Graphene oxide in palladium nanoparticle (GrafeoPlad): a new class of catalytic materials for heterogeneous catalysis

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By encapsulating graphene oxide in palladium metal nanoparticles and reporting the first application of the resulting metal-organic alloys to nitrobenzene hydrogenation with hydrazine at room temperature, we introduce a completely new class of catalytic materials dubbed herein "GrafeoPlad" for designing platinum-group metals doped with 3D entrapped graphene oxide. This new class of hybrid materials opens practically relevant new perspectives in many areas of today's catalysis science and technology.

Consisting of organic molecules 3D entrapped in the lattice structure of metal crystals, organically doped metals were introduced by Avnir in 2002 reporting the entrapment of Congo Red dye in silver.1 As simple as effective, the method involves concomitant dissolution in water of a metal salt precursor and of the dopant organic molecules, followed by reduction of the metal cations with a reducing agent. Employing a surfactant, the method was readily demonstrated to be effective also for the entrapment of water-insoluble organic molecules.1 In 2008 Avnir’s team also demonstrated the successful encapsulation of polymers in Cu and in Ag either by emulsifying the dopant molecules in water with a surfactant or by utilizing a solvent such as dimethylformamide.2 The subsequent year, reporting the encapsulation of Cu(II) and Fe(III) phthalocyanines in Ag nanoparticles, Pagliaro and co-workers in 2009 dubbed these materials “metal-organic alloys” (MORALs).3 Today, the applications of MORALs range from ionicomer@Ag for enhanced electrocatalytic anion-exchange membranes for hydrogen fuel cells4 through alkaloid@Cu for highly selective, waste-free, electrocatalytic asymmetric ketone hydrogenations.5

Avnir has reviewed advances in this completely new field of materials chemistry in 2014 and in 2018.6,7 Graphene has been widely studied as reinforcing material in different metal/graphene composite materials (generally made by mixing, compacting and sintering or by extrusion).8 For instance, graphene coated on both sides of a Cu foil via a chemical vapor deposition (followed by stacking and hot pressing numerous layers of numerous Gr/Cu/Gr foils) affords copper having an electrical conductivity 117% higher than pure copper.9 Other applications of graphene and metals include the use of graphene as support of metal nanoparticles10 or of single metal atoms11 for catalytic applications. Now, reporting the encapsulation of graphene in palladium metal nanoparticles, we introduce a completely new class of catalytic materials dubbed herein “GrafeoPlad” for designing platinum group metals doped with 3D entrapped graphene. Depicted in Scheme 1, the catalyst synthesis goes through the employment of water-soluble graphene oxide (GO).

### Scheme 1. Synthesis of GO@nPd, palladium-entrapped graphene oxide.

In detail, the catalytic material is prepared by adding a solution of 200 mg PdCl₂ (Sigma Aldrich, Milan, Italy) in 50 mL aqueous ethanol (H₂O:EtOH 1:1) kept under stirring with 452 μL of an aqueous solution of graphene oxide (GO, 8 mg/mL, purchased by Nanografí Nano Teknoloji, Turkey). After 30 min stirring, the mixture was added with 86 mg of powdered Zn (Sigma Aldrich, Milan, Italy). Thus suspensions nearly immediately turned to black due to formation of Pd nanoparticles embedding the GO. The mixture was left overnight to ensure complete reduction of Pd²⁺ cations and concomitant entrapment of the GO platelets, after which a solid black precipitate (GrafeoPlad or GO@nPd, where n stands for “nanoparticle”) was filtered through a paper filter (Whatman 5), washed with HCl 0.1 M to remove the excess of Zn, and dried overnight at 40 °C in an oven.

The transmission electron microscopy (TEM) experiments were carried out using a Thermo Fisher Scientific Talos L120C instrument operating at 120 kV. Samples were deposited on Cu-
The XRD diffractograms were obtained using a Rigaku Miniflex 600 diffractometer with Cu Kα radiation (λ = 0.1541 nm), acquiring data in the 10–80° 2θ range with a step size of 0.05° and a counting time of 8 s per step. The FTIR spectra were recorded with a JASCO FT/IT 4100 instrument, preparing the samples in KBr pellets, acquiring data in the 4000–6000 cm⁻¹ range. The catalytic reduction of nitrobenzene (99% purity, Sigma Aldrich, Milan) was carried out at room temperature using hydrazine hydrate (85% solution, Carlo Erba, Milan). In a typical reaction, 40 μL of nitrobenzene (3.9·10⁻⁴ mol) and 46 μL of hydrazine hydrate (8.04·10⁻⁴ mol) were dissolved in 6 mL of methanol in the presence of 3 mg of GrafeoPlad. The reaction was also carried out employing 63 mg of a commercial Pd/C (5 wt%) catalyst (Engelhard, Rome, Italy), containing the same amount of Pd. In each case, the reaction was monitored with a Shimadzu LC-10AD VP HPLC equipped with a RID-10A detector and Restek Ultra BiPh 5μm column (Restek, Cernusco Sul Naviglio, Italy) using a mixture H₂O:MeOH 1:1 as eluent. At the end of the reaction, the catalyst was recovered by centrifugation and washed using ethyl acetate.

The TEM photographs of GrafeoPlad show that the material is comprised of aggregated palladium nanoparticles (Figure 1, left), some of which clearly reveal (Figure 1, center) the presence of glassy GO layers on the edge of the aggregated nanoparticles. In other parts of the material the Pd nanoparticles are deposited over large GO layers (Figure 1, right).

The XRD diffractogram of GrafeoPlad (Figure 3) shows evidence that the material consists of graphene oxide entrapped in Pd nanoparticles (GO@nPd). Well-defined peaks around 40° and 46° in the diffractogram originate from the (111) and (200) crystal planes of Pd nanoparticles 9 nm in diameter (derived by the Scherrer equation).

Successful encapsulation of the GO layers is shown by the typical infrared absorption “fingertip” absorption bands in the FTIR spectrum in Figure 4: at 3424 cm⁻¹ and 3442 cm⁻¹ (O–H group stretching vibrations), 1721 cm⁻¹ (carboxylic C=O stretching) and 1637 cm⁻¹ (carbonyl C=O stretching), 2919 cm⁻¹ and 2849 cm⁻¹ (carbonil C–H combination bands), 1144 cm⁻¹ and 1094 cm⁻¹ (C–O stretching vibrations), and about 1380 cm⁻¹ due to the C–OH bond stretching frequency. In the case of GO, the shoulder peak at 1227 cm⁻¹ is ascribed to the C–O–C stretching mode.
Figure 4. FTIR spectrum for GO and GO@nPd.

Compared to the prepared GO, the C=O stretching of Pd-GO was slightly shifted to a shorter wavenumber, i.e., 1561 cm\(^{-1}\), suggesting the formation of Pd carboxylates for the GO entrapped in the Pd lattice.\(^{13}\)

As mentioned above, the catalyst was employed in nitrobenzene hydrogenation with hydrazine in liquid phase at room temperature. Figure 5 shows the kinetics of the hydrogenation next to the kinetics of the same reaction mediated by the commercial Pd/C catalyst. Both catalysts selectively afford aniline, with the commercial Pd/C rapidly affording complete conversion of the substrate after 15 min, whereas the conversion of nitrobenzene over GrafeoPlad after 60 min was about 75%.

Remarkably, the filtration test in which the catalyst is removed by filtration when reaction is not complete (after 5 min, in this case) proved that no active species of Pd are leached in solution due to complete absence of reactivity of the reaction filtrate upon filtering the catalyst (Figure 6).

Finally, the catalyst was reusable with only modest loss in activity between the first and the second reaction run (Figure 7), likely due to adsorption and partial pore blockage of the hydrophilic reactant and product molecules in the inner porosity of the partly hydrophilic GO@nPd nanoparticles comprising the catalyst.

The FTIR spectrum in Figure 8 of GrafeoPlad after mediating the hydrogenation of nitrobenzene with hydrazine shows that the signal due to carbonyl group (1637 cm\(^{-1}\)) decreases, whereas the signal at 1384 cm\(^{-1}\) due to the C-OH bond stretching frequency sharpens.

Figure 5. Kinetics of nitrobenzene hydrogenation with hydrazine mediated by GO@nPd and by commercial Pd/C (5 wt%).

Figure 6. Activity of the reaction mixture and of reaction filtrate upon removing the GO@nPd catalyst via filtration.

Figure 7. Conversion of nitrobenzene to aniline mediated by GO@nPd in five consecutive reduction runs.

Figure 8. FTIR spectrum for GO@nPd after mediating the reaction of nitrobenzene with excess hydrazine.
This outcome may be due to the Pd nanoparticles embedding the GO layers of GrafeoPlad catalyzing the reduction of graphene oxide carbonyl groups to alcoholic functions. We remind that the reduction of GO to graphene (reduced graphene oxide, RGO) with hydrazine requires prolonged (3 h) treatment of GO at 95 °C.14

We ascribe the good catalytic activity of GrafeoPlad to the electron donation from the extensive π-π bonds in the hexagonal carbon lattice of graphene oxide to the unoccupied orbitals of Pd nanoparticles, as it happens with the enhanced catalytic activity of Pd towards H₂ chemisorption, with graphene acting both as an electron reservoir and molecular pathway.15 Studies on Pd NPs deposited on graphene oxide suggest that the activity of the resulting catalyst, for example in cross-coupling reactions, is due to the single-layer hydrophilic sheet structure onto which polarized substrates such as aryliboronic acids easily adsorb and from which the less polarized biphenyl products can readily dissociate.16 GO and Pd/GO nanosheets, however, tend to self-assemble at relatively higher concentrations and temperatures, especially in aqueous media, requiring exfoliation of the GO sheets by surfactants to enhance the catalytic activity of the Pd/GO nanosheets.16

The 3D entrapment of graphene oxide in the crystal lattice of Pd is completely different from the 2D adsorption of Pd nanoparticles on GO, and opens the path to GrafeoPlad applications in catalysis with even higher efficacy and at substantially lower cost than Pd nanoparticles supported on GO,17 well beyond the catalytic reduction of nitrobenzene to aniline at room temperature reported herein.

For practical applications in which higher activity is required, the GrafeoPlad nanoparticles will be dispersed on large surface area supports ensuring enhanced accessibility of the reactants to the catalytic active species, as it happens with the MORAL made of Ag entrapping a molecular dye supported on TiO₂ nanotubes to catalyze methanol partial oxidation with unprecedented high activity and catalyst stability.18

The findings reported in this communication are general. GO entrapment is possible in many other metals, including all platinum-group (PGM) metals, opening the route to practically relevant applications of GrafeoPlad and GO@Metal hybrid materials belonging to Avnir’s MORALs6,19 in many of today’s relevant areas of catalysis science and technology.

Acknowledgements
This study is dedicated to Professor David Avnir on the occasion of his 75th birthday. We thank the Università degli Studi di Milano PSR2021_DIP_005_PI_CDPIN project for funding, and Dr Nadia Santo, Unitech NOLIMITS, Università degli Studi di Milano, for the TEM images.

Electronic supplementary information
A video with the catalyst preparation can be freely watched at the URL: http://bit.ly/4029FrS. High resolution TEM pictures depicting the GrafeoPlad catalyst prior and after use as well as the commercial Pd/C catalyst also prior and after use can be freely accessed at the URL: https://bit.ly/43wECAh.

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Notes
The Authors declare no competing financial interest.

Data availability
All data are available upon reasonable request by contacting the corresponding Authors.

References


