



## Glassy carbon modified by a silver–palladium alloy: cheap and convenient cathodes for the selective reductive homocoupling of alkyl iodides

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### ABSTRACT

Micrometer-thick layers of silver–palladium alloy were elaborated in order to modify the surface of glassy carbon electrodes. Such a surface modification can be readily achieved via a preliminary silver galvanostatic deposit onto carbon followed by a 'palladization' step, thanks to a simple immersion in acidic Pd<sup>II</sup>-based solutions producing a displacement reaction. The as-prepared metallic interfaces exhibit outstanding catalytic capabilities especially in the cleavage of carbon–halogen bonds while being chemically/electrochemically quite stable and relatively inexpensive. More specifically, the use of such glassy carbon/Ag–Pd electrodes in dimethylformamide (DMF) containing tetraalkylammonium salts (TAA<sup>+</sup>X<sup>-</sup>) makes the one-electron reductions of primary alkyl iodides possible; this reduction leads to the formation of homodimers in high yields. Formation of a free radical as transient resulted from the homocoupling reaction.

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### 1. Introduction

Searching for stable and efficient electrodes in the field of organic electrochemistry remains nowadays an important goal to specifically achieve new cathodic reactions,<sup>1</sup> in which the heterogeneous character of the electrode surface could play a crucial part. Widely used in the past, mercury-based electrodes are today unanimously banned due to their toxicity.<sup>2</sup> Noble metals as pure platinum or palladium constitute also interesting working electrodes within the cathodic domain but their high cost appears to be a major drawback. Alternatively, different carbon substrates (such as graphite or glassy carbon) could be first considered as universal solid working electrodes, although these electrodes cannot be used to achieve specific electrocatalytic reductions without surface chemical modifications (e.g., grafting, deposit of functionalized polymers). Recently, massive silver substrates modified by means of an unusual palladization treatment (Ag–Pd alloy formation in surface) have been used for the catalytic one-electron reduction of organic halides<sup>3</sup>. Unfortunately, the relative high cost of such electrodes and the quasi-irreversible modification of the silver surfaces rapidly appeared to limit the use of Ag–Pd alloy interfaces.

In the present Letter, we report on a very simple approach to modify the carbon surfaces by silver and palladium deposits, thus making possible an easy formation of free radicals obtained from

the electrocatalytic cleavage of primary alkyl iodides RI. In particular, the homocoupling reaction leading to the dimerization of those radicals is shown as a convenient method to produce a large panel of linear alkanes present in minor wax components. Using such a process, cross-coupling reaction can be considered and will be developed later. To date, the organic synthesis of these alkanes was typically achieved by means of Grignard's syntheses through the corresponding alkyl halides.<sup>4</sup> Thus the several preparation routes quoted in the recent literature appear quite complex.<sup>5–10</sup> However, reduction of alkyl bromides and iodides by metals like zinc,<sup>11</sup> lanthanum,<sup>12</sup> or indium<sup>13</sup> were also considered for the homocoupling (formation of linear paraffins with an even number of carbon atoms).

Our first set of data deals with the electrolytic reduction of 1-iodoalkanes (C<sub>n</sub>H<sub>n+1</sub>I with n < 20) led through very simple experimental conditions: use of an organic polar solvent like DMF without any special purification, choice of a common electrolyte like TAA<sup>+</sup>X<sup>-</sup> salts (note that alkali metal salts may be used as well). This paper essentially describes data obtained by means of potentiostatic electrolyses, but very simple cells can be used as well such as two-compartment electrolyzers equipped with a separator. The modified carbon plate acts as working electrode and the counter electrode (graphite, rhodium oxide, etc.) may be simply connected to a current generator. These cheap carbon/Ag–Pd electrodes can be re-used several times apparently without systematic rebuilding, whereas the RIs one-electron reduction enabled to achieve homocoupling reactions in high yield.

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## 2. Experimental

### 2.1. Elaboration of the modified carbon surfaces

The fabrication of working electrodes presented here with glassy carbon is very easy and certainly feasible for a wide variety of carbon materials. After a preliminary galvanostatic deposit of silver onto glassy carbon surfaces, an Ag–Pd surface was simply obtained by displacement reaction, thanks to a fast dipping into a fresh solution of palladium salt in acidic solution. Typically, onto a glassy carbon surface slightly polished, an electrochemical deposit of silver was achieved by using a plating bath composed of 1 g of AgNO<sub>3</sub> dissolved in 100 mL of 0.1 N HNO<sub>3</sub>. The galvanostatic deposit was obtained by using a current density of 0.25 mA cm<sup>-2</sup> (*Q* = 2 C cm<sup>-2</sup>). The resulting deposit was then treated either with a solution of 5 × 10<sup>-2</sup> M PdCl<sub>2</sub> in 0.1 N HCl (contact time: 3 min) or with a solution of 5 × 10<sup>-2</sup> M PdSO<sub>4</sub> in 0.1 N H<sub>2</sub>SO<sub>4</sub> (contact time: 12 min). To make the deposit thicker, two or three similar operations (Ag deposit followed by a palladization process) can be made. Afterwards, the deposit was thoroughly rinsed with water and then with acetone. Characterizations of the as-produced layers have previously been performed on massive silver substrate<sup>3</sup> by a combined SEM, HRTEM, EDS study. With quite short times of contact (i.e., less than 1 min) the as-produced layer appeared to be stable, whereas a treatment by sonication had no visible effect on the adhesion of micro crystals covering the carbon substrate. A selection of SEM images is depicted as a gallery in Figure 1, showing the surface evolution of the Ag layer before and after ‘palladization’ reaction.

### 2.2. Electrochemical procedure, salts, and solvents

In all experiments, the supporting salt concentration was fixed at 0.1 M using tetra *n*-butylammonium tetrafluoroborate (TBABF<sub>4</sub>) and tetra *n*-butylammonium hexafluorophosphate (TBAPF<sub>6</sub>) purchased from Aldrich in different dipolar solvents. Used solvents dimethylformamide (DMF) and acetonitrile (quality for analyses) were purchased from SDS and propylene carbonate (quality for syntheses) was purchased from Merck. It is worth noting that procedures given hereafter do not require specifically dry solutions.

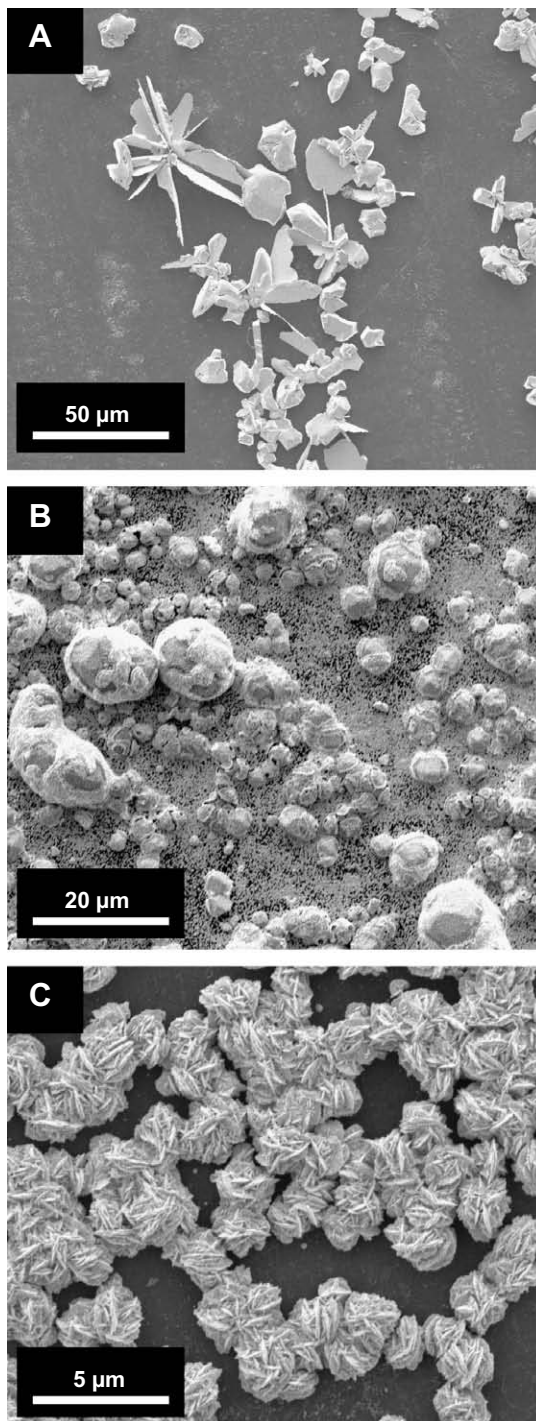
### 2.3. Electrochemical instrumentation and procedures

All potentials are given versus aqueous Saturated Calomel Electrode (SCE). The electrochemical instrumentation has already been described in detail.<sup>3</sup>

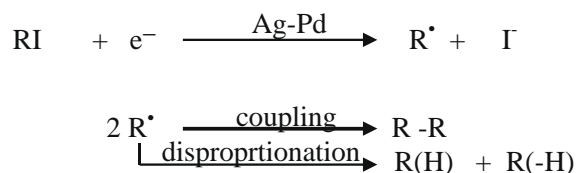
## 3. Results

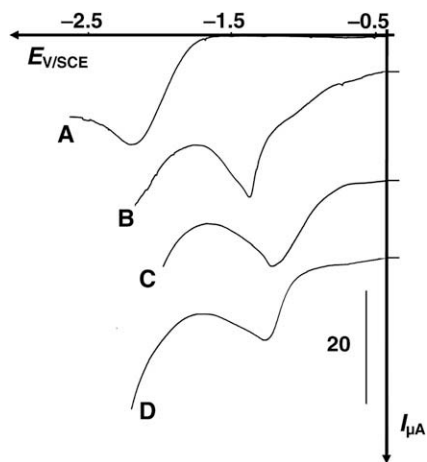
### 3.1. Voltammetries

Typical analytical results obtained with a glassy carbon/Ag–Pd micro-electrode are shown in Figure 2. Basically, the 1-iodobutane reduction is observed onto a regular glassy carbon interface at –1.9 V vs. SCE according to a two-electron process (curve A). With a modification of the surface by means of a silver deposit (curve B) or a Ag–Pd layer (curves C and D), the potential shift is spectacular reaching almost 1 V when the silver surface is reacted with a PdCl<sub>2</sub>-based solution. At those reduction potentials, the overall process turns to be one-electron since the free alkyl radical is no longer reduced. This can be observed on curve D that displays the peak current as half of the one obtained at carbon. Obtained steps with all RIs at GC/Ag–Pd electrodes were shown to be diffusion controlled and their peak currents were checked to be proportional upon RI concentration.



**Figure 1.** SEM images of silvered glassy carbon after a galvanostatic deposit (*Q* = 0.1 C cm<sup>-2</sup>). (A) Image of the GC/Ag surface without chemical treatment; (B) after displacement reaction using a PdCl<sub>2</sub>-based solution and a contact time of 5 min; (C) the previous GC/Ag–Pd surface after using for the catalytic reduction of 1-iodobutane (10 mmol L<sup>-1</sup> in DMF) at –1.3 V versus SCE (*Q* = 2.5 C cm<sup>-2</sup>).



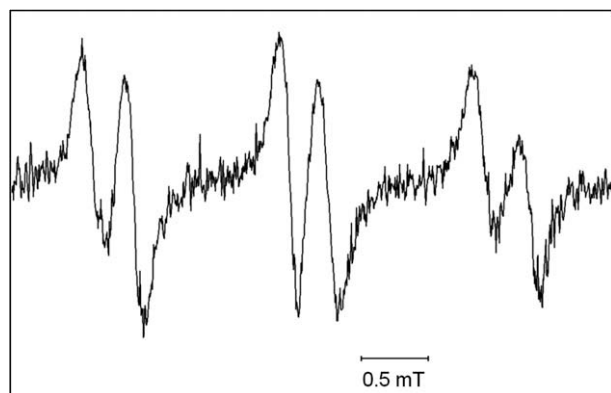


**Figure 2.** Voltammetric responses of a solution of 1-iodobutane (concentration:  $10 \text{ mmol L}^{-1}$ ) at different solid electrodes using  $0.1 \text{ M TBABF}_4$  in DMF as electrolyte. Apparent surface areas:  $0.8 \text{ mm}^2$ . Scan rate:  $50 \text{ mV s}^{-1}$ . (A) At glassy carbon; (B) at glassy carbon electrode covered by a galvanostatic deposit of silver ( $Q = 1.2 \times 10^{-3} \text{ C cm}^{-2}$ ); (C) GC/Ag electrode treated by a solution of  $\text{PdCl}_2$  during 15 s; (D) GC/Ag electrode treated by a solution of  $\text{PdSO}_4$  during 10 min (see text).

The one-electron process obtained at these new electrodes has been additionally verified thanks to ESR process. As a matter of fact, electrolyses of RIs achieved in the presence of *N-tert-butyl- $\alpha$ -phenylnitrone* (TBPN) in excess (see Fig. 3) led to a mono-electronic overall process with the appearance of a sole six-ray paramagnetic signal assigned to a nitroxide radical (trapping of *n*-octyl radical by TBPN). Thus, with 1-iodooctane, the spectrum gives the following parameters:  $g = 2.0066$ ,  $a_N = 14.69 \text{ G}$  and  $a_H = 2.85 \text{ G}$ .

### 3.2. Preparative electrolyses

Macroelectrolyses of primary RI compounds were potentiostatically achieved ( $-1.2 > E > -1.4 \text{ V vs. SCE}$ ) under argon atmosphere from two-compartment cells (volume of catholyte ranging from 8 to 25 mL). Quantities of electrolyzed RI were between 0.05 and  $0.5 \times 10^{-3} \text{ mol}$  with efficient areas of used GC/Ag–Pd electrodes of about  $5 \text{ cm}^2$ . After total completion of electrolyses (one-electron process occurred), the catholyte solution was mixed with water and then extracted with diethylether. The extract was twice rinsed with water and dried over magnesium sulfate. Systematically the mass of dry extracts corresponded to about 80 % of the theoretical value estimated for an exclusive formation of hydrocarbons.



**Figure 3.** ESR response after a potentiostatic electrolysis at  $E = -1.35 \text{ V vs. SCE}$  of 1-iodooctane (concentration:  $15 \text{ mmol L}^{-1}$ ) in DMF +  $\text{TBABF}_4$  medium with excess of TBPN (concentration:  $80 \text{ mmol L}^{-1}$ ). Working electrode: GC/Ag–Pd with an apparent surface area of  $3 \text{ cm}^2$ . The electrolysis was totally completed after  $1 \text{ F mol}^{-1}$ .

**Table 1**

Reduction of primary iodo-alkanes at GC/Ag–Pd cathodes. The experimental conditions are given in the text

1-Iodoalkane $\text{C}_n\text{H}_{2n+1}\text{I}$	R–R (%)	R(–H) (%)	R(H) (%)	Passed charge ( $\text{F mol}^{-1}$ )
$n = 4$	98	–	–	1.1
$n = 6$	98	–	–	1.05
$n = 8$	98	–	–	1.1
$n = 10$	97	–	1	1.1
$n = 12$	99	–	1	1.05
$n = 16$	27	42	27	1.15
$n = 18$	33	39	28	1.15
$\text{Ph}(\text{CH}_2)_3\text{I}$	99	1	–	1.0

Table 1 displays the main results obtained with a large palette of primary alkyl iodides. It is quite noticeable that all RIs characterized by a linear chain no longer than  $\text{C}_{12}$  led almost exclusively to homodimers. Thus, the GC/Ag–Pd electrodes offer a quite better selectivity than massive Ag–Pd cathodes as recently reported<sup>3</sup> since amounts found for R(H) and R(–H) were minor, at least with alkyl chains no longer than  $\text{C}_{12}$ . It is also worth observing that with very long chains ( $\text{C}_{16}$  and  $\text{C}_{18}$ ), the yield of dimers collapses and the reaction is no longer selective. It is expected that the coverage of the GC/Ag–Pd electrode by long chain alkyl radicals (building of a self-organized layer) prevents the catalytic reaction from occurring. In other words, long chain dimers are fairly insoluble and could block the capacity of the electrode as well.

### 4. Conclusions

The use of carbon electrodes modified by a very thin layer of an alloy Ag–Pd leads to spectacular results in the field of the reductive homocoupling of primary alkyl iodides. At least with chains no longer than  $\text{C}_{12}$  the coupling reaction is quasi quantitative. The simple way to produce these new cathodes, their low cost as well as their electrochemical stability allow considering this new electrochemical synthesis approach as extremely valuable for the formation of paraffins possessing an even number of carbon atoms. The method is worth being improved by the concept of many kinds of carbons now used as cathodic materials, in particular porous 3D materials.

### Acknowledgment

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