Few layer graphene decorated with Pd nanoparticles: synthesis, characterisation and catalytic applications in the electrochemical oxidation of alcohols

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Due to their unique graphitized basal planar structure, chemically inert nature and high conductivity, graphene and graphene-based composite materials are among the most promising alternatives as electrode materials in energy-related devices.[1,2] Graphene sheets decorated with metal nanoparticles are typical examples of emerging metal-carbon composites that currently attract special research efforts due to their enhanced potential for catalytic applications.[3] One of the most interesting is related to the electrocatalytic activity in alcohol oxidation reactions for energy production where metal-decorated graphene has been reported to be more efficient than any other commercially available material.[4] In this communication, we present first results on the CVD synthesis of few layered graphene (FLG), the formation of metal-graphene composites and the testing of these materials in the electrochemical oxidation of ethanol, ethylene glycol, glycerol and 1,2-propanediol.

FLG and FLG-MWCNT (multiwall carbon nanotubes) composites were prepared by ethylene CVD at 650°C.[5,6] TEM (Figure1a) and Raman spectra showed that the FLG sample contained few layered graphene flakes with thickness (as determined by the broadening of the x-ray powder diffractograms) ranging from 0.5-8 nm. In order to achieve better metal dispersion, all carbon samples were treated with nitric acid to introduce surface oxygen functionalities that will help anchoring the metal precursor. A suspension of 1 g of sample was placed in a 250 mL flask containing 100 mL of THF and sonicated for 15 minutes prior to the addition of 0.15 g [$Pd_2(dba)_3$] precursor and left stirring at 40°C for 3 days. The solid product was filtered and dried under vacuum, and then it was ground and reduced at 300°C in hydrogen (20 vol. % in Ar) . After reduction the sample was stored under argon.

The three samples were characterized via cyclic voltammetry (CV) with KOH 2M, Ethanol (EtOH) 10 wt. % KOH 2M, Ethylene glycol (EG) 10 wt. % KOH 2M, Glycerol (Gly) 10 wt. % and 1,2-propandiol (1,2-Prop) 10 wt. % KOH 2M aqueous solutions. The reference electrode was $Ag/AgCl/KCl_{sat}$ and all potentials were referred versus RHE. The working electrode was made as described below: each catalyst (about 40 mg) was dispersed in a solution of water and *i*-propanol (1.2:0.7 g) and sonicated for one hour; the resulting ink was dropped on a glassy carbon disk (about 5 mg) and a drop (2.5 µL) of a solution of AS-4 Tokuyama ionomer was added. The metal loading was about 30 µg cm^{-2}.

Figure 1 shows a TEM image of few layer graphene and (b) shows a graphene flake coated with Pd nanoparticles. A statistical count of the particle sizes for the samples yielded an average diameter of 8.4 nm for Pd/FLG and 8 nm for Pd/MWCNT. On the other hand, Pd/FLG-MWCNT showed an average particle size of 6.4 nm indicating the presence of a synergetic effect for the mixture of graphene and CNTs as a smaller Pd particle size was observed.

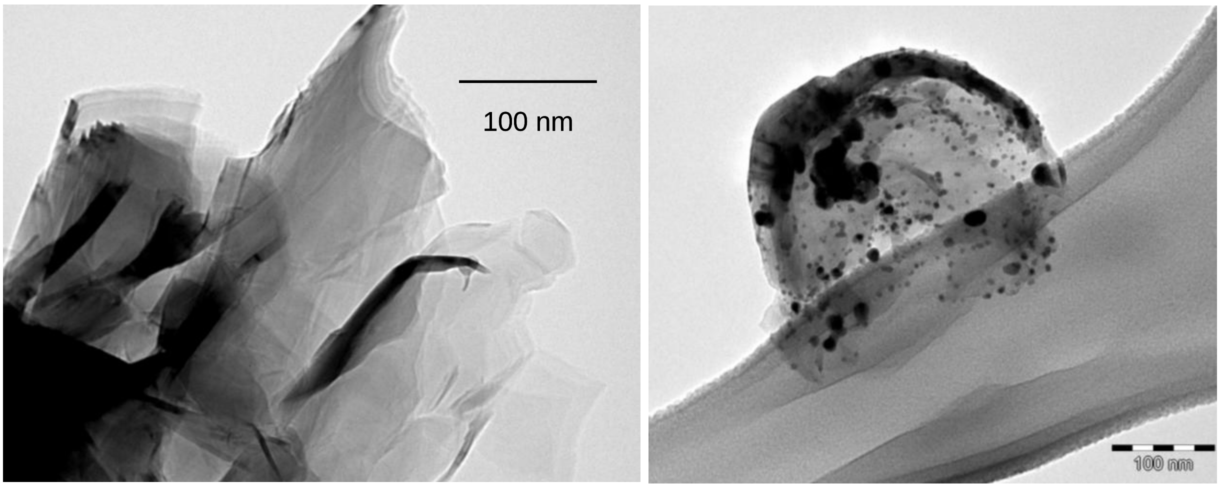

Figure 1. TEM micrographs of (a) few layer graphene, and (b) Pd/FLG catalyst.

Pd/FLG catalyst showed the highest performance toward the oxidation of ethanol with a peak current of ca. 100 mA cm^{-2} and a current at 0,5 V of ~ 10,5 mA cm^{-2}. The best catalyst for the other alcohols (1,2-propanediol, ethylene glycol and glycerol) was Pd/FLG-MWCNT with a very high values of current at 0.5 V and peak current densities. This improved performance is probably related to the presence of smaller Pd particles. These results are very promising, especially if compared to previously published results for Pd/CNT[7] that showed a current density peak of about 34 and 47 mA cm^{-2} toward ethanol and glycerol oxidation.

CONCLUSIONS

The synthesis and characterization of few layer graphene coated with Pd nanoparticles has been reported. The FLG-MWCNT composite substrate showed improved performances when compared to MWCNT or FLG substrates and this observation is related to the smaller particle size of the Pd on this substrate.

References

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