Intermix of metal nanoparticles-single wall carbon nanotubes

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By using physical mixtures of Pd/SWNTs (Pd nanoparticles on single-walled carbon nanotubes) and Pt/SWNTs, the composites show electro-catalytic properties comparable to corresponding alloys: readily electron exchange between the two metal nanoparticles via SWNT support at long range without direct atomic contact is responsible for the tunable alloy-like properties.

Bimetallic nanostructures (such as alloy, core-shell and Janus nanoparticles) have attracted significant attention due to their superior properties over monometallic counterparts in thermal, electro- or photo- catalytic applications.¹⁻³ For example, carbon supported monometallic Pt nanoparticles (NPs) display the excellent activity for the oxidation H₂ in PEM fuel cells. Recent research has showed that PtPd NPs also give remarkable activity. They contain less expensive Pt content and also offer higher CO tolerance than the corresponding monometallic Pt or Pd.⁴ These attractive attributes have been ascribed to a number of possible reasons, which include high intrinsic activity of Pd for H₂ oxidation; storage and spillover H₂ 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.⁵⁻⁷ In order to tailor catalytic activity, understanding on the structure-activity relationships with respect to morphology, shape, size, atomic position and composition of the bimetallic nanoparticles is crucially important. However, rationalization of the synergetic effects in bimetallic NPs at present is rather limited. In addition, the synthesis of bimetallic NPs is also challenging, which requires to place individual components in highly controlled manner. The type of synthesis methods and conditions adopted are crucially important to the final quality of the nanoparticles made. There are reports claiming the delicate controls in synthesising the nanostructures such as flame pyrolysis, laser ablation, chemical vapour deposition, etc.⁸⁻¹⁰ Notice that the typical procedures for their synthesis are often complex and involve harsh conditions, such as applying high

temperature at short duration for rapid mixing of components without excessive particle growth and aggregation.^{11,12} Despite the fine controls, metal segregation is still commonly taken place, causing phase separation and thus degrading catalytic performance.¹³ A simple synthesis method for bimetallic structures would therefore be useful.

Here, we show that by simply physical mixing a batch of solid sample of Pt NPs on single-walled carbon nanotubes (Pt/SWNTs) with another batch of solid sample of Pd/SWNTs at various proportions, the resulting composite materials without atomic mixing of the supported metal atoms exhibit electrocatalytic properties comparable to their corresponding alloy structures.

As seen from the ESI, the physical mixture of two batches of M/SWNTs (M = Pd and Pt) samples at different proportions, giving the resulting Pd:Pt atomic ratios of 7:3, 5:5, and 3:7. They were christened as Pd₇Pt₃/SWNTs, Pd₅Pt₅/SWNTs and Pd₃Pt₇/SWNTs, respectively, without involving any prior pre-alloy synthesis. The crystal and electronic structures of Pd and Pt in these samples were retained as their individual monometallic states after the mixing as confirmed by Raman, XRD, TEM, and XPS without any indication of alloy formation (see Figs. S1-S4, Tables S1-S3). Cyclic voltammograms (CVs) of Pt/SWNTs and Pd/SWNTs in Fig. 1 reveals typical hydrogen adsorption/desorption peaks below 0.3 V and formation/reduction of metal oxide layer above 0.5 V for the SWNTs-supported monometallic NPs. The double layer charges are also the same for all the samples. The diagnostic three anodic desorption hydrogen peaks and two cathodic adsorption peaks can be assigned to weakly and strongly bonded hydrogen adatoms on different facets of Pt and Pd NPs from acidified water (Fig. 1A).^{14,15} The peaks are sharp indicating that the adsorption/desorption processes on the metal surfaces are rather fast with respect to the scan rate. Also, the peaks are retained virtually the same sizes and positions during the scans. This suggests that no dissolution and replating of monometallic NPs during cycling are observed in this short time. However, the particle size distribution of NPs and the capacitive current of the SWNTs support and possibly also the local mass transport phenomena in small pores contribute to the slight diversion of this reversibility, especially at our practical scan rate. In contrast to Pt/SWNTs and Pd/SWNTs, Pd₇Pt₃/SWNTs, Pd₅Pt₅/SWNTs and Pd₃Pt₇/SWNTs show a single broadened peak at

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Figure 1 Cyclic voltammetry (A) and CO stripping (B) of Pt/SWNTs, Pd/SWNTs, Pd₇Pt₃/SWNTs, Pd₅Pt₅/SWNTs and Pd₃Pt₇/SWNTs recorded at a scan rate of 50 mV s⁻¹ in 0.5 M H₂SO₄ saturated with N₂. The peak potentials of CO stripping are plotted in (C).

0.16±0.010 V, which appears to be independent of the Pd:Pt ratios used. This feature was also observed for palladized platinum electrodes.^{4,16,17} Thus, the mixed solid samples show a striking similar electro-catalytic behaviour as bimetallic catalysts.^{4,16,17}

CO stripping voltammograms are shown in Fig. 1B and the peak potentials of CO stripping of different catalysts are presented in Fig. 1C. In all cases, no peaks were observed below 0.70 V demonstrating that the active sites on the surface of metal NPs were mainly occupied by CO molecules.¹⁸ Pt/SWNTs shows a CO oxidative stripping at lower peak potential (0.81±0.009 V) than that of Pd/SWNTs (0.99±0.008 V), which clearly suggests a facile electro-oxidation of the weaker bound CO by Pt than Pd.^{19,20} Interestingly, the stripping voltammograms for Pd₃Pt₇/SWNTs, Pd₅Pt₅/SWNTs and Pd₇Pt₃/SWNTs show splitting of the broad CO oxidation peak into two closely sub-peaks. The second one grows at the expense of the first one as higher Pd: Pt ratios are used. As seen from Fig. 1B, the broad CO oxidation peak of Pt/SWNTs also progressively shifts to 0.82±0.007, 0.87±0.006 and 0.90±0.005 V for Pd₃Pt₇/SWNTs, Pd₅Pt₅/SWNTs, and Pd₇Pt₃/SWNTs, respectively. Thus, the peak potential of the mixture appears to be tunable dependent on the Pd:Pt ratio (Fig. 1C). Similarly, PtPd co-synthesised alloy as PtPd^a (Fig. S5) also displays the intermediate CO stripping potential between monometallic Pt and Pd as that of 1:1 physical mixture of Pd/SWNTs and Pt/SWNTs.

Overall, the deviation of the peak potentials in H desorption/absorption and CO oxidation indicate a strong interaction between the two different metals in the mixed catalysts. Such interaction dominates the *in-situ* adsorption/desorption, resulting in new peak positions rather than two sets of characteristic peaks of Pd and Pt, respectively. However, in the mixed Pt/SWNTs and Pd/SWNTs samples, the supported Pt metal NPs on SWNTs should not have any extensive contact with Pd metal 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.⁴⁻⁷ It appears that simple electron transfer may have readily taken place

between Pd and Pt of different Fermi levels (FLs) via conductive SWNTs in a remote way.²¹ This electronic effect may play the

Figure 2 CV curves (A) and CO stripping (B) of SWNT-layer sandwiched electrodes recorded at a scan rate of 50 mV s⁻¹ in 0.5 M H₂SO₄ saturated with N₂. The peak potentials of CO stripping are plotted in (C).

SWNTs in a remote way.²¹ This electronic effect may play the dominant role in the resulting adsorptive/catalytic properties of bimetallic NPs, which cannot easily be segregated from other minor contributions in conventional catalysts. Apparently, the degree of back donation of CO attenuates when electrons are drained from Pd (lower FL) hence increasing the CO electro-oxidation activity with weaker CO binding.²¹ Simultaneously, the activity of Pt (higher FL) is decreased at higher potential over the electron richer Pt NPs from Pd NPs through the conductive SWNTs. Thus, this offers a simple means to modulate the adsorption and hence catalytic activity of monometallic NPs by other NPs via SWNTs.²²⁻²⁴

Clearly, the electron energy levels between the two metal NPs cannot be equilibrated in a homogeneous manner. The variations in the spatial separation of Pd NPs and Pt NPs by SWNTs at different mixed ratios leading to local differences in potentials have given rise to the two variable shouldered sub-peaks in the CO stripping. It is thus important to identify the efficiency of electron transfer between the two supported metal NPs using SWNTs as the spatial separator. To address this, sandwich-structured electrodes are designed and investigated (Fig. S6). A layer of Pd/SWNTs was first deposited on the electrode surface, on top of which 1-3 layers of SWNTs were deposited before the deposition of the outmost layer of Pt/SWNTs (with the same molar concentration of Pt in Pt/SWNTs as Pd in Pd/SWNTs). As a result, the adsorptive or catalytic changes to the Pd/SWNTs layer can be directly monitored, which is electronically modulated by the outer SWNTs and Pt/SWNTs layers. The SWNTs layers and the interface between layers cause great resistance to the electron transfer. As shown in Fig. 2A, increasing the SWNTs layers leads to the increase of the double-layer charge thickness in the potential range 0.23-0.50 V. This is due to the fact that the SWNTs layers increase the exposed surface areas of SWNTs and consequently the total charge on the surface of the electrode film.²⁵ Interestingly, all the sandwich-structured electrodes give one CO oxidation peak, the potential of which progressively shifts to approach the peak position of Pd/SWNTs with the increase of SWNTs layers. The peak potentials are 0.93±0.007, 0.95±0.005 and 0.98±0.005 V, corresponding to the electrodes with one, two and three SWNTs layers (Fig. 2B and 2C). Given that more SWNTs

layers resulting in higher resistance, the electron transfer becomes poorer, as a result, the CO oxidation peak stays closer to that of Pd/SWNTs as SWNTs layers increase. The higher current observed on sandwich-structured electrode is the result of doubled metal loading, extra SWNTs layers, and the increased surface area of top Pt/SWNTs layer which is deposited on rough surface of SWNTs layer rather than on a much smoother electrode surface.

Figure 3 CV curves (A) and CO stripping (B) of amorphous carbon-layer sandwiched electrodes recorded at a scan rate of 50 mV s^{-1} in $0.5 \text{ M H}_2\text{SO}_4$ saturated with N_2 . The peak potentials of CO stripping are plotted in (C).

We also introduced carbon layers (C= Vulcan-XC72 carbon) at the same quantity in a similar fashion this time in the sandwiched-structure (Fig. 3). The electrode with one carbon layer gives CO peak at $0.90 \pm 0.004 \text{ V}$. This value may indicate a similar electron perturbation from Pt NPs to Pd NPs through this carbon. On the other hand, we cannot exclude a degree of contact between the Pd/SWNTs and Pt/SWNTs in such small amount of carbon as the spatial separator due to the ineffective separation of this condensed form of amorphous carbon as that of SWNTs (cf. PdPt/SWNTs in Fig. 1). However, when two further carbon layers are inserted, the CO peak at $0.99 \pm 0.009 \text{ V}$ resembling to that of Pd/SWNTs is obtained. The oxidation peak of Pt is almost indiscernible in the case of the three carbon layers. Therefore, it can be concluded that the degree of electron transfer through the amorphous carbon is much weaker than that of SWNTs due to its higher inherent electrical resistance. SWNTs characterized with unusual high electron conductivity²⁶ facilitate the electron transfer, creating a conductive bridge between the two metal NPs at long range. This suggests that bimetallic catalysts supported on a highly conductive substrate such as SWNTs can tolerate metal segregation and relax the need of creating intimately alloy structures.

In summary, physical mixing of two different monometallic NPs supported on highly conductive SWNTs renders the electronic and catalytic properties comparable to alloyed bimetallic NPs. The Fermi level equilibration and the associated charge transfer between two different metal NPs in direct contact or through conductive mediator like SWNTs must at least partly explain the improved electrocatalytic properties of the bimetallic structure (see ESI).²⁷ We believe, the preliminary finding reported as this short communication note may open up a new but simple route for the preparation and engineering of bi- or multi-metallic catalysts in fuel cells or related technologies.

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