

Correlation between Carbon Spacer Ratio in 3D Reduced Graphite Oxide-Nanoribbon and Catalytic Performance of 3D carbon supported PtPd

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The design of decorating metal crystals on carbon materials was widely considered as milestone for the development of fuel cell due to the improved particle distribution, high electron conductivity as well as enhanced mass transportation<sup>1</sup>. Recently, one-atom layer thick graphene draw great attentions for its superior physical properties<sup>2</sup>. However, the strong restacking of graphene layers would lead the loss of effective surface area for supporting metal nanoparticles. To avoid this, we have firstly reported using nanoribbon (NR), a partially exfoliated multi-walled carbon nanotube, as effective carbon spacer to prohibit the restacking of graphene lattice. The previous results demonstrated that 3D carbon composite supported PtPd electrocatalyst showed enlarged electrochemical active surface area (ECSA) and enhanced mass activity for methanol oxidation reaction (MOR), which is a rate-determining electrode reaction for direct methanol fuel cells. In this study, a series of 3D carbon composite supported catalysts were prepared and their catalytic activities were also compared. We investigated the relationship between the carbon spacer ratio and catalytic performance.

Graphite oxide (GO) and nanoribbon (NR) were prepared by modified Hummers' method.<sup>3</sup> The as prepared GO and NR mixtures with different weight ratios (9:1, 5:5, 1:9) have been reduced concomitantly with Pt and Pd ions by chemical method<sup>4</sup> to form novel 3D hybrid catalyst with high active surface area. The products were characterized by BET, TEM, SEM, XRD, TG and ICP. And the electrochemical measurements were done using standard three-electrode system.

The weight ratios between GO and NR were selected as 5:5, 1:9 and 9:1 to investigate the 3D structure formation as well as their relationship to the catalytic activities. Generally, as shown in Fig. 1, PtPd nanoparticles with average sizes of 3.5 nm, 3.6 nm, 3.9 nm, 4.2 nm and 5.3 nm were formed and distributed among different carbon substrates with increased amount of NR.

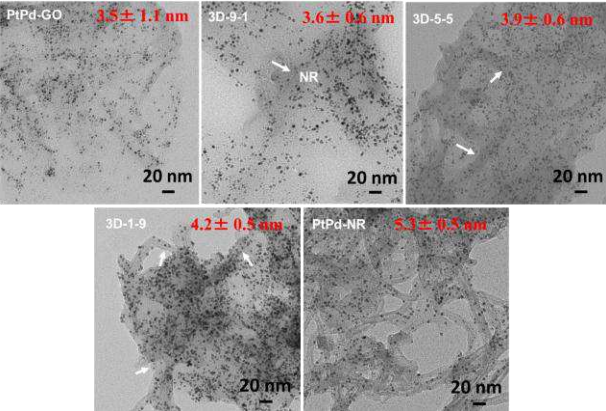


Fig. 1 TEM images all the catalysts with different carbon spacer ratios.

TEM images show the morphology changes of 3D carbon composite by varying the carbon spacer ratios. As

NR increases, more spacers were intercalated with graphene layers, however the aggregations of tubular NR occurred when the NR ratio increased beyond 50%. When only NR was used for supporting PtPd nanoparticles, both aggregations and layer structures were observed since the open parts in NR tended to overlap with the similar structures in the neighbor NRs. In addition, when the spacer ratio was high, the particle size became larger due to the less amount of functional groups.

Fig. 2a shows Cyclic Voltammograms (CVs) of all the catalysts with distinct hydrogen adsorption/desorption region, double-layer region, and the surface oxide formation/reduction region. The electrochemical surface areas (ECSA) calculated from the hydrogen adsorption-desorption charge ( $Q_H$ ) for each sample were 50, 72, 164, 87 and 56  $m^2/g_{Pt}$  respectively. Methanol oxidation reaction (MOR) measurements (Fig. 2b) showed the mass specific activities ( $I_m$ ) for each catalyst were 176, 274, 565, 458 and 345  $mA/mg_{Pt}$ .

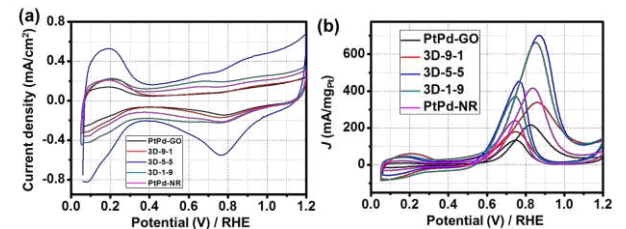


Fig. 2 (a) Comparative CVs in  $N_2$  saturated 0.1 M  $HClO_4$  solution at scan speed of 20 mV/s and (b) CVs of all the catalysts in 0.1 M  $HClO_4$  and 0.1 M methanol solution at scan speed of 20 mV/s.

As shown in Table 1, when increasing the amount of NR, surface area of graphene has been effectively increased due to the formation of 3D structure. Similarly, the ECSA value and mass activity of the catalyst also showed the same trend until the GO/NR was 5:5. Beyond this ratio, the surface area of carbon composite decreased and the ECSA value and mass activity toward MOR were suppressed due to the strong aggregations between the NRs, since NRs tended to aggregate into large rod through interactions between the open parts.

Table 1. Summary of different catalysts

| Catalysts | BET of carbon support ( $m^2/g$ ) | Particle size (nm) | Metal loading (wt%) | ECSA ( $m^2/g_{Pt}$ ) | $I_m$ (MOR) $mA/mg_{Metal}$ |
|-----------|-----------------------------------|--------------------|---------------------|-----------------------|-----------------------------|
| PtPd-GO   | 17.2                              | $3.5 \pm 1.1$      | Pt: 18.3, Pd 4.0    | 50                    | 176                         |
| 3D-9-1    | 21.2                              | $3.6 \pm 0.6$      | Pt: 16.7, Pd: 4     | 72                    | 274                         |
| 3D-5-5    | 51.6                              | $3.9 \pm 0.6$      | Pt: 18.6, Pd: 3.7   | 164                   | 565                         |
| 3D-1-9    | 50.5                              | $4.2 \pm 0.5$      | Pt: 8.8, Pd: 1.8    | 87                    | 458                         |
| PtPd-NR   | 36.9                              | $5.3 \pm 0.5$      | Pt: 16.9, Pd 3.4    | 56                    | 345                         |

In conclusion, the restacking of graphene layers could be most effectively prohibited by taking a proper amount of carbon spacer. PtPd nanocrystals supported on 3D carbon with 50% NR spacer showed the highest ECSA value and activities in the methanol electrooxidation due to the enlarged surface area, small particle size as well as homogenous distribution.

References

1. Y. Qiao and C. Li, J. Mater. Chem., **21**, 4027, (2011).  
2. S. Guo, S. Dong and E. Wang, ACSNANO, **4**, 547, (2010).  
3. Hummers, Jr and R. E. Offeman, J. Am. Chem. Soc., **80**, 1339, (1958).  
4. B. A. Kakade, T. Tamaki, H. Ohashi, T. Yamaguchi, J. Phys. Chem. C, **116**, 7464, (2012).