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Photocatalytic carboxylation of C—H bonds promoted by popped graphene oxide (PGO) either bare or loaded with CuO

Angela Dibenedetto[c,d], Jiaguang Zhang[b], Mateusz Trochowski[e], Antonella Angelini[b,c], Wojciech Macyk[e], Michele Aresta[a,d,*]

[a] IC2R srl., Via Casamassima km 3, 70018 Valenzano, BA, Italy
[b] Department of Chemical and Biomolecular Engineering, NUS, 2 Engineering Drive 4, Singapore 117585, Singapore
[c] Department of Chemistry, University of Bari, Via Orabona, 4, 70125 Bari, Italy
[d] CIRCC, via Celso Ulpiani 27, 70126 Bari, Italy
[e] Faculty of Chemistry, Jagiellonian University, ul. Ingardena 3, 30-060 Kraków, Poland

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ABSTRACT

Popped graphene oxide (PGO), either bare or loaded with CuO (or Cu_2O), has been characterized for its photoelectrochemical properties and used for the first time as photocatalyst for CO_2 insertion into C—H bonds, a challenging reaction of great industrial interest. PGO joins, thus, the restricted number of modified polymeric C-species (fullerenes and carbon nanotubes-CNT) having photochemical activity. Using acetylacetone as test molecule and bare PGO, two isomeric carboxylic acids were formed with *ca.* 3.5% yield under white (solar) light irradiation that was enhanced to over 10% after deposition of CuO on PGO. Under the reaction conditions, CuO alone gave only minor traces of the carboxylated products. Therefore, the two components together produce a synergistic effect that reinforces the photocatalytic activity of each of them. Interestingly, both PGO and CuO@PGO do not have the correct potential for the generation of the radical anion $CO_2^{\cdot -}$, therefore the reaction mechanism of formation of the carboxylated products cannot imply the formation of C—C bond *via* radical coupling. Most likely, the one-hole oxidation of acetylacetone to the relevant radical is the starter of the carboxylation process that implies the transfer of two electrons to CO_2. The possible implicacy of HCO_2H in the carboxylation has been demonstrated by the presence of such compound in the photocatalytic reaction mixture under CO_2 and by the direct carboxylation of *acac* with formic acid under dinitrogen in the same operative conditions as with CO_2.

1. Introduction

The synthesis and structure of PGO from GO and some of the catalytic properties of the former loaded with transition metals (TMs@PGO) have been recently reported [1]. Although the structural features of PGO (and GO) have been quite extensively described in Ref. 1, the photoelectrochemical-PEC properties were not. In this paper we describe the PEC properties of PGO and CuO@PGO and report for the first time on their use in photochemical reactions bearing to the formation of C—C bonds. The direct introduction of a carboxylic acid moiety (—CO_2H) onto an organic substrate is an area of crucial industrial interest. The formation of a carboxylate moiety today requires complex and harsh procedures (oxidation of alkyl moieties or partial oxidative demolition of aromatic rings such as naphtalene to afford benzene-o-dicarboxylic acids, or else hydrolysis of cyanides) that may eventually have a quite low carbon utilization fraction, producing large amounts of waste. New sustainable synthetic methodologies are welcome that can both reduce the production of waste, including the emission of CO_2 into the atmosphere, and save fossil carbon through the recycling of carbon, stepping from a “linear to a cyclic C-economy” [2–5]. The direct carboxylation of an organic substrate *via* CO_2 insertion into a C—H bond would respond to the requisites of a *sustainable chemistry* and contribute to *recycling carbon* [3]. The C—H bond activation is not easy to perform under controlled conditions in thermal catalytic reactions. Photocatalytic reactions might be more successful, as we have recently shown using ZnS decorated with Ru nano-particles [6,7]. Photochemical reactions would implement a new route to carboxylates, making use of cheap and abundant solar energy within a single step carboxylation reaction, making use of recoverable and recyclable non-soluble catalytic materials and avoiding the production of waste. In such photocarboxylations, the involvement of the radical anion $CO_2^{\cdot -}$ has been demonstrated to occur [6,7]. In electro-

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* Corresponding author at: IC2R srl., Via Casamassima km 3, 70018 Valenzano, BA, Italy.
E-mail address: michele.aresta@uniba.it (M. Aresta).

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chemical processes, the $1e^-$ reduction of CO_2 proceeds through an uphill electron transfer with formation of the carbon dioxide radical anion. The redox potential of the $CO_2/CO_2^{\cdot -}$ couple in water amounts at −1.9 V *versus* standard hydrogen electrode (SHE), making the process strongly unfavorable (in dry organic solvents the situation is even worse, as the potential is −2.1 V *vs* SHE) [8]. This extremely low potential is justified by the large reorganization energy necessary for the transition from the linear CO_2 free molecule to the bent (133°) radical anion. Multi-electron reduction processes of carbon dioxide coupled to proton transfer (Eqs. (1)–(5)) lead to more stable products and therefore such reactions are thermodynamically preferred: yet their selectivity is difficult to control [6–22] and, in fact, several products are often concurrently formed:

$$CO_2 + 2H^+ + 2e^- \rightarrow HCOOH \; E^\circ = -0.61\ V \tag{1}$$

$$CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O \; E^\circ = -0.53\ V \tag{2}$$

$$CO_2 + 4H^+ + 4e^- \rightarrow HCHO + H_2O \; E^\circ = -0.48\ V \tag{3}$$

$$CO_2 + 6H^+ + 6e^- \rightarrow CH_3OH + H_2O \; E^\circ = -0.38\ V \tag{4}$$

$$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O \; E^\circ = -0.24\ V \tag{5}$$

One photon can induce the transfer of one electron in a photochemical reaction, according to the photoequivalence law of Stark and Einstein. Therefore, the probability of one-electron process is much higher than that of a multiple-electron process. The energetic stability of carbon dioxide molecule ($\Delta G_f^\circ = -394\ kJ\ mol^{-1}$) constitutes a strong limitation to CO_2 reduction and makes this reaction highly endergonic [23].

Photocatalytic carboxylation of organic compounds under mild conditions may become a novel approach to carbon dioxide utilization [6,7]. In general, the basic concept of photocatalytic carboxylation is the C—C bond formation with coupling of two radicals: an organic one and $CO_2\cdot^-$, as we have shown to occur with ZnS [6,7]. Interfacial electron transfer at the surface of irradiated semiconductors brings to organic radicals formation [24–26]. Kisch et al. have reported the coupling of organic radicals photogenerated at CdS resulting in C—C and C—N bond formation [27]. Yanagida and coworkers suggested that CdS would promote an intermolecular addition to C═O bond (alkylation of CO_2) [28]. In such reactions, electrons from the excited photocatalyst were able to reduce both carbon dioxide and the organic substrate (*e.g.* aromatic ketones, benzyl halides), while triethylamine was consumed as a sacrificial electron donor. The carboxylic acid was thus formed upon radical–radical anion coupling.

In this paper, we describe a photocatalytic system based on popped graphene oxide (PGO) or PGO loaded with copper(II) oxide. Both systems enable the carboxylation of acetylacetone affording two isomeric carboxylic acids. The reaction is very selective and other side-products are not formed when the correct solvent is used. As discussed below, the mechanism results to be different from that discussed in Refs. 6, 7, 27and 28, due to the different properties of PGO/CuO@PGO with respect to ZnS/Ru@ZnS and CdS.

2. Results and discussion

2.1. Materials characterization

PGO is a compound of general molecular formula C_xO_y (for the elemental analyses see the Experimental Section) containing several functional groups such as epoxy, carbonyl and hydroxyl groups, attached to sp^3 and sp^2 hybridized carbons [29]. The structural and physical features of GO and PGO have already been described in ref. 1. Here we report some newly investigated properties, mostly photochemical, but not only. ^{13}C—CPMAS-NMR spectrum of PGO (See Fig. 1, SI) displays three main broad resonances at 64.7, 74.1 and 107.57 ppm, suggesting the presence of C—O and C—C bonds of different nature.

According to the literature [27] the most intense signals at 74.11 and 64.7 ppm can be ascribed to epoxy(1,2-ether)groups and tertiary alcohols, respectively. The peak at 107.57 ppm is due to C═C bonds. The low intensity signals at 25.8, 37.6 ppm are relative to quaternary carbon atoms [30].

XPS analyses (See Fig. 2, SI) have confirmed the presence of the functional groups listed above. C═O and O—C═O moieties were also detected even if in low concentration that justify their absence in the ^{13}C NMR spectrum. In particular, 19% of the total carbon is in the oxygenated forms C—O (14.544), C═O (2.18) and O—C═O (2.91).

Loading PGO with CuO produced a material with minor structural differences with respect to the starting PGO as revealed by Raman analyses (See Fig. 3a–b, SI): D bands at *ca.* 1330 cm^{-1} originate from defects of the polycrystalline graphene, while G bands at *ca.* 1575 cm^{-1} result from the single crystal graphene. The intensity ratio, I_D/I_G, can be used to determine the disordered extent of the carbon material. PGO has a ratio of 4.1, larger than that in CuO@PGO (2.7), indicating that the Cu species affect the structure of PGO, resulting in a material with less defects in the graphene sp^2 structure.

SEM analysis (See Fig. 4, SI) reveals the presence of particles of irregular shape and dimension. EDS analyses coupled to SEM confirm the presence of copper species (green spots in Fig. 4-right). Noteworthy, XPS analyses reveal that the copper distribution between the surface and the bulk is uneven. In fact, if one compares the amount of Cu found by XPS on the surface (1.1-1.8%) with the total amount of copper in the sample (9.2%, see Analytical Data in the Experimental Section), finds that maximum *ca.* 20% of copper is on the surface and the remaining portion must be in the bulk. The Cu(I)/Cu(II) ratio is equal to 1/8.83 so about 90% of copper is in the oxidation state Cu(II).

The XRD profile of nanosized CuO@PGO (See Fig. 5, SI) confirms the spot distribution of nanosized CuO (enlarged peaks attributable to tenorite) on PGO.

The UV–vis spectra (250–1100 nm) of materials are presented in Fig. 1. All materials with PGO exhibit absorbance in the whole studied range. Bare CuO and Cu_2O have absorbance onsets at about 900 nm and 700 nm respectively. The CuO@PGO and Cu_2O@PGO spectra resemble that of bare PGO in the range from 700 to 1100 nm, but there is an evident change below 650 nm.

As it will be discussed below, Cu_2O is inactive in photocatalysis in the present case. So, there was no reason to carry out a complete physical and structural characterization of Cu_2O and the relevant Cu_2O@PGO. We carried out photochemical characterization in order to figure out whether impurities of Cu(I) could deeply affect the properties of Cu(II)- materials, but fortunately this is not the case. As a matter of fact it was very difficult to exclude the presence of Cu_2O in CuO-based materials, as shown by XPS.

The observed decrease in absorbance of CuO-PGO-materials originates from deposited copper oxides which affect the spectroscopic properties. The deposited CuO (and Cu_2O) may scatter the light, causing the decrease of absorbance. To estimate the optical band gap of two bare materials (CuO and Cu_2O) the Tauc transformation was used [6,7]. Assuming that CuO is a direct band gap semiconductor [31], the band gap energy was found to be 1.49 eV. The same method was used to determine the band gap energy of Cu_2O (1.97 eV), which is also a direct band gap semiconductor [32].

2.2. Photoelectrochemical measurements

The bare copper(II) oxide reveals cathodic photocurrents over the whole absorption range at the potential of −0.4 V *vs.* Ag/AgCl (Fig. 2). The spectral range of photocurrent generation encompasses the whole range of absorbance. Other materials were practically inactive under similar conditions. This suggests, that CuO shows the highest efficiency in photoinduced interfacial electron transfer (IFET).

During the experiment reported in Fig. 3 an almost 400 times more