Electrocatalysis at palladium nanoparticles: Effect of the support nitrogen doping on the catalytic activation of carbon–halogen bond

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ABSTRACT

Pd nanoparticles (NPs) were deposited electrochemically on three differently modified glassy carbon (GC) supports: pristine GC, nitrogen implanted GC and Ar implanted GC. The aim of such an approach is to discriminate whether the electrocatalytic activity of Pd NPs toward the activation of carbon–halogen bond is preferentially driven by chemical or morphological defects. Modified GC electrodes were prepared by ion implantation whereas Pd was deposited according to a double-step potential deposition in a 1 mM $PdSO_4 + 0.1$ M H_2SO_4 solution.

The electrodes were fully characterized by X-ray photoemission spectroscopy, which allowed the identification of several different N-based defects. Pd NPs morphology, dimension and distribution were investigated by scanning electron microscopy. The outcomes indicate that the electrodeposition of Pd NPs on nitrogen-implanted GC results in smaller catalyst particle sizes and higher particle dispersion with respect to pristine GC. The palladium nitrogen-implanted electrode was tested in the electrochemical reduction of benzyl chloride, showing that Pd NPs result in a much higher catalytic activity than bulk Pd and Pd NPs loaded on the pristine GC electrode.

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1. Introduction

Activation of the carbon–halogen (C—X) bond is a highly explored field in organic electrochemistry since it finds huge application in organic synthesis [1,2], in the control over radical polymerization [3,4], in pollutant degradation [5–7] and in mechanistic investigation on dissociative electron transfer (DET) [8–11]. The main drawback associated with the electrochemical activation of C—X is the very negative potentials required, and this is particularly true in the case of organic chlorides, which represent the most investigated ensemble among organic molecules containing a nucleofuge group. This has boosted over the last decade the research of electrode materials active toward the C—X bond breaking, and, so far, Ag, Cu and Pd were found to possess extraordinary electrocatalytic properties [12–16]. However, attempts to improve catalytic activity by changing from bulk electrode to nanoparticles (NPs) dispersed on a support, or by introducing a second or a third metal have not yet led to the desired improvements [17,18].

In principle, the catalytic activity can be increased either by a fine dispersion of the NPs or by modulating the electronic properties of the catalyst NPs by interaction with support chemical or morphological defects; as an example, a way to enhance the durability of the catalyst support assembly in the case of oxygen reduction is to strengthen the catalyst NPs support interaction by introducing into the substrate defects that can act as trapping sites for anchoring the catalyst NPs [19,20]. In this regard, Minguzzi et al. have recently observed that the electrochemical activation of a carbon surface in acidic media introduces oxygen functional groups which enhances the stability and the electrocatalytic activity of Ag NPs toward the C—X bond activation [21].

Among various forms of carbon, glassy carbon (GC) is the most important for use as an electrode in electrochemistry, since it shows very low electrical resistivity, it is non-porous and impermeable to gases, it has high chemical resistance and the widest potential range observed for graphitic carbon electrodes and, last but not least, it can be easily polished and managed [22]. This renders GC an optimal material for a basic investigation on how the chemical modifications of the support can affect the activity of the loaded catalyst. The chemical modification (hereafter referred to as doping) of a GC surface is generally performed by the adsorption or by the covalent bonding (grafting) of molecular catalyst or electronic mediators. Another option is to synthetize a doped GC by thermolysis of suitable carbon precursors (usually polymers) containing the desired heteroatoms [22,23] or by the mixture of resins and an inorganic source of heteroatoms, such as boric acid and ammonia [24]. In the present case, following a different approach, nitrogen

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functional groups have been introduced on a GC support by N_2^+ and N^+ ion implantation, producing a modified N-GC support. Here it will be shown that the presence of nitrogen functional groups on the carbonaceous support can influence the nucleation and growth of metal NPs and promote their catalytic activity toward activation of the C—X bond.

In the present case, palladium was employed as metal NPs because of its excellent hydrogenation ability, which makes it an excellent catalyst in the electrochemical dechlorination of organic chlorides in aqueous media or organic–aqueous mixture [25–27]. The Pd NPs electrochemical deposition on N-GC (Pd@N-GC) has been carried out in a 1 mM $PdSO_4$ + 0.1 M H_2SO_4 solution by a double-step potential deposition.

The N_2^+ and N^+ ion implantation, besides the introduction of new functional groups, leads to the formation of an increased number of morphological defects; this open a new issue about the possibility of disentangling the effects connected to the presence of new functional groups from those deriving from the morphological defects introduced by ion implantation. In order to discriminate between the two effects, we have performed the deposition of Pd also on pristine GC (Pd@GC) and on an Ar^+ implanted GC (Pd@Ar-GC) samples, and used them as an internal reference to gauge the results. In particular, Ar-implantation determines relevant morphological defects, consisting in a re-hybridization of carbon atoms from C_{sp^2} to C_{sp^3}, but cannot induce chemical defects [28].

The prepared GC electrodes were fully characterized by X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM), and the electrochemical reactivity was tested for the reduction of benzyl chloride, which so far is considered as a standard test molecule for investigating carbon—halogen bond activation.

2. Experimental

2.1. Chemicals

CH_3CN, (WWR, HPLC grade) was distilled over CaH_2 under a N_2 atmosphere. Tetraethylammonium tetrafluoroborate ($TEABF_4$) (Fluka, >98%) was recrystallized twice from EtOH and dried in a vacuum oven at 70 °C. Benzyl chloride (Fluka, ≥99.5%) and $PdSO_4$ (Alfa Aesar, 99.95%) were high-purity reagents and were used without further purification. Deionized water used for the experiments was previously twice distilled from $KMnO_4$.

2.2. Preparation and characterization of Ar-GC and N-GC substrates

The N- and Ar-GC samples were prepared by using the ion beam produced by the ion gun (Thermo VG Scientific) under the same conditions: 2.2×10^{-6} mbar background of N_2 or Ar, a beam energy of 500 eV and exposure time of 10 min, with an incidence angle of the ion beam equal to 45° with respect to the sample surface (the ion current measured during this treatment was 2.0 μA and the total dose of implanted atoms was around 5×10^{16} ion cm^{-2}). The nitrogen/argon dose was evaluated to be about 15 at%.

The XPS characterization of the samples was performed in a UHV chamber (base pressure <5×10^{-9} mbar), equipped with a double anode X-ray source (Omicron), a hemispherical electron analyzer (VG Scienta). All XPS measurements were performed at room temperature, using non-monochromatic Mg-Kα radiation ($h\nu$ = 1253.6 eV) and a pass energy of 50 eV and 20 eV for the survey and high-resolution spectra, respectively. The calibration of the binding energy (BE) scale was carried out using Au 4f as reference. The N 1s and C 1s peaks were deconvoluted into individual components (after Shirley background removal) using symmetrical Voigt

functions, whereas the Pd 3d photoemission peaks were deconvoluted into chemical-shifted components using Doniach–Sunjich shape functions. In both cases, the χ^2 minimization was ensured by the use of the nonlinear least-squares routines.

SEM investigations were performed with a dual-beam FEI Nova 600i instrument, with a semi-in-lens cold cathode field emission scanning electron microscope source.

2.3. Electrochemical instrumentation

Electrochemical measurements were carried out either by use of a computer-controlled Autolab PGSTAT30 potentiostat or an EG&G PARC Model 273/A potentiostat. The electrocatalytic activity of the nanostructured surfaces for benzyl chloride reduction was investigated by means of cyclic voltammetry (CV) and was carried out in a three-electrode cell with a GC, either modified or unmodified, or Pd disk as working electrode. The counter electrode and the reference electrode were a Pt wire and Ag|AgI|Bu$_4$NI (0.1 M) in CH_3CN, respectively. The latter was calibrated after each experiment against the ferrocenium/ferrocene couple. The potentials measured against the Ag|AgI|I$^-$ reference electrode were converted to the SCE scale, to which all potentials in the paper are referred, by using $E^0_{Fc+/Fc}$ = 0.391 V vs. SCE in CH_3CN [12]. The working electrodes were built from a GC plate (Tokai GC-20) and 2-mm diameter Pd wire (Alfa Aesar, 99.999%) and were polished to a mirror finish with silicon carbide papers of decreasing grain size (Struers, grit: 500, 1000, 2400, 4000) followed by diamond paste (3-, 1-, 0.25-μm particle size). They were then cleaned in ethanol in an ultrasonic bath for about 5 min. In several cases a slight passivation of the Pd electrode, resulting in a poor reproducibility of the data, was observed during the electrocatalytic experiments. When this happened, the electrode was activated by CVs until cathodic discharge.

The Pd NPs on GC, Ar-GC and N-GC were freshly prepared before each experiment by electrodeposition of Pd on an exposed area of 3-mm diameter GC disk. The GC samples (8 mm diameter) were either clamped in a Kel-F mask or enveloped in Teflon tape. The electrochemical deposition of Pd NPs was carried out in a three-electrode cell containing 1 mM $PdSO_4$ solution in 0.1 M H_2SO_4. GC, Ar-GC and N-GC disks were set as working electrode, while the counter electrode and the reference electrode were a Pt wire and a Hg|Hg$_2$SO$_4$|K$_2$SO$_4$ saturated electrode, respectively. The reference electrode was separated from the working electrode compartment through a salt bridge which avoided any contamination of the working electrode. The conversion of the potential measured vs. Hg|Hg$_2$SO$_4$|SO$_4^{2-}$ to the SCE scale is obtained by addition of +0.373 V to the measured value. All experiments were carried out at 25 °C.

3. Results and discussion

3.1. Preparation of Pd nanoparticles (NPs) on pristine and doped GCs

We first investigated the redox reactions of palladium on GC by CV in 1 mM $PdSO_4$ + 0.1 M H_2SO_4 solution. The first negative-going scan obtained under these conditions shows no well-defined cathodic peak for the reduction of Pd^{2+} to Pd(0). CV obtained starting at an initial potential of 0.3 V vs. SCE and scanning in the negative direction at variable negative potential limits indicate that Pd deposition starts at a potential more negative than −0.05 V vs. SCE, which coincides with the equilibrium potential. This was confirmed by the appearance of a PdO peak on the reverse scan and by XPS measurements revealing the presence of Pd over the GC surface. A similar experiment has been carried out at N-GC, though in