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Efficient Pt electrocatalysts supported onto flavin mononucleotide–exfoliated pristine graphene for the methanol oxidation reaction

M. Ayán-Varela[a,*], R. Ruiz-Rosas[b], S. Villar-Rodil[a], J.I. Paredes[a], D. Cazorla-Amorós[b], E. Morallón[b], A. Martínez-Alonso[a], J.M.D. Tascón[a]

[a] Instituto Nacional del Carbón, INCAR-CSIC, Apartado 73, 33080 Oviedo, Spain
[b] Instituto Universitario de Materiales, Universidad de Alicante, 03690 San Vicente del Raspeig, Alicante, Spain

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ABSTRACT

Due to its large surface area, high electrical conductivity as well as mechanical and thermal stability, pristine graphene has the potential to be an excellent support for metal nanoparticles (NPs), but the scarce amount of intrinsic chemical groups/defects in its structure that could act as anchoring sites for the NPs hinders this type of use. Here, a simple strategy based on the stabilization of pristine graphene in aqueous dispersion with the assistance of a low amount of flavin mononucleotide (FMN) is shown to yield a material that combines high electrical conductivity and abundance of extrinsic anchoring sites, so that pristine graphene–metal (Pd and Pt) NP hybrids with good dispersion and metal loading can be obtained from FMN–stabilized graphene. The activity of these hybrids towards the methanol oxidation reaction (MOR) both in acidic and alkaline media is studied by cyclic voltammetry (CV) and their stability investigated by chronoamperometry. The pristine graphene–Pt NP hybrid prepared by this simple, eco–friendly protocol is demonstrated to outperform most previously reported pristine graphene– and reduced graphene oxide–metal NP hybrids as electrocatalyst for the MOR, both in terms of catalytic activity and stability, avoiding at the same time the use of harsh chemicals or complex synthetic routes.

1. Introduction

Owing to the increasing demand of sustainable alternatives to the environmentally troublesome fossil fuels extensively used nowadays, direct methanol fuel cells (DMFCs) have attracted significant attention over the last years as an efficient portable power source for electronic devices [1,2]. This interest is due to the easy transport, storage and manipulation of liquid fuels, as well as to the high energy conversion efficiency and low operation temperature and pollutant emission associated to DMFCs [3,4]. On the other hand, DMFCs suffer from two remarkable disadvantages: (1) methanol crossover in the electrolyte membranes from the anode to the cathode and (2) sluggish kinetics of the methanol oxidation reaction (MOR) [5–7]. To address the former issue, a lot of effort has been focused on the development of new proton and anion exchange membranes [8,9]. To mitigate the latter limitation, a common strategy involves the use of suitable electrocatalysts to overcome the activation barrier associated to the MOR. In this regard, it is well known that Pt is the most active metal electrocatalyst [10–12], but other metals (e.g., Pd, Ni, Co or Cu) and metal alloys are also explored because of their lower cost and better tolerance to poisoning by CO [13–16]. In addition to the electrocatalyst itself, proper selection of a good support material is a critical issue, due to its potential influence on the size, distribution and morphology of the metal component. For application in DMFCs, ideal supports must have a large surface area, high conductivity and should be able to anchor and stabilize ultrafine metal nanoparticles (NPs), avoiding their aggregation.

Carbon materials, such as carbon nanotubes [17], carbon black [18], ordered mesoporous carbon [19], carbon nanofibers [20] and graphene [21], have emerged over the last years as suitable supports for metal NPs towards fuel cell applications. In particular, graphene exhibits a unique two-dimensional honeycomb atomic structure with large surface area, structural, mechanical and thermal stability as well as high charge carrier mobility and electrical conductivity [22,23]. These attractive features make graphene an excellent support for metal NPs, with a potential to

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[*] Corresponding author: Tel.:+ +34 985 11 90 90 fax: +34 985 29 76 62.
E-mail address: m.ayan@incar.csic.es (M. Ayán-Varela).

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enhance their electrocatalytic activity. Currently, the most common route to synthesize metal and other NPs onto graphene materials as supports takes advantage of the peculiar characteristics of a well-known derivative of graphene, i.e. graphene oxide (GO). GO boasts good dispersibility in water and some organic solvents, which facilitates the deployment of wet colloidal NP preparation methods, and is also extensively decorated with oxygen functional groups, which serve as tight anchoring sites for the nucleation and growth of the NPs [21,24–26].

However, the use of GO-based or reduced graphene oxide (RGO)–based supports in electrocatalytic applications has also significant drawbacks. For instance, the presence of oxygen functional groups, which cannot be completely removed by the usual reduction approaches, degrades the electrical conductivity of the carbon lattice and compromises its stability under the harsh electrochemical conditions of fuel cells [27]. Therefore, finding alternative graphene materials that can escape the limitations of GO but exhibit at the same time its main attractions would be highly desirable. Pristine graphene flakes and sheets are in principle an obvious option in this regard, because their oxide-free nature endows them with high electrical conductivity and chemical/electrochemical stability. Indeed, a few recent studies have focused on metal NP-pristine graphene systems as electrocatalysts for alcohol fuel cells [28–33]. Such studies relied either on graphene layers synthesized by chemical vapor deposition (CVD) [28,31–33] or on flakes obtained by direct, ultrasound-assisted exfoliation of graphite powder in organic solvents, such as *N*-methyl-2-pyrrolidone (NMP) [29,30]. Nevertheless, the use of these specific types of pristine graphene is not without its disadvantages. For example, the synthesis of CVD graphene is a relatively complex process that requires high temperatures, whereas NMP is a high boiling point and non-innocuous solvent that encumbers further processing of the exfoliated graphene flakes (in this regard, production/processing in water would be clearly preferable). More generally, the absence (or very low density) of chemical groups and defects in pristine graphene materials makes their uniform decoration with firmly anchored NPs harder to attain. Thus, the deployment of simpler and safer methodologies towards the production of efficient pristine graphene–metal NP electrocatalysts for MOR is still in great demand.

A solution to the mentioned limitations of pristine graphene-supported electrocatalysts could be based on the use of certain amphiphilic molecules with the ability to strongly adsorb onto graphene and play a dual role: (1) they would act as colloidal stabilizers to afford the production and processing of pristine graphene flakes in aqueous medium and (2) they would serve as anchoring sites to allow extensive and uniform decoration of the flakes with metal NPs. In this respect, we have very recently demonstrated the utility of flavin mononucleotide (FMN), an innocuous and safe derivative of vitamin B_2, as an exceedingly efficient dispersant of pristine graphene flakes in water [34]. Significantly, very low fractions of FMN (FMN/graphene mass ratios down to 0.04) are able to colloidally stabilize high graphene concentrations (up to $\sim 50\,\mathrm{mg\,mL^{-1}}$), and the amphiphile is strongly adsorbed onto the graphene surface via π-π interactions, thus avoiding any significant structural alteration of the carbon lattice. As a result, FMN-based graphene films were shown to exhibit very high electrical conductivity. In addition, the adsorbed FMN molecules served as efficient extrinsic anchoring sites for the nucleation and growth of metal NPs on the graphene flakes. All these results suggest that FMN-based metal NP-pristine graphene hybrids could possess a strong potential as high performance electrocatalysts for MOR, but studies along this line have not yet been undertaken. Hence, in the present work we have prepared Pt and Pd NPs onto FMN-stabilized graphene flakes and investigated their use as electrocatalysts for MOR. The results indicate that these hybrids exhibit improved electrocatalytic activity in relation to many other graphene-based systems, and therefore constitute a highly competitive option for use in DMFCs as a result of, e.g., their simplicity of preparation or use of completely innocuous reagents (FMN).

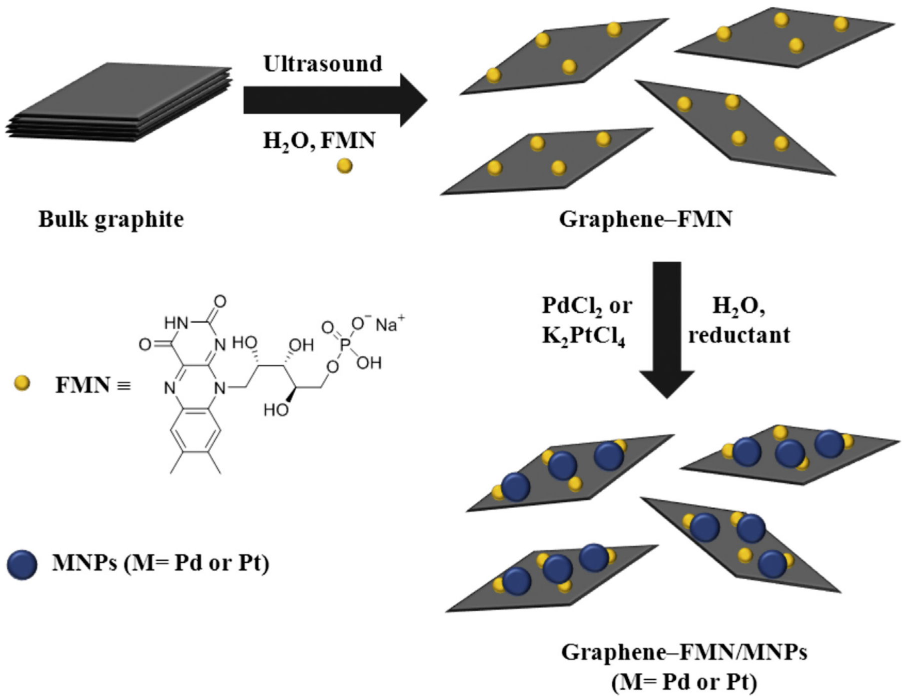

Fig. 1. Schematic of the FMN-assisted exfoliation and stabilization in water of pristine graphene, followed by the preparation of pristine graphene–metal NP hybrids.