub> precursors together for the co-reduction. The CO oxidation peak of PtPd/SWNTs is found to locate between that of Pt/SWNTs and Pd/SWNTs, which is the same as the mixed samples.

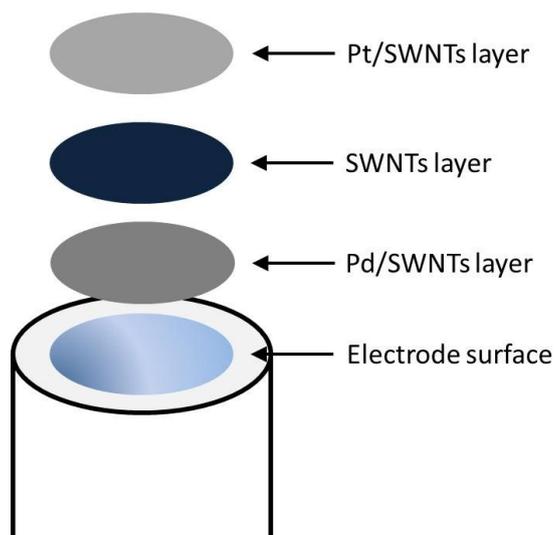


Figure S6 Schematic of sandwich electrode preparation. 6  $\mu\text{L}$  of Pd/SWNTs ink was firstly deposited on electrode surface and air dried. Six  $\mu\text{L}$  of SWNTs ink was then deposited onto the Pd/SWNTs layer and dried. Finally 6  $\mu\text{L}$  of Pt/SWNTs ink was deposited on top of SWNTs layer. To prepare sandwich-structured electrode with two or three SWNTs layers, the procedure of depositing SWNTs layer was repeated once or twice before the final Pt/SWNTs layer was applied. SWNTs and carbon inks were prepared following the recipe of catalyst ink, i.e., 6 mg of SWNTs or XC-72 and 100  $\mu\text{L}$  of Perfluorosulfonic acid-PTFE copolymer were ultrasonically dispersed in 1000  $\mu\text{L}$  of 2-propanol for 30min. Then 6  $\mu\text{L}$  of ink was dropped on the glassy carbon electrode.

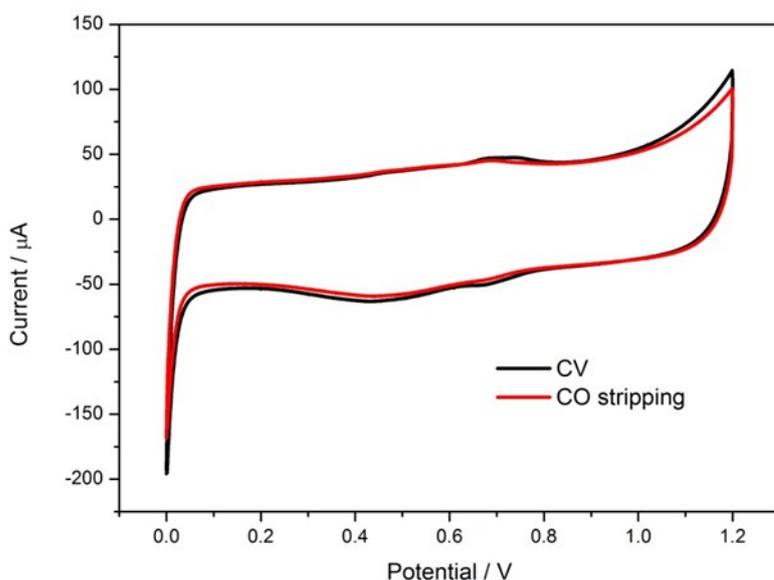


Figure S7 the CV and CO stripping of pure SWNTs. Two curves are almost identical, indicating no contamination from Fe, which is used as a catalyst for preparing SWNTs by CVD method.

NB: After purification in argon steam at 900 °C for 4 h to oxidize the amorphous carbon and graphite particles, SWNTs were refluxed in 6 M HCl overnight to dissolve any metal particles, especially Fe metal particles which was used as a catalyst for preparing SWNTs by CVD method. XRD patterns of Pt/SWNTs and Pd/SWNTs (Fig S2) showed no signs of Fe (or any other metal). Pure SWNTs ink without metal loading was used to prepare an electrode to perform CV and CO stripping. No signal belonging to metal contamination could also be observed (Fig S7).

### **Electronic effect through SWNTs at long range**

First, as stated in the introduction of the main manuscript, recent research has showed that PtPd NPs give remarkable activity for electrochemical oxidation of H<sub>2</sub> in PEM fuel cells. They contain less expensive Pt content but can also offer higher CO tolerance than the corresponding monometallic Pt or Pd. These attractive attributes have been ascribed to a number of possible reasons, which include high intrinsic activity of Pd for H<sub>2</sub> oxidation; storage and spillover H<sub>2</sub> from Pd to regenerate CO

poisoned Pt sites in close proximity; electronic (ligand) effects or geometric effects due to their characteristic atomistic structure in the PtPd structure. It is difficult to disentangle these effects from a bimetallic structure. Particularly, the local changes in d-band center position and filling of Pt modified by Pd in a close proximity by both the electronic or geometric effects as bimetallic alloy, core-shell or janus particles are commonly employed in literature to explain the improved catalytic properties.

However, in our physical mixture of Pt/SWNTs and Pd/SWNTs, our EDX analyses of 8 randomly chosen spots of Pd<sub>5</sub>Pt<sub>5</sub>/SWNTs presented in Table S1 showed none of them containing both Pt and Pd. Also, the binding energies of Pd 3d in Pd/SWNTs and Pd<sub>5</sub>Pt<sub>5</sub>/SWNTs are almost identical to each other (see Table S2) (The binding energies of Pt 4f in Pt/SWNTs and Pd<sub>5</sub>Pt<sub>5</sub>/SWNTs also resemble to each other (Table S3)). Thus, in the mixed Pt/SWNTs and Pd/SWNTs sample, the supported Pt NPs on SWNTs should not have any extensive contact with Pd NPs. The previous assignments to the local electronic or geometric effect or hydrogen spillover on Pt atoms by neighbour Pd atoms in close proximity do not seem to play any significant role to account for the observations. There is also no electronic band mixings or hybridizations (no change in d-band center position) as commonly occurred in alloy structure.

The classical Fermi level equilibration and the associated charge transfer between two different metals in direct contact or through conductive mediator such as SWNTs must at least partly explain the improved electrocatalytic properties of the bimetallic structure. A recent theoretical article [3] using the Fermi level equilibration and the associated charge transfer to account for different electrocatalytic properties of multimetallic nanosystems in comparison to systems composed of pure metals is given for the interested readers to get further information.

## **Reference:**

- [1] I. V. Anoshkin, I. I. Nefedova, D. V. Lioubtchenko, I. S. Nefedov, A. V. Räsänen, *Carbon*, 2017, **116**, 547-552.

[2] M. Tominaga, N. Watanabe, Y. Yatsugi, *J. Electroanal. Chem.*, DOI: <https://doi.org/10.1016/j.jelechem.2016.11.042>.

[3] P. Peljo, J. A. Manzanares, H. H. Girault, *Langmuir* 2016, **32**, 5765–5775.