

## Fabrication of graphene-PtPd alloys with high electro-catalytic activity for ethanol oxidation

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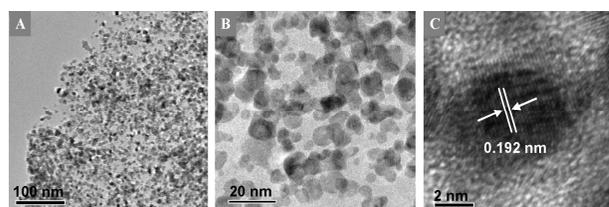
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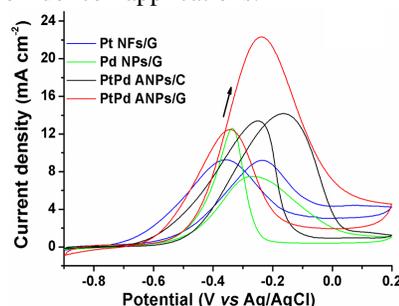
Recently, direct ethanol fuel cell (DEFC) has drawn increasing attention as a promising kind of power source due to the lower toxicity, lower membrane permeability and higher energy density of ethanol. However, a significant challenge in the development of DEFC technology is the need for highly active catalysts for the ethanol oxidation reaction (EOR) in an acid or alkaline environment that involve complete oxidation per ethanol molecule to CO<sub>2</sub>, which is difficult to implement at low temperatures. Pt-based alloy (Pt-M) catalysts, which enhance electro-catalytic activity due to their increase of Pt d-band vacancy and more favorable Pt-Pt inter-atomic distance, are well studied and widely used in DEFC [1]. In addition, in order to further maximize the activity of Pt-M catalysts and minimize the use of precious metals, it is helpful to load Pt-M catalysts on the surface of supporting nano-materials with low cost, high surface area, and good electrical conductivity. As a newly developed two-dimensional (2-D) carbon support, graphene has received considerable interest due to its outstanding physical and chemical properties [2, 3]. There are more and more examples of Pt-M alloys/graphene hybrids demonstrated to date [4]. However, in order to avoid aggregation of nanoparticles (NPs), many recent methods rely on specific capping agent for surface stabilization. Unfortunately, the presence of these agents around the NPs leads to decreasing their activity sites, which severely affect their chemical activities. Therefore, it is meaningful to develop surfactant-free method to synthesize Pt-M alloys/graphene hybrids.

Here, we described a green, one-pot and surfactant-free route to fabricate PtPd alloy NPs on graphene (PtPd ANPs/G) sheet. As a low-cost and green solvent, ethanol was used as the reductant in this preparation. In addition, graphene sheets were used as a supporting material and stabilizing agent for the deposition of PtPd ANPs. The morphology, structure and composition of the resulting PtPd ANPs/G sheets were characterized by transmission electron microscopy (TEM), high resolution TEM and high-angle annular dark-field scanning TEM (HAADF-STEM). Fig. 1A-C shows the representative TEM images of PtPd ANPs/G at different magnifications. Low-magnification TEM images (Fig. 1A and B) show that all the PtPd ANPs are uniformly distributed on the graphene surface. The absence of isolated PtPd ANPs in the product indicates a strong interaction between graphene and PtPd ANPs. The HRTEM image in Fig. 1C demonstrates the average diameter of the PtPd ANPs is about 7.6 nm. The inter-planar spacing is 0.192 nm, which agrees well with the (200) lattice spacing of face-centered-cubic (fcc) Pt and Pd. The elemental distribution of the PtPd ANPs/G catalyst was studied by HAADF-STEM technique. The results revealed that both Pt and Pd have a homogeneous distribution on the nanoparticles, suggesting the formation of an alloy structure.



**Fig. 1** (A-C) Representative TEM (A, B) and HRTEM (C) images of PtPd ANPs/G hybrids.

EOR was studied to investigate the electro-catalytic performance of the catalysts. Fig. 2 shows the cyclic voltammetry (CV) curves of EOR in Pt NFs/G, Pd NPs/G, PtPd ANPs/C and PtPd ANPs/G at 50 mV s<sup>-1</sup> in 1.0 M NaOH containing 1.0 M ethanol. The onset potential of ethanol oxidation for PtPd ANPs/G was -0.50 V, which is more negative than that of other three catalysts. Moreover, the maximum current density of PtPd ANPs/G reaches at 22.4 mA cm<sup>-2</sup> in the forward scan, while that for Pt NFs/G, Pd NPs/G and PtPd ANPs/C is 9.1, 7.5 and 14.2 mA cm<sup>-2</sup>, respectively. The ratio of the forward anodic peak current (I<sub>p</sub>) to the backward anodic peak current (I<sub>b</sub>) for PtPd ANPs/G is 1.81, which is higher than other three catalysts. These results indicated that the as-prepared PtPd ANPs/G hybrids showed a higher electro-catalytic activity and better tolerance towards CO poisoning, which may provide an insightful way to develop advanced electro-catalysts for fuel cell applications.



**Fig. 2** CVs of Pt NFs/G (blue line), Pd NPs/G (green line), PtPd ANPs/C (black line) and PtPd ANPs/G (red line) at 50 mV s<sup>-1</sup> in 1.0 M NaOH containing 1.0 M ethanol.

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### References

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