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Title page

Immobilization of fullerene C₆₀ at cathodically polarized glassy carbon for generation of thin nucleophilic layers and their carboxylation and alkylation.

Jacques Simonet^{[a]*} and Viatcheslav Jouikov^[a]

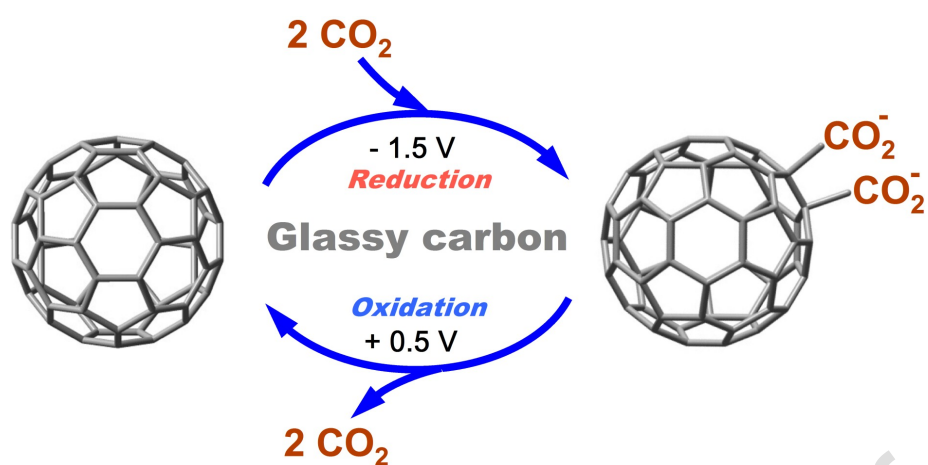
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Graphical Abstract



Journal Pre-proof

Immobilization of fullerene C₆₀ at cathodically polarized glassy carbon for generation of thin nucleophilic layers and their carboxylation and alkylation.

Jacques Simonet ^[a]* and Viatcheslav Jouikov ^[a]

The present contribution is dedicated to Professor Jean Lessard (University of Sherbrooke, Canada) for his significant contribution in the fields of catalysis and organic electrochemistry.

Abstract: Fullerene-C₆₀ deposited onto solid substrates (glassy carbon, gold) was polarized between 0 V and -2 V vs. Ag/AgCl/KCl_{sat} (aq) in polar aprotic solvents (dimethylformamide or acetonitrile) containing tetramethylammonium salts in the presence of electrophilic reagents, namely primary haloalkanes (Hal = Br, I) and carbon dioxide. The electrogenerated reduced forms of C₆₀ (C₆₀⁻ to C₆₀⁴⁻, fullerene polyanions), show high reactivity towards various electrophiles which permits preparing C₆₀ dicarboxylates whose formation was established through coulometric integration. Importantly, anodic oxidation (E_p ≈ +1 V) of thus produced C₆₀ dicarboxylates led to the complete regeneration of C₆₀ via a Kolbe bis-decarboxylation.

1. Introduction

At the present time, carbon remains a basic material for building solid electrodes. Glassy carbon (GC), graphite and graphene are commercially available in different forms easily adaptable to specific purposes and are commonly used for different applications. Additionally, the development of chemistry of fullerenes [1] and particularly of C₆₀ allows preparing the materials of high conductance due to the insertion of alkali and alkaline earth metals [2], especially of K⁺ and Rb⁺. Echegoyen [3,4] reported that C₆₀ shows six successive reversible cathodic transitions within the range -1...-3.3 V (vs Fc⁺/Fc) in toluene-acetonitrile. More recently [5-10], other reports were published, using aprotic polar solvents such as acetonitrile (ACN) and dimethylformamide (DMF), that are easier to handle despite the difficulty of keeping the electrolytes sufficiently dry during the experiments. Unfortunately, the modifications of C₆₀ via any cathodic process affecting its initial structure led to a profound loss of the cathodic activity at the potentials lower than -2 V, which therefore ruins any possibility of using fullerenes for

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building (via grafting procedure) modified solid surfaces. Consequently, using specific fullerene-based carbon materials for creating polarized surfaces with intrinsic redox properties appears to be a goal almost impossible to reach.

Additionally, the stability of C_{60} polyanions in polar solvents depends on the nature of counter-cations ($n\text{-Bu}_4\text{N}^+$, $n\text{-Hex}_4\text{N}^+$, K^+) and on their protonation when the residual moisture content might be higher than 500 ppm. Such non-constructive effects were reported to provoke a gradual decay of C_{60} mechanically immobilized onto different conducting solid substrates (smooth GC, Au or Pt) [5-6].

The present contribution aims to develop these opportunities and to point out the reactivity of reduced forms of C_{60} (electrogenerated polyanions) toward soluble electrophilic organic molecules such as organic halides (alkyl bromides and iodides) and toward carbon dioxide.

Concerning the reactivity of cathodically activated C_{60} with classical electrophiles commonly used in organic electrochemistry (such as alkyl halides and carbon dioxide), the literature is quite limited. While studies concerning CO_2 are nowadays most often oriented to its use as a reagent [11], one may quote that CO_2 (used as its saturated solutions in DMF or ACN) reacts with different reduced forms of graphite [12], graphene [13], and with the reduced unsaturated inclusions in GC [14] when these materials serve as cathodes. Additionally, when several transition metals like Au and Cu are used as cathodes, their carboxylation can be realized also [15-17]. Further development of this approach exploits the redox catalysis for modifying the C_{60} layers.

2. Experimental Section

In the present contribution, the electrochemical activation of C_{60} (limited to the cathodic domain) has been developed in *polar aprotic solvents* (DMF and ACN, dried by addition of activated neutral alumina till an average water content of less than 500 ppm). Tetramethylammonium salts (TMA^+ essentially associated with BF_4^- or ClO_4^- anions) were used as supporting electrolytes at a concentration 0.1 M. The choice of TMA^+ salts arises from the fact that they do not undergo Hofmann elimination and cannot act as a source of protons at cathodically polarized solid surfaces [18].

Fullerene C_{60} (purity of 99%) was purchased from TCI. The disk electrode for fullerene deposition was 3 mm in diameter in case of glassy carbon (GC) and 1 mm for gold. Before the deposition of C_{60} , the electrode surface was polished with silicon carbide paper (Struers 500 and 1200) and then rinsed with water, alcohol, and lastly with acetone. The C_{60} powder was then deposited by pressure/rubbing on these surfaces. The method of modification of thus deposited

C₆₀ by electrophiles is based on the works of Fry [19] and Lund [20-24] regarding “redox catalysis” using cathodic reduction of polyaromatic molecules in the presence of sufficiently electrophilic reagents.

The carboxylation was achieved with saturated solutions of CO₂ obtained by bubbling the gas in DMF (at 25 °C, the concentration of CO₂ is about 0.2 M L⁻¹). Then, the C₆₀ deposited on the electrode was cathodically activated between 0 V and -1.8 V; after the carboxylation, the modified surfaces were rinsed with water, acetone, and finally dried at 50 °C. The thus obtained carboxylated C₆₀ deposits both onto GC and onto gold showed a good stability in the contact with air.

This approach successively applies as well to the systems obtained by insertion of C₆₀ into thin layers of suitable conducting polymers or even more simply taking fine mixtures (e.g. 50/50 w/w) of C₆₀ with graphene. Due to π,π -interactions [25], the latter system is very stable in DMF. For instance, a variety of mixtures of C₆₀ with industrial graphenes such as XGnP graphene grade C (specific area 750 m²/g, available from XG Sciences Inc) or carbon nanotubes (MWCNTs with the average diameter 10-20 nm, from Arkema) reveal a good stability of the electrodes during the scans.

3. Results and Discussion

3.1 Reactivity of the reduced forms of C₆₀ toward organic electrophiles.

Before performing the carboxylation on polarized solid materials, voltammetry of the smooth GC covered with a C₆₀ deposit was carried out in dry DMF (Figure 1A). Four consecutive reversible reduction steps (I, II, III and IV) were observed (Figure 2) within the potential range from 0 V to -1.9 V. Upon repetitive scans, the intensity of the reduction peaks rapidly decreased. In the presence of an organic electrophile (Figure 1B, *n*-iodo-propane), the voltammetric response upon cycling the potential was dramatically modified. Additional reduction steps appeared beyond -0.8 V attesting to the reaction of iodopropane with the reduced forms of C₆₀. Due to the fact that at GC in DMF/TMABF₄ the iodide is reduced according to a two-electron step (-2.0 V, Figure 1B), it is assumed that the additional peaks located behind peak II (marked with * and **) correspond to the S_N2 processes, especially when the reaction between the fullerene dianion C₆₀²⁻ and the iodoalkane is fast, which is seemingly the case. Otherwise, another possible reaction scheme might be that discussed by Lund [21] for redox catalysis in the case of polyaromatic compounds (anthracene and pyrene anion radicals as reducing species or/and nucleophilic reagents) and aliphatic halides (as electrophiles). This peculiar feature corresponds to a fast coupling between the anion radical of the “catalyst” (the cathodically doped aromatic compound) and the radical issued from one-electron reduction of the haloalkane. In the

case of solid polyanions, however, their nucleophilic reactivity is more pronounced than the radical reactivity, which favors S_N2 reactions.

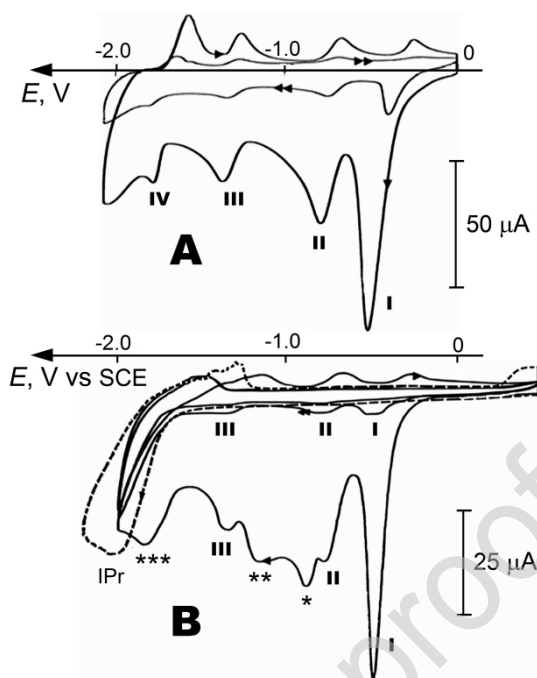


Figure 1. Cathodic voltammetry of thin layers of C_{60} deposited onto smooth solid surfaces. Electrolyte 0.1 M $TMABF_4$ in dry DMF, scan rate 100 mV s^{-1} . (A) C_{60} on gold (area 0.8 mm^2). First and second scans. (B) C_{60} on smooth GC (area 7 mm^2) in the presence of 1-iodopropane ($6 \times 10^{-3} \text{ mol L}^{-1}$). Integration of the one-electron reduction current I in the second scan corresponds to $\approx 4.2 \times 10^{-9} \text{ mol cm}^{-2}$ of fullerene remaining at the interface.

On the contrary, at very negative potentials, step *** could be assigned to a slow redox catalysis since a large amount of C_{60} was consumed via alkylation during the preceding steps. Step IV totally disappeared giving place to a broad step (-1.9 V) that could attest that catalytic alkylation is almost total and practically all the deposited C_{60} has been consumed. This is confirmed by a large depletion of the oxidation steps relative to the original transitions I, II, III and IV. The reduction currents observed in the second scan are much smaller than in the absence of the iodoalkane, which confirms high reactivity of the latter toward reduced forms of fullerene. Other haloalkanes (1-iodohexane and 1-bromooctane) were used in this process under similar conditions leading to comparable results.

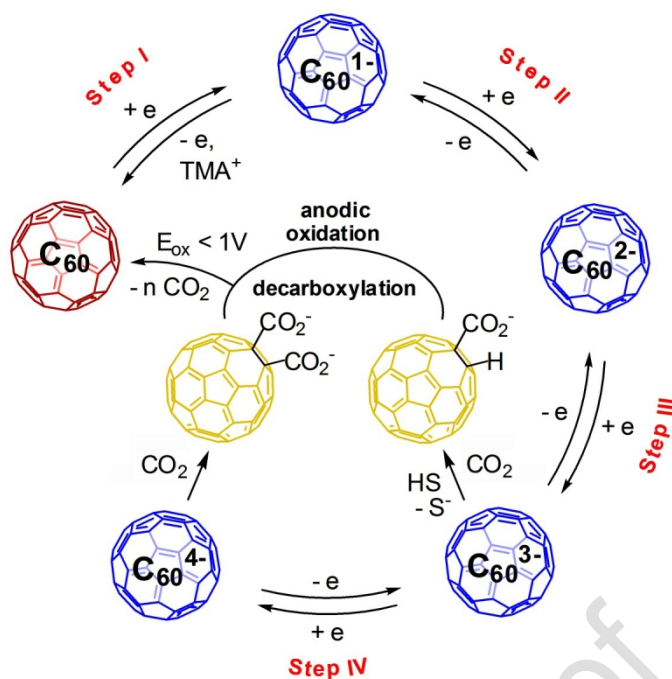


Figure 2. The redox steps (between -2.1 V and +1.1 V) of C_{60} deposited onto GC, without and in the presence of CO_2 . Other carboxylated forms, e.g. $[C_{60}(CO_2^-)_n]^{(4-n)-}$ ($n = 1$) might be formed from tetraanion C_{60}^{4-} while deeper carboxylation (with $n = 3, 4$) is less probable because of low-nucleophilic nature of intermediate mono and dianions, see text. Eventual protonation of C_{60} polyanions from the residual moisture is also schematically shown.

3.2 Use of organic bi-electrophilic reagents at modified C_{60} deposits

A further development of the findings described in the previous section was the cathodic activation of C_{60} in the presence of bi-electrophiles such as 1,3-dibromopropane and 1,6-diiodobutane under similar conditions (DMF containing TMA salts). In order to improve the stability of the reactive carbon layer (so far containing C_{60} alone), fine mixtures of C_{60} with natural Ceylon graphite flakes or with industrial graphene in a 1:1 mass ratio have been deposited onto glassy carbon and gold (Figure 3). This trick permitted to improve physical stability of the deposit due to π - π interactions between the electroactive fullerene and the graphite micro-plates that are themselves electrochemically inactive within the considered potential zone (0...-2.0 V) and to decrease (or totally suppress) the solubility of reduced C_{60} species (the polyanionic forms). Note that below -2 V, the reduction of the stabilizing matrix occurs causing the release of the retained C_{60} . Figure 4, comparing the stability of a pure C_{60} layer with that of its 1:1 mixture with the commercial graphene (XGnP, 750 m^2/g), illustrates the efficiency of this approach and a tremendous difference in stability of C_{60} redox systems. In a striking contrast to the rapid depletion of currents in the case of C_{60} deposited alone (Fig. 4A), all

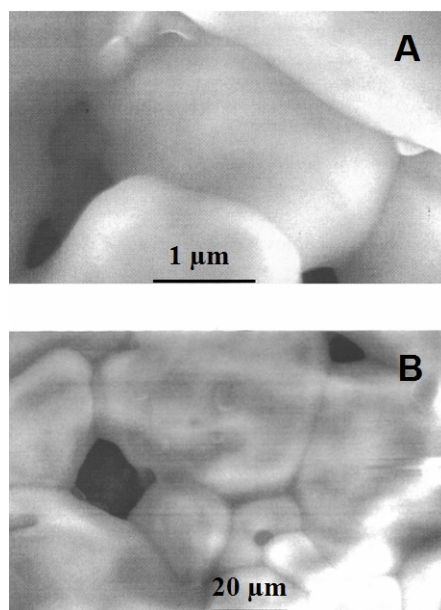


Figure 3. SEM views of the deposits (before carboxylation) of C_{60} on glassy carbon: (a) C_{60} alone and (b) in the mixture $\{C_{60} + \text{graphene}\}$.

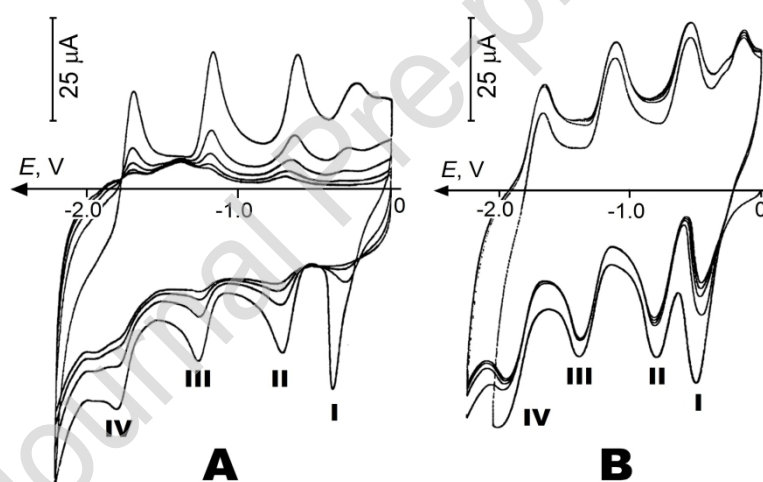


Figure 4. Voltammetric responses (6 scans) of: (A) C_{60} deposited onto a GC electrode; (B) a mixture of C_{60} with industrial graphene (50/50 w:w). DMF/0.1 M $TMABF_4$, scan rate 50 mV s^{-1} .

of four redox steps of fullerene are stable and practically unchanged during the consecutive scans in the case of the deposited C_{60} /graphene mixture (Fig. 4B). The superficial concentration of active C_{60} units in this mixed layer, estimated through coulometric integration, was $(3.0 \pm 0.2) \times 10^{-8} \text{ mol cm}^{-2}$ (for the case shown in Fig. 4B). When fullerene stabilized with graphene or graphite (both electro inactive in the range of reduction of the fullerene) is reduced in such layers, its reduced nucleophilic forms readily react with bi-electrophiles like 1,3-dibromopropane or 1,6-

diiodohexane, leading to a polymeric material inactive up to -2 V (Figure 5) where C_{60} units are connected with $(CH_2)_3$ or $(CH_2)_6$ linkers.

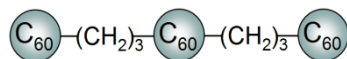


Figure 5C shows the two reduction peaks of anthraquinone immobilized (2×10^{-8} mol cm^{-2}) at the C_{60} /graphene interface using 2-bromomethyl-anthraquinone in the same process. For comparison (Figure 5D), a GC electrode of the same geometrical area was also shown to react in a similar way though with a significantly lower efficiency (providing anthraquinone coverage of 6×10^{-9} mol cm^{-2} only), underlining the specific role of C_{60} embedded into the interfacial graphitic layer.

Furthermore, gold surfaces can also be modified with bi-electrophilic reagents using the pre-deposited fullerene layers. This process is depicted in Figure 6. The deposited covalently linked poly-fullerene layer has a pronounced radicalophilic character allowing its modification through grafting of organic radicals electrogenerated within the potential range 0...-1.6 V. A large panel of organic halides carrying electro-active groups (benzyl, allyl) may thus react with C_{60} via radical grafting as illustrated in Figure 5B for 1,3-dibromopropane.

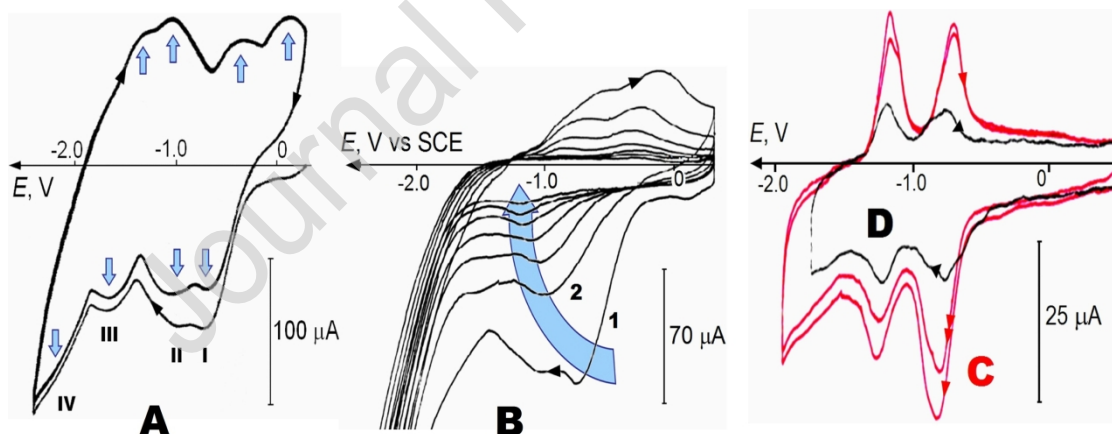


Figure 5. (A) Voltammetry of a mixture $\{C_{60} + MWCNT\}$ (50/50 w:w, deposited onto polished GC electrode, area 7 mm^2) in DMF containing $TMABF_4$. Six consecutive scans at the scan rate 50 $mV s^{-1}$. (B) Modification of this electrode in the course of seven successive scans in the presence of 1,3-dibromopropane (7×10^{-3} mol L^{-1}). (C) Response of 3-methylantraquinone grafted to the C_{60} /MWCNT interface via one-electron reduction of 2-bromomethyl anthraquinone. (D) For comparison, the response of a GC electrode after the same treatment as in (C).

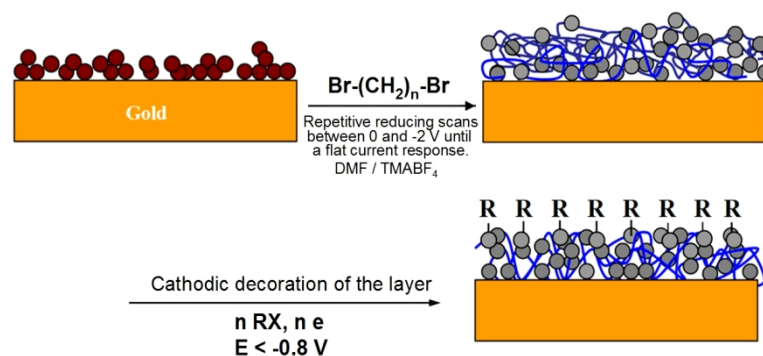


Figure 6. Modification of a C_{60} /gold interface providing a polymeric coverage by the reaction of the reduced forms of C_{60} with α,ω -dihaloalkanes (e.g. 1,3-dibromopropane and 1,6-diiodohexane) taken in excess.

3.3 Reactivity of reduced C_{60} with carbon dioxide

As shown in 2.1, the reduced forms of C_{60} layers deposited onto Au or glassy carbon can be considered as efficient poly-nucleophilic materials. Further illustration of this is that the reduction of C_{60} in the presence of CO_2 (saturated solution in DMF) leads to carboxylated thin layers. Figure 7 shows the voltammograms of the fullerene deposited on Au (A) and GC (B) in the presence of CO_2 in DMF/0.1 M $TMABF_4$ solutions. During the first scan, the cathodic response of the C_{60} /GC interface shows two steps, I and II (with E_p 's more positive than -1.0 V) specific to the reduction of C_{60} to $[C_{60}]^-$ and $[C_{60}]^{2-}$ respectively. Their reversibility (at vertex potential $E = -1.0$ V) demonstrates that monoanion and dianion of the fullerene do not react with CO_2 . The behavior of C_{60} /Au layers within this interval of potentials is similar. Upon the excursion of the potential down to -2.0 V, the peaks I and II show no more reversibility. The next reduction step (III) also appears without an anodic counterpart and a new huge reduction peak emerges at $E < -1.5$ V (Figure 7).

In the second scan, a partial (Fig. 7B) or a total loss (Fig. 7A) of electroactivity is observed demonstrating an efficient carboxylation of tri and tetra-anions of C_{60} . Carbon dioxide is only weakly active towards classical nucleophiles ($[C_{60}]^-$ and $[C_{60}]^{2-}$ are not enough nucleophilic for their efficient carboxylation), so the observed feature attests that the polyanions $[C_{60}]^{3-}$ (peak III) and $[C_{60}]^{4-}$ (included in the broad and intense peak at $E < -1.5$ V) are much more potent nucleophiles able to react with CO_2 (Fig. 2, steps III and IV, each followed by reaction with CO_2). At the potentials more negative than -2 V, the carboxylation of different types of carbons may occur through the generation of CO_2 anion radical ($E_{CO_2} < -2.2$ V [16,26]); however, it does not concern the present report as the potential of the process was strictly controlled not to exceed -2.0 V. With gold support, quite comparable results were obtained.

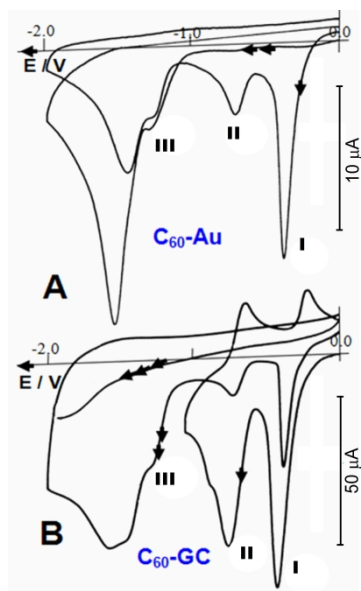


Figure 7. Voltammetric reduction of C_{60} in the saturated solution of CO_2 in DMF / 0.1 M $TMABF_4$. Deposition of C_{60} onto (A) gold (area 0.8 mm^2) and (B) GC (area 7 mm^2). First and second scans at the scan rate 50 mV s^{-1} .

In this case, a sharp peak ($E = -1.55 \text{ V}$) during the repetitive scans attests to the superficial carboxylation of gold under these conditions [17].

The carboxylation of C_{60} through the present cathodic activation was confirmed by FTIR analyses of the obtained interfaces ($\nu_{C=O}$ $1700\text{-}1600 \text{ cm}^{-1}$, δ_{CH} $1440\text{-}1230 \text{ cm}^{-1}$, δ_{OH} 930 cm^{-1}).

3.4 C_{60} and Kolbe reaction

What is the anodic stability of the carboxylated C_{60} units? The oxidation of organic carboxylates (Kolbe reaction) at different anodes is a well known process in solution electrochemistry principally leading to free radicals [27]. Much less common is the anodic cleavage of carboxylates grafted onto solid conductors, the process relating to the oxidation of carboxylated glassy carbon and graphene [13,14]. The anodic behavior of carboxylated C_{60} deposited onto carbon is illustrated in Figure 8. The reduction of this layer (a large cathodic peak at $E < -1.0 \text{ V}$ marked as Red) is associated with the appearance of a massive oxidation step (Ox) during the reverse scan to the boundary (γ). On the reverse scan, from 1.2 V to -1.2 V (γ to δ), not reaching the step Red, the peak Ox does not appear on the anodic branch (back to $+1.2 \text{ V}$). At the same time, two oxidation peaks IIa and Ia appear confirming the reversibility of steps I and II, and therefore the formation of the decarboxylated species $[C_{60}]^{n-}$ ($n = 1$ and 2). As was shown above, these latter are poorly nucleophilic and unable to react with CO_2 . Importantly, these two oxidation peaks were absent on the anodic branch following first cathodic scan from 0 V to -2.0

V (boundary β). This fact along with the intense cathodic process (Red) and the large associated anodic peak (Ox) during the reverse scan may attest to the reductive carboxylation of the fullerene through its more nucleophilic forms $[C_{60}]^{n-}$ ($n = 3$ and 4), generated at the steps III and IV (see Fig. 1 and 2). Importantly, the reversibility of steps I and II in the second cathodic scan from γ to δ and the absence of the oxidation step at ≈ 1.0 V - a crucial feature of this process - attests to the regeneration of fullerene from carboxylated C_{60} upon electrooxidation and therefore, to a *reversible carboxylation of C_{60}* . Remarkably, the efficient immobilization /stabilization of C_{60} at a smooth GC surface due to its embedding into an electro-inactive matrix (graphene, MWCNT) enables a very good stability of its current responses within the used range of potentials (-2.0 to 1.0 V), which permits a reliable coulometric comparison of the interfaces considered.

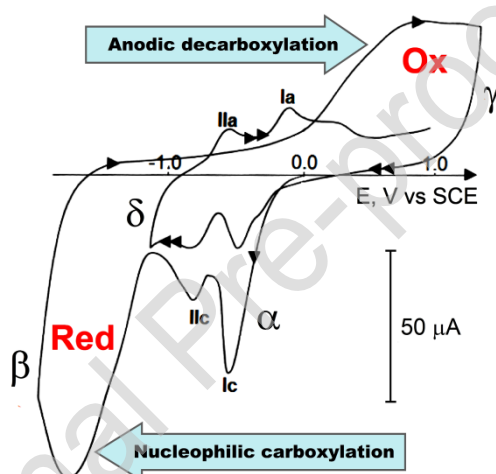


Figure 8. Voltammetry of C_{60} deposits on GC in DMF + 0.1 M TMBF₄ saturated with CO₂. Scan rate 50 mV s⁻¹. Electrode area 7 mm². The scan departs from 0 V (α) to -2.0 V (vertex β) then returning to +1.2 V (γ), followed by a novel cathodic excursion of the potential up to -1.2 V (δ).

As an example, the voltammetry of a C_{60} -graphene deposit on GC is shown in Figure 9A. Integrating the currents of the corresponding cathodic and anodic processes reveals that the amounts of electricity during the carboxylation (step B) $Q_B = 1.6 \times 10^{-3}$ C, and Kolbe decarboxylation (step C) 1.6×10^{-3} C, are strictly equivalent. Moreover, the coulometry of the yellow zone (A), the two one-electron "reference steps" (Ic and Iic), which correspond to the formation of non-nucleophilic fullerene anions $[C_{60}]^-$ and $[C_{60}]^{2-}$ respectively, provides $Q_{I+II} = 1.5 \times 10^{-3}$ C. This coulometric value corroborates the consumption of two electrons in the Kolbe process, unambiguously attesting to the carboxylation-decarboxylation of two sites during the

voltammetric cycle (Fig. 2). From this amount of electricity, $Q_{\text{IC+IIC}} \cong Q_{\text{Red}} = Q_{\text{Ox}} = (1.5-1.6) \times 10^{-3} \text{ C}$, the amount of fullerene carboxylated was estimated at $1.1 \times 10^{-7} \text{ mol}$ of C_{60} per cm^2 considering that carboxylation and decarboxylation of one C_{60} unit each corresponds to a two-

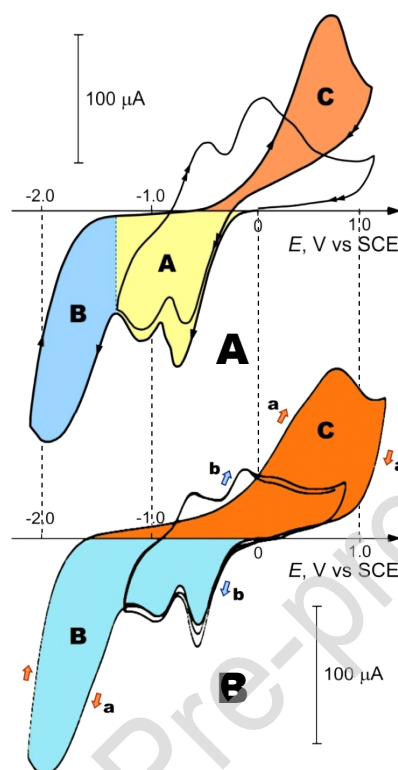


Figure 9. Oxydo-reduction of the carboxylated C_{60} -graphene interface (see text) deposited onto GC in DMF / 0.1 M TMABF_4 . Scan rate 50 mV s^{-1} . (A) In the presence of CO_2 . First scan: starting from 0 V to -2.1 V then returning to +1.1 V. Second scan is limited to -1.3 V not allowing the carboxylation of C_{60} . Consequently, the corresponding to Kolbe reaction oxidation step C does not appear. (B) Same conditions as in (A) but after the removal of CO_2 during 10 min bubbling of argon into the cell. Both the carboxylation of C_{60} and its Kolbe decarboxylation are still present. The amounts of electricity corresponding to these processes are equivalent suggesting CO_2 has been retained in the C_{60} -graphene system.

electron transfer. The amount of electricity involved (with a very good reproducibility) and the easiness of decarboxylation, by analogy with vicinal decarboxylation of organic 1,2-dicarboxylates through the Kolbe bis-decarboxylation [27-29], support di-carboxylation of $[\text{C}_{60}]^n$ at vicinal or conjugated positions allowing an easy di-decarboxylation back to the double bond(s) in the anodic process.

Stability of thus obtained carboxylated system was tested when CO_2 was entirely removed from the electrolyte by purging with dry argon during 10 min. Amazingly, the electrode kept the

imprint of carboxylation-decarboxylation even in a total absence of the external carbon dioxide. The relative intensity of steps I and II progressively diminishes while both carboxylation (B) and decarboxylation (C) gain in importance (Figure 9B). Current integration confirmed that the amounts of electricity remain equal at B and C ($2.9 \times 10^{-3} \text{ C}$ in Figure 9B) suggesting that a sufficient amount of CO_2 remains entrapped in the C_{60} /graphene phase for maintaining the process.

These results underline that the reduced forms of C_{60} deposited onto gold or GC interfaces alone or in combination with carbon forms (graphene, MWCNT), non-reducible at the applied potentials, constitute efficient poly-nucleophilic materials that readily react with appropriate electrophiles. As depicted in Figure 7, out of four reduced states $[\text{C}_{60}]^{n-}$, two (with $n = 3$ and 4, formed at $E < -1.2 \text{ V}$) are nucleophilic enough to react with CO_2 providing carboxylated fullerenes.

4. Conclusion

The present contribution demonstrates an exceptional capacity of C_{60} to stock electrons in a reversible manner within a range of moderately cathodic potentials (0...-2.0 V). Thus, under simple experimental conditions (DMF/0.1 M TMABF_4), four easily accessible reduction steps permit the cathodic doping of C_{60} immobilized on GC or gold. Electrophilic haloalkanes readily react with cathodically doped C_{60} (deposited on these supports) in an $\text{S}_{\text{N}}2$ process to give an alkylated material. Using bifunctional α,ω -dihaloalkanes permits also to covalently cross-link the fullerene matrix by alkyl chains and to prepare a stable radicalophilic carbonaceous interface suitable for radical grafting (within the potential range 0 to -1.6 V) of organic halides carrying various functional groups. As an example, methylanthraquinone radical was grafted to the C_{60} /graphene interface, but other types of modified surfaces should be possible to obtain through this procedure as well.

Making use of the electrophilic reactivity of CO_2 , electrogenerated fullerene polyanions (at $E < -1.2 \text{ V}$) were transformed into dicarboxylated C_{60} units whose two-electron oxidation at moderate anodic potentials leads to the regeneration of the starting fullerene.

When fullerene is embedded into graphene, an amazing stability of this interface to the repetitive scans within 0 to -2.0 V cathodic range was demonstrated for the first time. This system constitutes a new solid poly-redox interface possessing reducing and nucleophilic properties. Although the attempts to stabilize C_{60} at conducting solids have been recently undertaken [30,31], the proposed approach seems universal offering huge possibilities for building modified thin layers on the conducting surfaces. The polyanionic forms of C_{60} in the

mixture with inactive (within the working potentials range) carbon nanoforms are devoid of solubility, which allowed accurately assessing their content in the layer and realizing first chemically reversible carboxylation-decarboxylation of the fullerene-C₆₀. This innovative approach expands the possibilities of the electrochemistry of fullerenes and it can be applied for triggering radical processes, for redox catalysis and, in general, for building new chemically modified electrodes using these extraordinary compounds. The use of the mixtures C₆₀/graphene appears to be of an exceptional interest for fixing C₆₀ into conducting carbon matrixes, though this topic is beyond the scope of the present contribution and this aspect is only shortly presented here.

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Declaration of interests

x The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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