



A synchrotron-based spectroscopic study of the electronic structure of N-doped HOPG and PdY/N-doped HOPG



M. Favaro ^{a,1}, G.A. Rizzi ^a, S. Nappini ^b, E. Magnano ^b, F. Bondino ^b, S. Agnoli ^a, G. Granozzi ^{a,*}

^a Department of Chemical Sciences, University of Padova, Via Marzolo 1, 35131 Padova, Italy

^b IOM-CNR, Laboratorio TASC, Area Science Park Basovizza, s.s. 14 km 163, 5 Basovizza, 34149 Trieste, Italy

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ABSTRACT

N-doped Highly Oriented Pyrolytic Graphite (HOPG) (obtained by ion implantation) was used as a model system for mimicking the effect of N-doping in sp^2 hybridized carbon based supports. The electronic structure of such system has been carefully characterized by means of spectroscopic techniques adopting synchrotron radiation. We demonstrate that it is possible to tailor different functional groups simply by tuning the annealing temperature after ion implantation. On such chemical modified HOPG, PdY catalyst nanoparticles have been deposited under strictly controlled conditions in ultra-high-vacuum (UHV) and the nanoparticle/support interactions studied by photoemission. The formation of the Pd₃Y alloy is evidenced by core level shift in Y 3d and Pd 3d states due to charge transfer.

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1. Introduction

The best way to reach the goal of stable, efficient and cost effective electrocatalytic materials for fuel cells is to use a rational design of the metal catalyst/support assembly. In this respect, the approach based on studies of model electrodes can be of value and their outcomes can be capitalized to implement efficient real electrodes to be properly tested in real working conditions.

In particular, HOPG (Highly Oriented Pyrolytic Graphite) is a reliable sp^2 -carbon model substrate that represents a simplified playground where the interaction between the catalyst nanoparticles (NPs) and the support can be easily studied.

HOPG is a carbon-based material made by high-temperature decomposition of gaseous hydrocarbons, often acetylene, followed by hot pressing at high pressure and temperature [1]. Pyrolytic carbon usually has a single cleavage plane because the single graphene sheets crystallize with an ordered stacking, as opposed to graphite that forms microscopic randomly-oriented zones. Because of this peculiar structure, pyrolytic carbon exhibits several unusual anisotropic properties [1].

Usually, a strong NP/support interaction is beneficial to reduce several degradation processes (e.g. agglomeration, detaching...) therefore increasing the electrode stability. A viable strategy to enhance the catalyst NPs/support interaction is associated with the introduction of

substrate defects that can act as trapping sites for anchoring highly dispersed catalyst NPs. In general, morphological defects introduced by a carbon atom re-hybridization (sp^2 to sp^3) and amorphization of the substrate are beneficial to increase the NP/support interaction [2]. On the other hand, extended amorphization of the support is detrimental with respect to the substrate conductivity, so a trade-off is needed. One route to minimize the conductivity decrease while maximizing the NP/support interaction is to resort to extrinsic chemical defects (such as boron, nitrogen and sulfur) rather than to morphological defects. They can be introduced by means of doping, and specific interactions, possibly modulating the electronic charge of the catalyst NPs, can be produced. Therefore the modification of the support allows tailoring the electronic properties of the catalyst.

In the last few years, chemical doping of sp^2 -carbon materials by nitrogen has been studied [3–6], and excellent stability and high performances over time of the NP/support assembly have been obtained [5,7]. Moreover, specific chemical interactions can trigger enhanced chemical reactivity so that even normally inert materials become highly reactive. Even more interestingly, it has been fully demonstrated that a properly doped support can become catalytically active itself [5,8].

In this study, N-doped HOPG (obtained by ion implantation, hereafter N-HOPG) was used as a model system for mimicking the effect of N-doping in sp^2 hybridized carbon based supports. The outcomes of this study can be also of relevance in the field of metal NPs/graphene composites for advanced energetics, since the special properties of these composite systems stem from very subtle electronic interactions (i.e. interfacial hybridisation), which very often involve specific defects of the sp^2 carbon lattice [9–11]. On such chemical modified HOPG, metal catalyst NPs have been deposited under strictly controlled

* Corresponding author.

E-mail address: gaetano.granozzi@unipd.it (G. Granozzi).

¹ Current address: Advanced Light Source (ALS), Joint Center for Artificial Photosynthesis (JCAP), Lawrence Berkeley National Laboratory, 1 Cyclotron Rd., M/S 6R2100 Berkeley, CA 94720, United States.

conditions in ultra-high-vacuum (UHV) and the NP/support interactions studied by the premises of surface science. We have herein considered PdY NPs as a potentially innovative catalyst. Actually, large efforts are currently devoted to test Platinum Group metals (PGMs) alloys with Rare Earth (RE) metals in order to reduce the content of the PGM while maintaining a sufficient catalyst activity and durability [12].

We report herein a detailed study of the chemical and electronic properties of N-HOPG based on several synchrotron-based surface techniques, namely High Resolution Photoemission Spectroscopy (HR-PES), Resonance Photoemission Spectroscopy (Res-PES), Near Edge X-ray Absorption Fine structure Spectroscopy (NEXAFS) and Low Energy Electron Diffraction (LEED). This study fully confirms the observations already obtained in our previous works [13–15] on HOPG and N-HOPG based on standard photoemission, and provides new insights in the electronic properties of these modified systems, with a detailed study of the valence band (VB). Moreover, on such HOPG and N-HOPG substrates we have deposited in UHV ultrathin films of Pd and Y and prepared by thermal annealing Pd₃Y alloyed NPs, as demonstrated by the use of HR-PES.

2. Experimental

Concerning the morphology, pure HOPG shows microcracks with varied length and width [16]. The existence of these cracks in crystallites of polycrystalline graphite was proposed firstly by Mrozowski [17]; for this reason, these features are usually known as *Mrozowski cracks*. In situ observations show that these cracks tend to close up heating HOPG at high temperature. For this reason, in order to obtain a clean and flat sample surface, annealing in UHV has been performed after the peeling (by scotch tape) of HOPG (Mikromasch, ZYB) in air, according to the procedure depicted in Fig. 1.

The ion implantation by nitrogen has been performed at room temperature (r.t.) and with a pressure of the precursor gas equal to $2.2 \cdot 10^{-6}$ mbar. In order to obtain a short projected range of ions into the target (to have chemical defect localized close the surface, in the case of N-implantation) and, at the same time, to study the surface morphology and chemistry upon nitrogen implantation, the energy of the incident ions was set to 100 eV, as reported in our previous study [15].

Pd and Y were evaporated in situ by e-beam bombardment from a high purity Pd rod and Y flakes, respectively (the last mentioned were contained in a Mo crucible). The deposition rate were equal to 0.25 MLE/min for Pd and to 0.10 MLE/min for Y (1 MLE (monolayer equivalent) corresponds to 2.26 Å [18] and to 1.77 Å [19] for Pd and Y, and represents the interlayer spacing between (111) planes in ten pure metals, respectively).

The characterization of the prepared systems was performed in situ, using HR-PES, Res-PES, NEXAFS and LEED at the Bach beamline

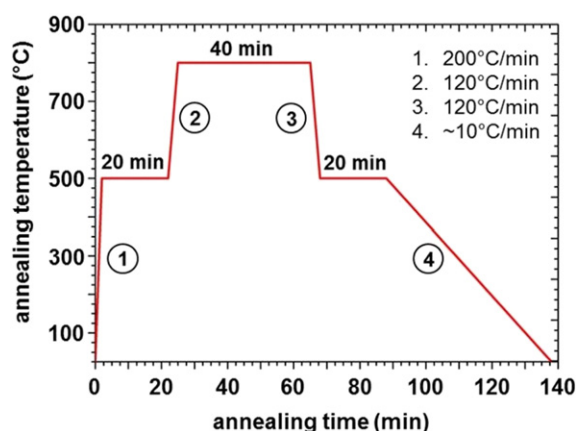


Fig. 1. Thermal annealing cycle carried out on the HOPG sample after the introduction in the UHV system.

operating at the Elettra Synchrotron Facility. Photoemission data were collected at RT with a SCIENTA R3000 analyzer set in transmission mode, using a photon energy of 595 eV (with a total energy resolution of 100 meV). C 1s and N 1s peaks were separated into individual chemically shifted components (after Shirley background removal) using a *Doniach–Sunjic* shape for the sp^2 component and symmetrical Voigt functions for the fitting of the molecular-like C and N 1s components. The χ^2 minimization was ensured by the use of nonlinear least squares routine. NEXAFS measurements on C and N K-edges were performed in Total Electron Yield (TEY) mode.

3. Results and discussion

3.1. Characterization of N-doped HOPG

In this part, we will provide a detailed characterization of N-HOPG using synchrotron light-based techniques. Fig. 2 reports HR-PES data obtained on annealed HOPG, at Bach beamline. Fig. 2a reports the C 1s peak of HOPG, acquired with a photon energy of 595 eV. The peak shows a *Doniach–Sunjic* shape, with a FWHM of 0.35 eV. The high cleanliness of the surface and the low presence of defects is also highlighted by the survey scan reported in inset in Fig. 2a and by the NEXAFS measurements reported in Fig. 2b.

For the NEXAFS measurement acquired in p polarization mode (*out of plane*) it is possible to observe the typical $1s-\pi^*$ sharp transition at 285.0 eV [20], whereas the $1s-\sigma^*$ transitions (between 290 and 315 eV) can be measured in s polarization mode (*in plane*) [20].

The effect of the different implantation energies can be visualized by the LEED patterns reported in Fig. 3. The LEED pattern of the pure support (Fig. 3b) is a superposition of the diffraction patterns of the single orientational domains present in HOPG [21]; because ZYB grade HOPG has little distortion angles between adjacent mosaic tessellation ($\approx 0.4^\circ$), the pattern is not characterized by single spots, but it assumes a circular geometry [16] due to the overlap of all the single domain diffraction spots (such as the *Debye–Scherrer* phenomenon that occurs in X-ray diffraction of powders, see Fig. 3a). Fig. 3c shows that the implantation at 100 eV leads to a weaker and more diffuse LEED pattern, because of partial surface amorphization with the consequent loss of crystalline order. On the other hand, ion implantation performed at higher energies (500 eV) generates a heavily amorphous surface [13,14], which eventually gives no diffraction. Thus, the surface does not show a LEED pattern, as shown in Fig. 3d.

In order to have a deeper physical insight into ion implantation procedure, Monte Carlo simulations of the N-implantation in HOPG have been carried out assuming the *Kinchin–Pease* modeling [22] of the ion-target atom interaction.

Under the experimental conditions of the N-implantation, performed by using common ion guns, the nitrogen plasma contains both N^+ and N_2^+ ionic species. By simulating the interaction of both the species with the carbon support and taking the average, Monte Carlo simulations give a *projected range*, R_p , and a *full width at half maximum* (FWHM) of the distribution, ΔR_p , equal to 7.9 Å and 10.3 Å for 100 eV implantation, and to 18.6 Å and 17.3 Å for implantation at 500 eV. Preliminary studies using standard photoemission and Monte Carlo simulations, demonstrated that it is possible to tune the projected range of the implanted atoms [13–15] and that no significant change occurs in the type or in the relative concentration of the chemical functionalities introduced by N implantation.

Fig. 4a and b reports the multippeak analysis of the C 1s and N 1s signals of the as-implanted N-HOPG, acquired in normal emission (NE) and grazing emission (GE) at Bach beamline (using a photon at 595 eV). The implantation was performed in situ at using 100 eV ions. In the case of C 1s, four components at binding energy (BE) of 283.7, 284.4, 285.5 and 286.5 eV, can be resolved. According to literature, they can be assigned to carbon vacancy (dangling bonds) [23,24], to sp^2 hybridized carbon forming the pure graphitic lattice, to sp^3

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