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An innovative anodic approach for efficient immobilization of an acetylenic triple bond via silicon-carbon bond scission

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ABSTRACT

The anodic scission of silicon-carbon bonds is successfully applied for the efficient covalent coverage of conducting solid surfaces with propynyl groups under quite simple conditions. The anodic cleavage of propynyl trimethylsilanes $(Me)_3Si\text{-}C \equiv C\text{-}CH_2R$ in acetonitrile containing tetraalkylammonium salts leads to a dense grafting of the propyne $C \equiv C\text{-}CH_2R$ units onto glassy carbon, gold, and platinum surfaces. When R is a good leaving group (e.g. bromide), versatile electrodes might be prepared upon their polarization alternately (i) anodically and (ii) cathodically. A first example in which the anodic acetylation is immediately followed by cathodic immobilization of graphene and fullerene is reported.

1. Introduction

Glassy carbon is still considered as an efficient electrode material within the cathodic domain [1, 2]. At the same time, most of the processes of fixation of organic moieties at the GC interface have been reported to occur through the addition of electrogenerated free radicals, mainly within the cathodic range [3–5]. Additionally, grafting processes with the radicals generated from the oxidation of alcohols [6], amines [7], and carboxylates [8] have been reported. On the other hand, the intrinsic cathodic charge of various carbon materials gives them a polynucleophlic character [9–11], making possible many efficient grafting processes reviewed recently [12].

The fact that different forms of carbon can be anodically charged in the presence of suitable reactive anions [13, 14] has been much less exploited. For instance, graphite can efficiently incorporate bromine in a manner obviously similar to the insertion of Br^- into anodically charged carbon [13]. From this work emerges the idea of anodic generation of electrophilic centers at the carbon surface. Indeed, the capability of a wide variety of carbons (e.g. glassy carbon, graphites and fullerenes) to be anodically charged at potentials more positive than $+1.5$ V vs. $Ag/AgCl/KCl_{sat}$ enables the formation of electrophilic centers on their surface which, in the presence of trimethylsilyl (TMS) substituted derivatives R-TMS, opens up new possibilities for modifying carbonaceous interfaces. This concept was considered in a recent work [14] originally developed to enable allylation and benzylation of different carbon materials. This process stresses the elevated kinetic instability of silicenium cations, in particular TMS^+, due to their extreme electrophilicity. Very efficient reactions of such species with a large variety of both π- and σ-electron donors have been reported. The oxidative cleavage of C—Si bonds, enhanced by the excellent leaving-group ability of TMS^+ cations, is covered in several reviews (see e.g. [15]). Along the same lines, allyl and benzyl nitrates have been formed under oxidative conditions from allyl and benzyl trimethylsilanes [16].

Recent work by Geiger [17, 18] underlined the interest in solid electrodes that can trap chemical functions via terminal lithio-activated ethynyl derivatives, permitting one to immobilize $R\text{-}C \equiv C\text{-}$ units onto gold and carbon surfaces. The present contribution focuses on a new activation process, simple to achieve, using the anodic reactivity of Si—C bonds (with TMS^+ as a leaving group [19]), which is applied to the immobilization of propynyl groups on solid surfaces such as carbon and gold.

2. Experimental

The present contribution focuses on the oxidation of trimethylsilylated compounds TMS-R with the R substituent being 1-propyne (**1**), 3-bromo-1-propyne (**2**) and 4-iodo-phenyl-1-propyne (**3**). All products are commercially available from Alfa Aesar. Anhydrous polar solvents – acetonitrile (ACN) for oxidation and *N*,*N*-dimethylformamide (DMF) for cathodic processes – were used to prepare 0.1 M solutions of electrochemical grade tetramethylammonium and tetrabutylammonium salts (essentially with BF_4^-, ClO_4^- and PF_6^- anions). Fullerene C_{60} ($>$ 99.0% purity) was purchased from TGI. Graphene was obtained in the laboratory by cathodic exfoliation of natural graphite [13].

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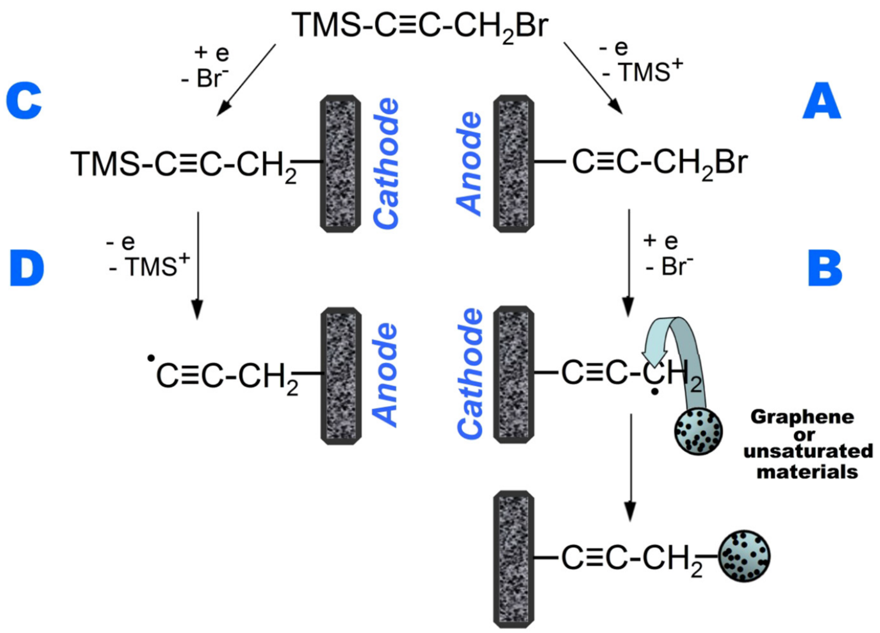

Scheme 1. TMS-C ≡ C-CH$_2$X as a versatile ambifunctional grafting agent.

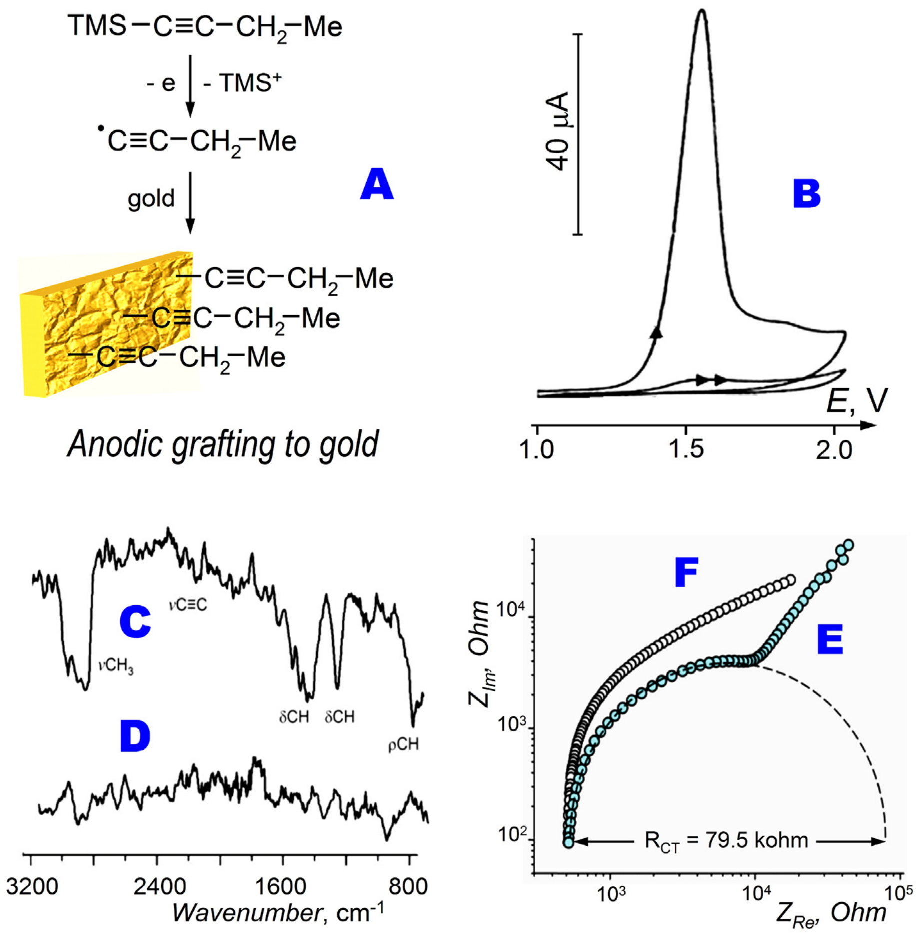

Fig. 1. Anodic modification of solid surfaces with TMS-R compounds. (A) Propynation at gold through a radical process. (B) Anodic oxidation of TMS-propyne (6 mmol L^{-1}) at a gold microelectrode (0.8 mm^2) in AN/0.1 M TMABF$_4$. Two first scans. Scan rate 50 mV s^{-1}. (C) FTIR spectrum of the layer obtained from the anodic oxidation of TMS-propyne **1** (12 mmol L^{-1}) at +1.54 V at smooth gold. (D) For comparison, FTIR response of Au surface before addition. (**E**) Nyquist plots of the reduction of chloranil (3 mmol L^{-1}) in ACN/0.1 mmol L^{-1} TBAPF$_6$ at a smooth Au electrode with freshly immobilized propyne layer. (F) Same as in (E), at the non-modified surface. $E = -1.16$ V, $\Delta E = 10$ mV. Frequency range from 0.306 MHz to 43 MHz.

In this first contribution on the use of ethynylic TMS derivatives for the efficient decoration of solid electrodes, only smooth glassy carbon and gold surfaces (0.8 mm^2) are described. The electrodes were polished with silicon carbide paper (Struers 500 and 1200) and consecutively rinsed with water, ethyl alcohol and acetone.

All potentials are referred to Ag/AgCl/KCl$_{sat}$ system in water.