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Efficient immobilization of 9,10-anthraquinonyl moiety at solid interfaces through 2-(bromomethyl)anthraquinone one-electron cleavage

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ABSTRACT

We report here a new and very efficient method for the coverage of different carbon materials with 9,10-anthraquinone attached via a methylene linker. The method is based on one-electron reduction of 2-(bromomethyl)anthraquinone (AQ-CH_2-Br) to a free radical AQ–CH_2• which was readily achieved using propylene carbonate (PC) as solvent containing tetrabutylammonium iodide. This way, the radical AQ–CH_2• adds to the abovementioned carbons forming very stable and dense covalently bound anhraquinonyl methane layers ($\Gamma \approx 2 \times 10^{-9}$ mol cm^{-2}). The grafting could be performed by constant potential electrolyses ($q < 0.5 \times 10^{-3}$ C mm^{-2}).

1. Introduction

The cathodic reduction of alkyl halides (RX with X = I or Br) caused great interest. In particular, many studies deal with the direct and indirect C – X bond cleavage processes [1,2]. Quite generally, the reduction at carbon electrodes corresponds to a two-electron hydrogenolysis.

Among activated organic halides, benzyl bromide certainly presented first exception. Its reduction at silver in two well-separated one-electron steps [3] and the immobilization of benzyl radicals at glassy carbon were reported [4]. In a similar way, "allylation" and "propargylation" of GC using unsaturated bromides were achieved [5]. Beyond significantly activated organic substrates, free radical grafting from neutral organic species appears quite unusual. Fortunately, it was amended by using the cationic substrates such as functionalized aryl diazonium salts nowadays widely employed as an almost canonical pathway for solid surface decoration [6].

Arylation of carbon is sought for in many important applications regarding sensing and catalysis and it certainly appeals for simple and efficient grafting ways. Until now, most of aromatic π-acceptors (e.g. nitroarenes) were immobilized at electrodes via the diazonium method. The modification of carbon surfaces by 9,10-anthraquinone moiety (AQ) has been extensively studied during recent years. Thus, a pathway using oxidation of Boc-protected diamines was applied for carbon grafting [7]. Other methods like Kolbe oxidation of an anthracene carboxylate [8] (possibly via a radical intermediate) were recently reported. An original recipe used 2-anthraquinone-diazonium preliminarily adsorbed for reaction onto edge-plane carboxylated pyrolytic graphite electrodes [9]. Superficial concentrations of grafted anthraquinone moieties were generally small and resistive films were often observed suggesting multilayer processes at carbon surface. Additionally, anthraquinone was gold-thiol immobilized by rigid norbornylogous bridges [10].

We now report a simple and efficient grafting process based on a one-electron cathodic cleavage of AQ–CH_2Br with transient formation of AQ–CH_2• in high dielectric permittivity organic solvents in the presence of a tetraalkylammonium iodide as supporting salt. The key step of the process is the in situ conversion of RBr into RI ($E_{RBr} < E_{RI}$) expected to occur at the interface (I^- adsorbed). Therefore, since the global two-electron scission of the C – I bond now occurs in two neatly separated steps, the free radical transient is selectively produced and may be efficiently attached to the GC surface. The starting bromide is commercially available or easy to synthesize. The – CH_2 – link between the acceptor and the surface is extremely short, unexpectedly allowing rather fast heterogeneous electron transfers. The proposed method can be extended to a large series of π-acceptors. Cathodic responses of attached films were mainly studied in polar solvents and first attempts of AQ–CH_2• grafting onto Au and Pt were achieved.

2. Experimental section

Electrolyses were essentially carried out in propylene carbonate (PC) containing 0.1 M Bu_4NI (TBAI) with an eventual addition of ethylene carbonate (EC) used in mixture 50/50 (v:v). In principle, experiments described in this work did not need special treatment of electrolytic

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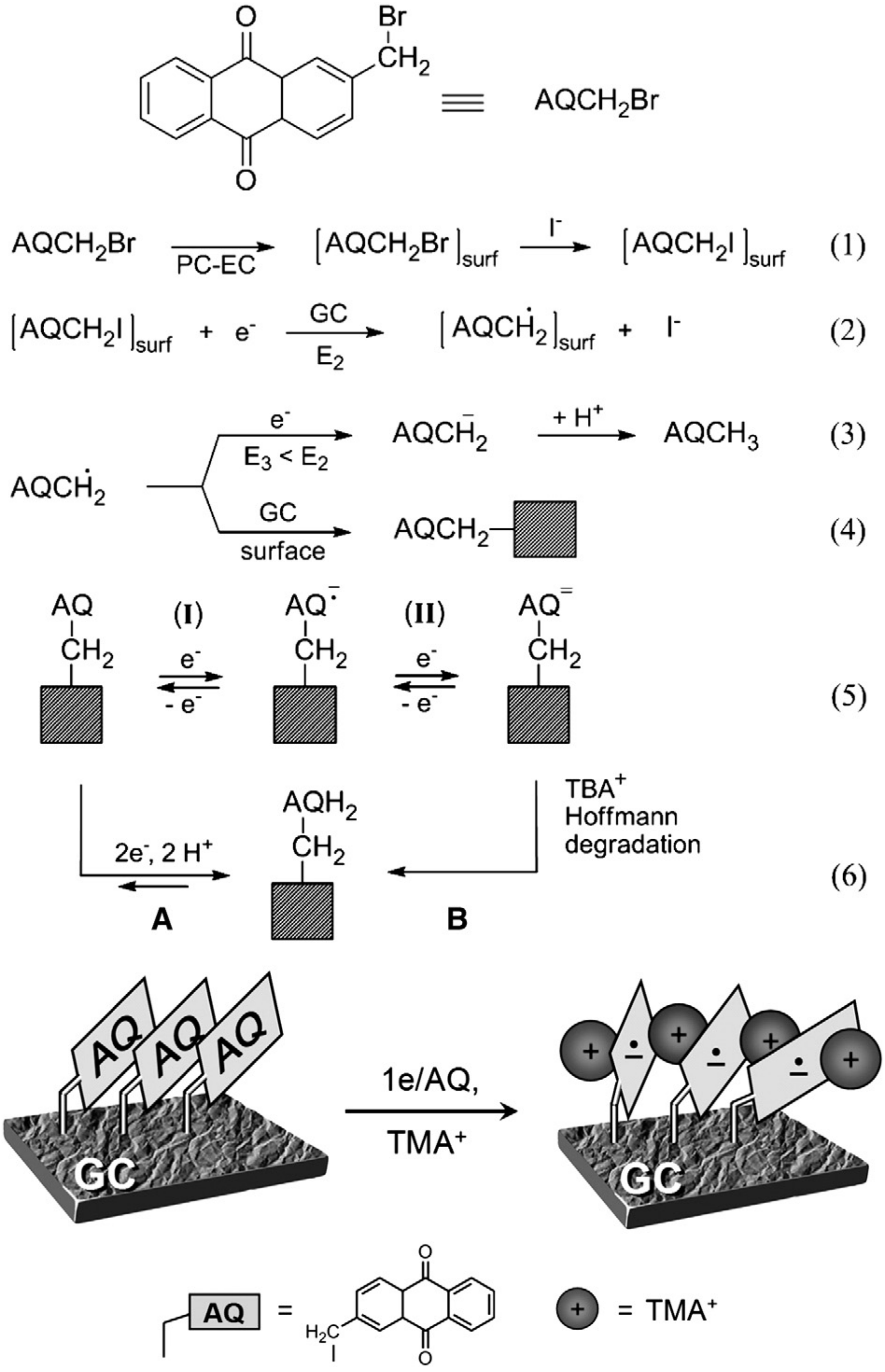
solutions. Specific cycling of adsorbed anthraquinone at solid electrodes (GC, gold, platinum) was achieved in N,N-dimethylformamide (DMF) or acetonitrile (ACN) containing 0.1 M $TBABF_4$ or $TMABF_4$. The potentials are referred to aqueous $Ag/AgCl/KCl_{(sat)}$. The electrochemical instrumentation has been previously reported [5].

The electrodes have an apparent surface area of 0.8 mm^2 (GC, Au, and Pt). GC electrodes of apparent surface area of 0.2 and 7 mm^2 were also used. All carbon samples were from Tokai Carbon Co. (GC Rod). Anthraquinone deposits at solid freshly polished electrodes were achieved in two different ways: a multi-scan at the level of the first step (formation of free radicals, Scheme 1) or through fixed-potential electrolysis (direct reduction of $AQ–CH_2–Br$). After deposit, the interface was sonicated during 10 min.

Before being modified, all electrodes were carefully polished with silicon carbide paper (Struers) or with Norton polishing paper (types 02 and 03). In all cases, electrochemical measurements and deposits were performed using three-electrode cells separated with a fritted glass. All electrolytic solutions were made oxygen-free by efficient argon bubbling.

2-(Bromomethyl)-anthraquinone, electrolytes and solvents used in the present work were purchased from Aldrich and employed without further purification.



Scheme 1. One-electron reduction and grafting of 2-(bromomethyl)anthraquinone and further reduction of the grafted layer in the presence of TMA+ cations.