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Thin porous palladium layers modified by cathodically doped graphene and organic donors

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Abstract

Thin porous layers of palladium deposited onto gold or Pd bulk metal treated by cathodic reduction in the presence of CsI under super-dry conditions were tested to establish their reactivity toward electrolytes. Specifically, an iono-metallic layer [Pd_4^-, TMA^+ {$TMABF_4$}] was found to be generated in tetra-alkylammonium salts, especially TMA^+, BF_4^-. This material is then taken as a starting substrate for *in situ* exchange between BF_4^- and many electrogenerated organic acceptor anions. Importantly, the list includes doped graphene and electro-active conducting organic polymers in their basic form. Thus, for example, an intriguing Pd–graphene layer can be created as a relatively thick interface, and may be either doped or un-doped, depending on the applied potential. The method was also shown to work with many organic acceptors (coronene, anthraquinone, etc.) immobilized in their reduced state. The proposed method suggests a new strategy for building stable composite materials of considerable interest for use as electrodes and/or in 3D redox applications.

Keywords: Doped palladium metal; Palladium–graphene electrode; Metal–carbonaceous donor composites.

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1. Introduction

It is usual to consider precious metals like platinum and palladium to be totally un-reactive toward electrons and ions. Most researchers working in organic electrochemistry or organometallic chemistry (whatever the overall conditions concerning solvents and salts) therefore still consider these materials as ideal electrodes, free of side reactions with other reagents. However, recent work [1-6] on the behaviour of Pt used as a cathode in super-dry aprotic polar solvents showed high reactivity when applied potentials are < -2 V vs. Ag/AgCl. Furthermore, as well as reduction in poly-anions (similarly to Zintl metals), the cathodic insertion of electrolytes (alkaline metal and tetra-alkylammonium salts) has been observed [4]. This means that both Pt and Pd could be considered as cathodic materials under

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specific conditions, leading to the emergence of a new generation of modified interfaces with applications in the field of electrocatalysis [7,8].

Quite intriguingly, these recent observations revealed the generation of poorly conducting "iono-metallic" layers which totally cover the concerned metal until a quasi overall inhibition of electron transfer. The thickness of these modified layers depends on the electrolytes used and might reach several tens of microns. The exact stoichiometry of the iono-metallic complexes has been determined: with palladium, the general surface reaction was found [4] to correspond to the following equation:

$$4\ Pd + e^- + 2\ \{MX\} \longrightarrow \{Pd_4^-\ M^+, MX\} + X^- \quad (1)$$

where M^+ is an alkaline metal cation or TAA^+ cation. A variety of anions could be employed (for example BF_4^-, PF_6^-, ClO_4^-). Halides I^- and Br^- could also be used, but in this case the layer stoichiometry is changed [4]. The generation and stability of iono-metallic structures depend crucially on the nature of the inorganic anion. In particular, inorganic anions X^- selected for their electrochemical stability are likely to be exchanged with carbanions, principally those electrogenerated *in situ* at the cathode surface and within the metallic bulk in the course of successive scans. The reactivity of electrogenerated anion-radicals and dianions (mainly from organic π-acceptors) formed at potentials *less* negative than the threshold of the Pd cathodic step (corresponding to reaction (1)) resulted in significant modification of the iono-metallic layer through inorganic anion ↔ organic anion or dianion exchange. This has been demonstrated [4,7] for platinum in the presence of π-acceptors under super-dry conditions (electrolytes $TBABF_4$ or CsI in DMF in the presence of activated neutral alumina). The highly intriguing insertion of organic species *in their reduced form(s)* can be obtained under very simple conditions (a potential of about -2 V is applied to the precious metal cathode) assuming that the organic compound is electroactive at less negative potentials than the one permitting the metal doping. Additionally, one may imagine that the irreversible formation of mono-anions – as in the case of carbanions derived from the cathodic cleavage of carbon–heteroatom bonds – could also lead to insertion, as well as the cathodic doping of organic conducting polymers (e.g. electrogenerated polyfluorenes, owing to the relative acidity of the fluorene C-H function in position 9 [9,10]). Basic forms of polymeric substances such as these could be formed simply at the interface of electrogenerated bases (EGBs) obtained by the reduction of electroactive impurities and therefore acting as base catalysts. Importantly, the cathodic doping of certain allotropic forms

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of carbon (graphene, C_{60}, fullerenes) reactive under electron transfer to their poly-anionic transients is of great interest in generating porous dual metal–carbon materials expected to show high 3D reactivity.

The present preliminary work is focused on porous palladium layers generated by cathodic treatment of Pd in the presence of CsI, or very thin galvanostatic Pd deposits on gold electrodes (gold does not afford iono-metallic transients [11,12]). Thanks to the exclusive use of TMA^+ salts that appear to eliminate the Hofmann degradation (known to generate protons and then alter the neutrality of the media towards electrogenerated organic anions), the redox potentials of some sample iono-metallic layers modified by π-acceptors are measured. Additionally, the reactivity of the iono-metallic layer towards the electrogenerated anionic forms (derived from the scission of RX type compounds or doping of graphene) is clearly demonstrated. In all cases, the experimental conditions are specified in the figure captions.

2. Results

The use of a palladium electrode in super-dry conditions appears to open new avenues of research in the study of conducting organometallic surfaces, layers, and/or materials that can possibly be modified by electrogenerated bases. As an example, Figure 1 shows that the electrochemical insertion of π-acceptor reduced entities is real. Curves A correspond to the charge (> -2 V) and discharge (≈ -0.5 V) of palladium. Addition of 1,4-diacetylbenzene (DAB) to the solution and further reduction at a pre-modified surface allows the deposition/insertion of redox species for which the electrochemical response in a solution free of DAB resembles that of DAB (two reversible steps) but strongly shifted towards more anodic potentials (ΔE > +1.2 V). Repetitive cycling results in the progressive disappearance of signals, presumably due to the gradual oxidation of the deposit when scans up to + 0.5 V are made. Importantly, slow rate scans up to -2 V result in the regeneration of the original signal (through a new reductive generation of the transient organo-iono-metallic layer, possibly limited by the diffusion rate of TMA^+ through the bulk metal).

In fact many organic acceptors were found to be suitable candidates to be embedded in the bulk metal (depending on the total amount of electricity injected into the system). Using this method, coronene, pyrene, dinitrobenzene, anthraquinone, acenaphthenoquinone, and acenaphthylene (Scheme 1) were efficiently inserted in palladium, probably through exclusive exchange with BF_4^-. After electrolysis, complexes {palladium, TMA^+, organic acceptor reduced forms} were found to be poorly oxidized by air in the course of the work-up. Such chemically modified interfaces used as electrodes may involve a new process of

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redox catalysis in which the catalyst is not immobilized by a conventional method (e.g. via radical grafting), but through efficient and easy embedding of organic anions (for example, via the two-electron scission of the carbon–heteroatom bond).

It is also important to consider the cathodic capability of palladium to directly permit insertion of acceptors not through exchange, but under electron transfer during a concomitant reduction. Thus, organic anions and electrogenerated polymeric anionic forms (possibly under the action of electrogenerated bases) may also react with graphene – pre-charged at -2 V – as depicted in Scheme 1.

This response is obtained with many π-acceptors (triphenylene, dinitrobenzene, anthraquinone, chloranile, bi-benzyle, diacethylbenzene, etc.). Astonishingly, the peak potentials assigned to the presence of acceptor reduced forms (now considered as donors towards the iono-metallic palladium phases), are all significantly shifted to a more positive potential range (up to $\Delta V \approx +1.0$ V). Figure 2A shows the response of anthraquinone trapped in the iono-metallic layer. The double redox response is quite different to that of free anthraquinone in the same solution at a platinum or smooth gold electrode (potential shifts > 1 V), strongly supporting the hypothesis of a structural change in the palladium surface through addition of the acceptor to the surface. The first step **(I)** in Figure 2A may be assigned to the anodic response of the organic radical anion fully inserted as a donor species into the metallic phase, while step **(II)** corresponds to the occurrence of the dianion in the bulk Pd. In the course of scans towards negative potentials, peak **(II)** is larger; however, in the course of the reverse scan, peak **(I)** (associated with the presence of the anion radical) turns to be fairly huge, which supports a prior dianion oxidation. Significantly, the increase in steps **(I)** and **(II)** when re-doping along a short scan up to the Pd charge threshold may regenerate reducing centres located at (or very close to) the electrode surface after modification.

Moreover, Figure 2B shows that acenaphthenoquinone also reacts with the electrochemically generated iono-palladium intermediate, leading to a deep blue layer which is totally stable when in contact with di-oxygen after work-up.

Furthermore, the as-produced surfaces were shown to favour redox catalyses at a potential < -1 V, possibly due to the occurrence of reduced forms (radical anion of the acceptor) at the Pd interface. (For example, 1-iodopropane can be indirectly reduced under these conditions with a potential gain of 0.5 V.) The method should be seen as a new process

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for chemical modification of metallic interfaces, with a limited amount of organic species easily activated electrochemically by mean of a cathodic pulse.

3. Charge-discharge of palladium–graphene layers

Since graphene can be electrochemically reduced in aprotic conditions (a poly-anion is formed after successive electron transfers onto graphene micro-flakes), it was interesting to consider whether such reduced materials could react with charged palladium.

Figure 3 depicts the cathodic charge (according to the double peak C1) of the Pd–graphene layer. The specific reduction of palladium (only observed in super-dry solvents) is superimposed on that of the graphene already described under rather similar conditions [13,14]. Interestingly, multi-step C1 increases during the scans while the anodic peaks A1 (discharge of Pd) and A2 (assigned to implication of the graphene poly-anion in the palladium layer) behave differently. A charge with pre-functionalized graphene was also successfully obtained. The resemblance with acceptor immobilization can be seen (see Scheme 1). The use of marked graphene (e.g. by means of 1,4-anthraquinone or ferrocene) clearly confirms the selective reactivity of graphene toward doped palladium by simple analysis of the resulting sonicated Pd electrodes (as clarified in the graphical abstract).

4. Conclusions

This communication reports the unexpected insertion of reduced acceptors and/or poly-anionic forms, possibly electrogenerated, in metals such as palladium matrixes. Preliminary work on platinum reduction and the concomitant insertion of π-acceptors is strongly improved with palladium as a host for several reasons: (i) a very sharp and clear discharge of the reduced iono-metallic layer is obtained with this metal; (ii) clear redox steps can be obtained with many π-acceptors (comparison between curves B and C in Figure 1); (iii) there is evidence of a palladium complex (probably including the anion-radical of the acceptor), stable in the presence of air, that allows further studies of the exact stoichiometry, provided *total* insertion within the layer is obtained. Additionally, the present report stresses the exclusive use of TMA^+, which strongly facilitates the formation of the iono-metallic complex and the exchange with acceptors. This is probably due to the stability of TMA^+ in contact with electrogenerated bases as a result of the much weaker impact of the Hofmann degradation of the salt.

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The other main point stressed in this report is that reduced poly-anionic forms of graphite (and graphene as an exfoliation product) can be reactive towards palladium and form a stabilized metal–graphene material (already described with Ag and Au [13]), which is reported to be very reactive both chemically and electrochemically.

The method is – for the moment – exclusively based on the exchange of the anion of the electrolyte involved during the cathodic doping of the metal. Importantly, the insertion relies on a preliminary treatment that implies the n-doping of the metal under unusual conditions (exclusive use of super-dry electrolytes [14]). Preliminary experiments emphasize that insertion of inorganic and organic anions can also be achieved by direct mixed electrolyses that involve both the metal and the pro-base. It is hoped that use of this technique will make it possible to design new polyvalent 3D materials based on Pd.

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Figure Captions

Figure 1. Cathodic reduction (and insertion) of diacethylbenzene (DAB: 10 mM L^{-1}) in DMF/$TMABF_4$ under super-dry conditions. (A) Pd-Au electrode. Scan rate 50 mV s^{-1}. (B) The same solution at a smooth gold electrode (0.8 mm^2). (C) Electrode (A) after the two scans, rinsed and dried, and then cycled in DMF + 0.1 M $TMABF_4$.

Figure 2. Charge of a palladium sheet (total surface area ≈ 4 cm^2) in super-dry conditions:
(A) modification of a Au-Pd electrode by $TMABF_4$ and then insertion of anthraquinone. Response of the electrode in DMF after rinsing. Scan rate: 50 mV s^{-1}.
(B) Deposition at Pd reduced in CsI 0.1 mol L^{-1} in DMF. Palladium sheet (total surface area ≈ 4 cm^2). Total charge 10 C followed by a contact with a super-dry solution of acenaphthenoquinone 10 mmol L^{-1} in DMF for 5 minutes. The *stable* blue coloured zone (on the left side) is assigned to acenaphthenoquinone dianion *trapped* within the reduced Pd phase.

Figure 3. Electrochemical multi-charge of a *thin* layer of graphene deposited onto a Pd microelectrode (area: 0.8 mm^2). Electrolyte: DMF/$TMABF_4$. Scan rate: 50 mV s^{-1}. Notice that the reduced graphene (possibly obtained by exfoliation of deposited natural graphite), occurring in **C1** (successive steps 1, 2, and 3) for generating a poly-anion acting as a poly-nucleophile.

Scheme 1. Concomitant charge of palladium (according to reaction (1) in super-dry conditions, electrolyte A^-,M^+) together with reduction of organic acceptors or contact with a carbonaceous charged material. Reactivity of electrogenerated anionic species from 1,4-dinitrobenzene and that of deposited graphene micro-flakes (implication of poly-anion obtained by a multi-electron transfer occurring at the Pd charge potential at <-2 V). The alternative use of electrochemically marked graphenes (e.g. through use of redox markers such as anthraquinone (AQ) or ferrocene (Fc)) allows the integration of certain reduced carbonaceous products within the superficial palladium space to be confirmed, despite the fact that a sonication rinsing is carried out.

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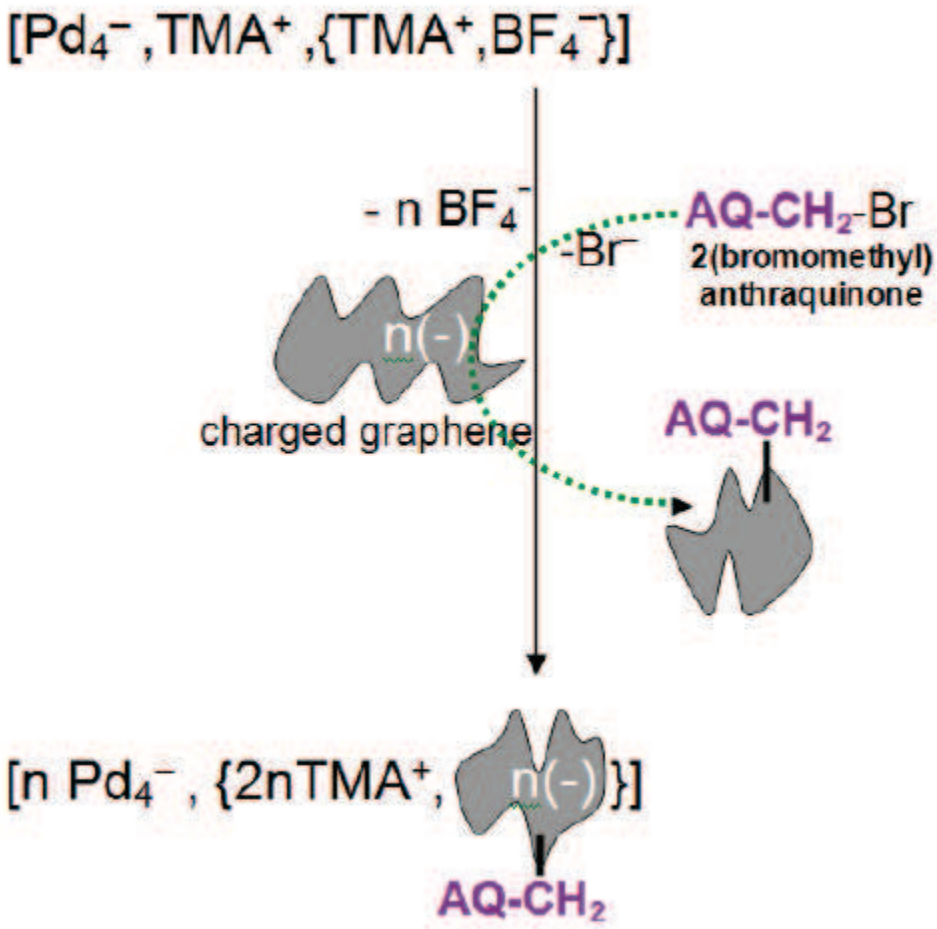

Graphical abstract

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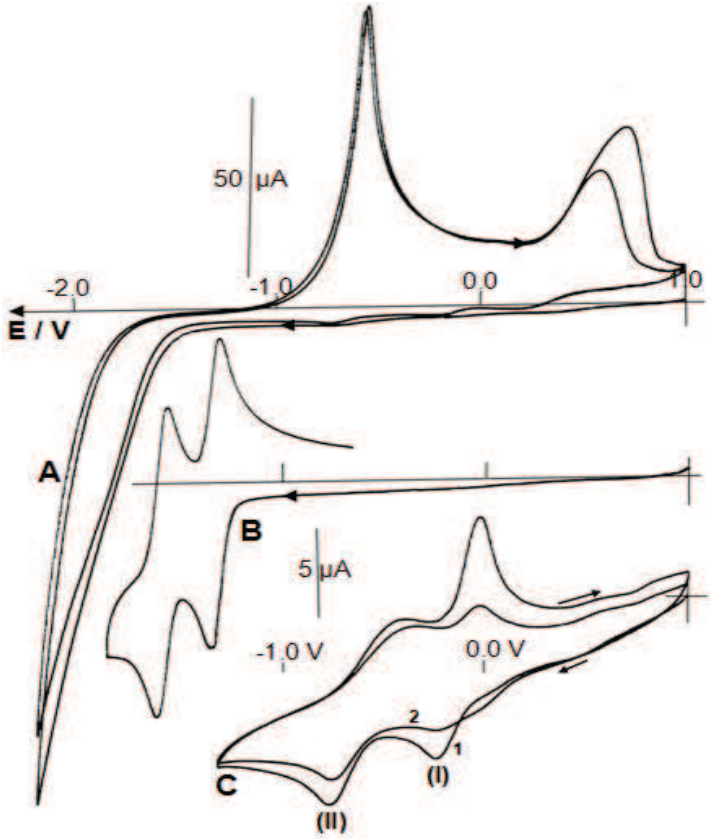

Figure 1

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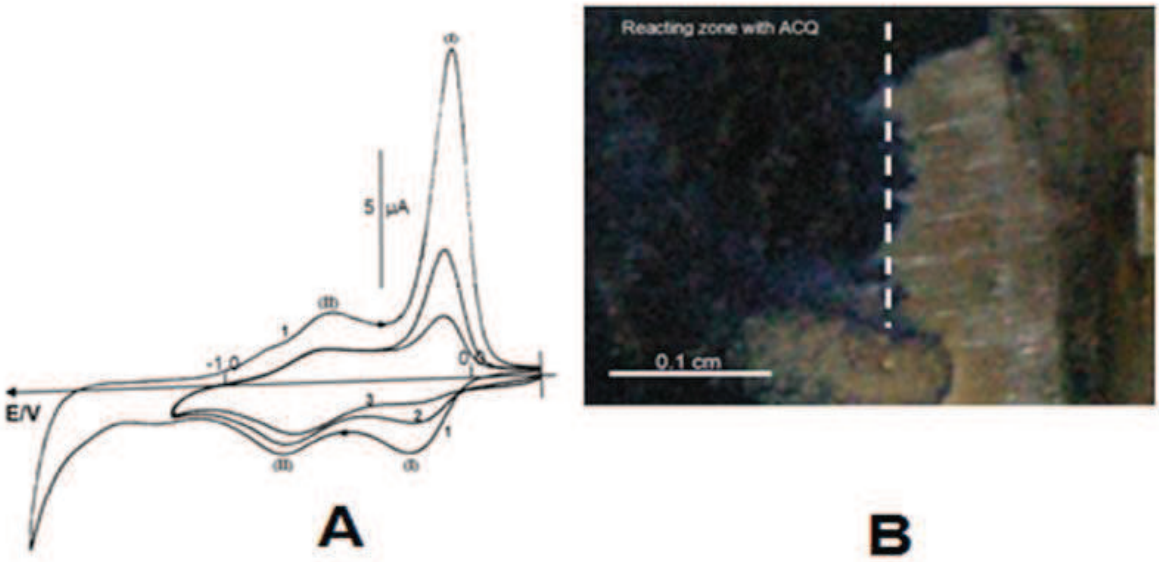

Figure 2

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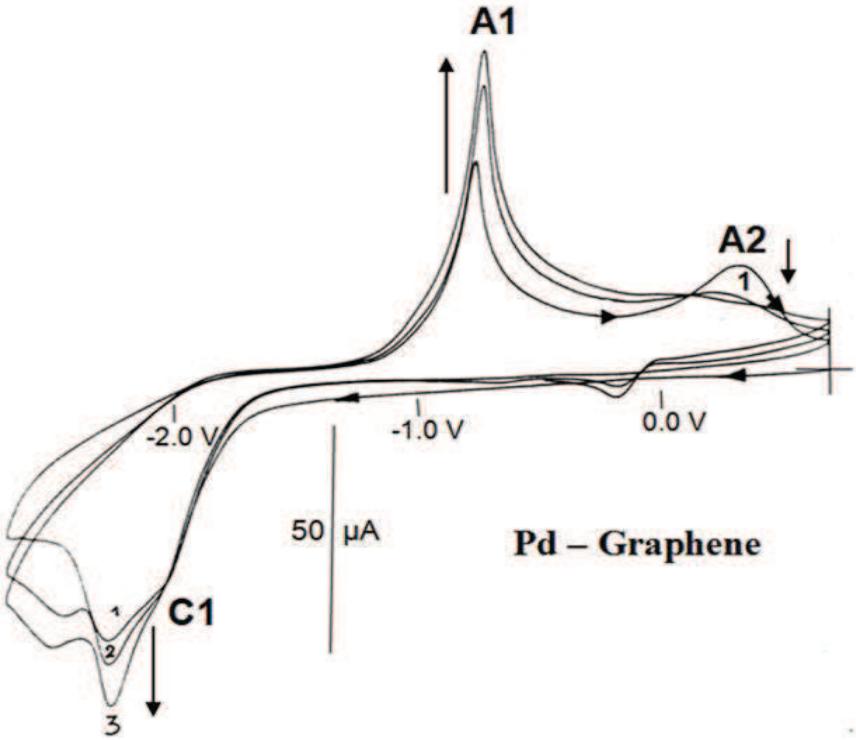

Figure 3

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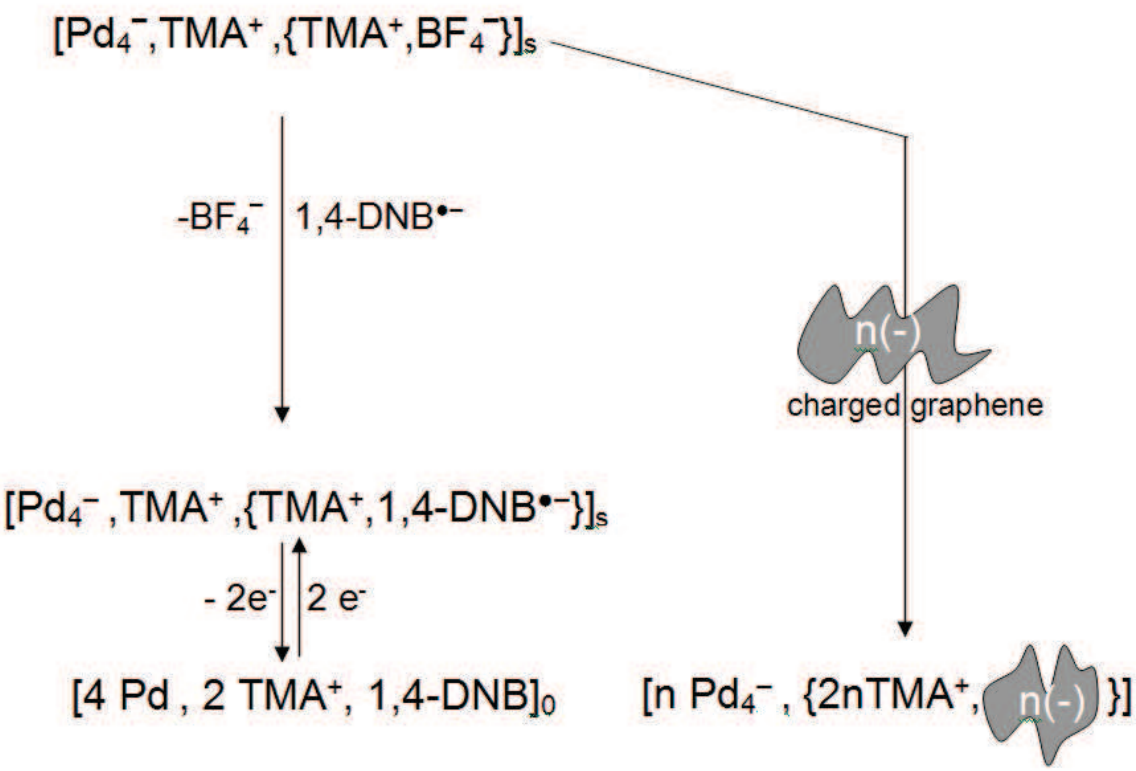

Scheme 1

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Highlights

- Electrochemical reduction of porous Pd layers used as electrodes incorporate anionic forms of doped carbonaceous derivatives.
- Graphite, graphene, polyarenes reduced as poly-anions may react with doped Pd.
- Graphene (or graphite via an *in situ* exfoliation process) through mixed electrolyses with Pd leads to Pd–graphene stable composite materials.
- Organic acceptors in contact with doped Pd produce quite stable redox systems.

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