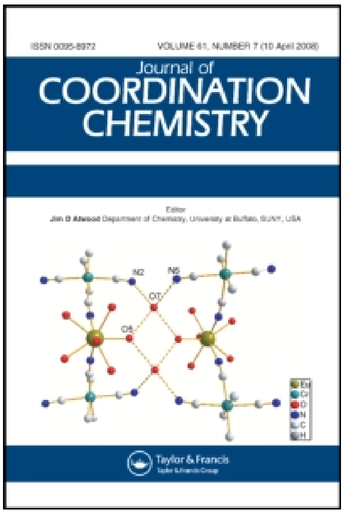

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A Supramolecular Cobalt-Porphyrin-modified Electrode, toward the Electroreduction of Co_2

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Short Communication

A SUPRAMOLECULAR COBALT–PORPHYRIN-MODIFIED ELECTRODE, TOWARD THE ELECTROREDUCTION OF CO_2

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The electro-reduction of carbon dioxide was studied by using a glassy carbon electrode modified with Co(II)-tetrabenzoporphyrin as adsorbed layers or as a supramolecular system. In order to obtain the supramolecular electrode, 4-aminopyridine was chemically bonded to the electrodic surface. On this surface, a first layer of porphyrins was anchored by the pyridine as a fifth ligand. Packed on the first layer of porphyrins, a supramolecular system is formed. The electrode modified with physically adsorbed layers of porphyrins does not show catalytic response toward the electroreduction of CO_2. However, the supramolecular electrode is very stable and shows a high catalytic response.

Keywords: Supramolecular; CO_2; Porphyrin; Cobalt; Electrode

Supramolecular chemistry, the subject of many recent studies [1,2], arises from units linked by weak unions, like hydrogen bonds, π interactions or electrostatic attractions [1]. In some cases, studies have focused on engineering aspects of chemistry [3–5]; in others, on biological model systems [6,7]. On the other hand, carbon dioxide reduction, catalyzed by transition metal complexes, has been widely studied due to its relevance to environmental chemistry and energy production [8]. In this work, we compare the electrocatalytic response toward reduction of CO_2 of an electrode surface modified with tetrabenzo-Co-porphyrins (Co-TBP) as a supramolecular system (see Scheme 1A) or as layers of adsorbed porphyrins. Figure 1 shows the structure of the porphyrin used in this study. Normally, in order to obtain supramolecular structures of stacked porphyrins, dendritic units are preferred because hydrophobic interactions are favorable [1]. The first step of the modification implies that an amine (4-aminopyridine) is covalently linked to the electrode surface according to an experimentally optimized

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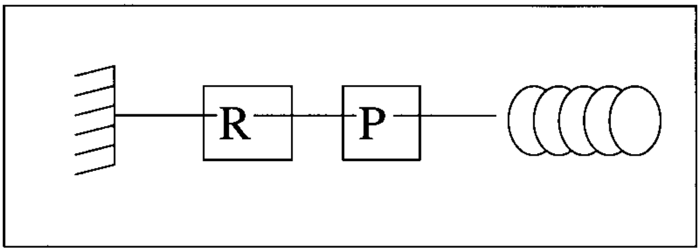


SCHEME 1A Simplified scheme corresponding to the electrode with an amine, **R**, covalently attached. **P** corresponds to the first porphyrin binding to the amine. Over this porphyrin, the stacked supramolecular system is formed.

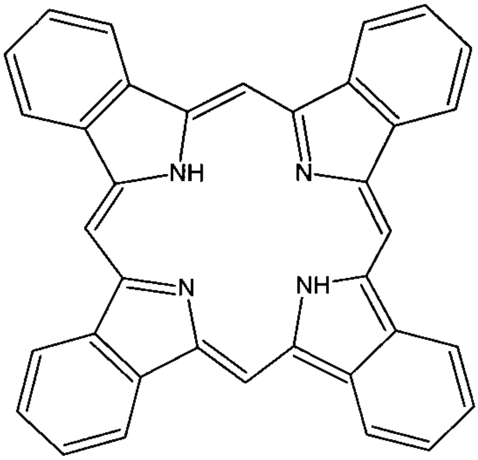


FIGURE 1 Structure of the free ligand of tetrabenzoporphyrin. When complexed by a metal the two hydrogens are replaced by cobalt.

method [9,10]. The electrode (glassy carbon) was submerged in a solution (ethanol/ 0.1 M tetrabutylammonium perchlorate (TBAP)/0.5 M 4-aminopyridine) at fixed potential (+1.60 V *versus* Ag/AgCl) for 2 min. After this treatment the electrode was submerged in an ultrasonic bath for 15 min in an aqueous pH 6.8 (phosphate/biphosphate) buffer solution. In order to check the binding of the amine to the electrode surface, a hydrogen evolution reaction (HER) was used [9,10]. Figure 2 shows the shift in the potential of HER that proves the amine is covalently attached [9,10]. After this treatment, the amino-modified electrode was submerged in a solution (dimethylformamide (DMF)/1 mM porphyrin) that was refluxed at 170°C for 2 h. During the reflux, a "monolayer" of axially bonded porphyrins was formed on the electrode surface. Stacked by π interactions, columns of porphyrins are formed over the first layer of chemically bonded Co-TBP. The shape of the column is unknown. Probably, the units are linked through the ring forming a side to side interaction (see Scheme 1B). In order to check the formation of a supramolecular modified electrode, it is necessary to compare the response of this electrode and different Co-TBP modified electrodes. Figure 3 shows the voltammetric response of glassy carbon and 4-aminopyridine-electrodes under N_2 and CO_2 atmospheres. The catalytic response toward the

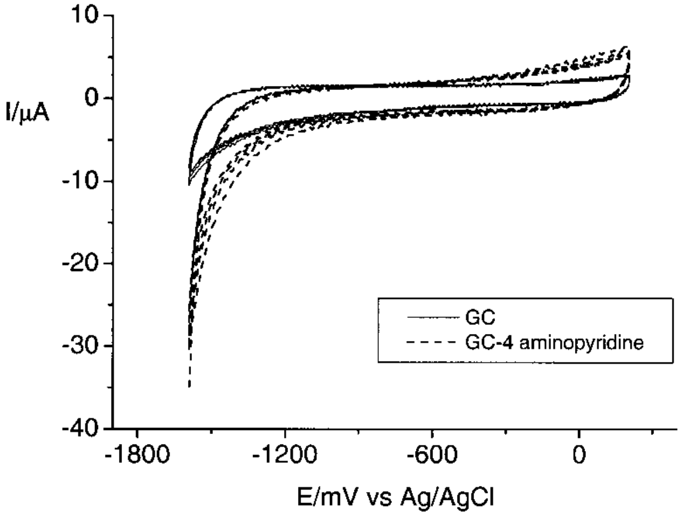
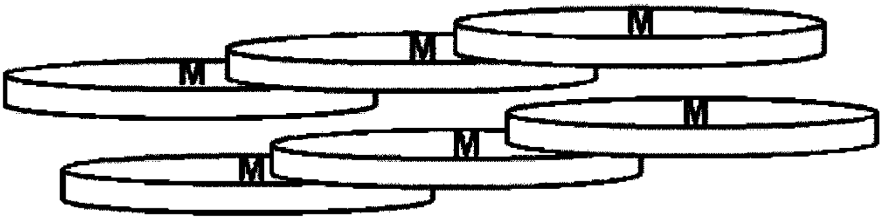


FIGURE 2 Voltammetric response of the amino-modified electrode toward the hydrogen evolution reaction (HER). The responses correspond to various consecutive cycles. Scan rate: $0.2\,V\,s^{-1}$. Electrolyte: phosphate/biphosphate pH 6.8 buffered aqueous solution.



SCHEME 1B Simplified scheme showing the interactions through the rings (side to side) of the porphyrins.

reduction of CO_2 in both systems is practically the same showing that the amine does not catalyze this reaction compared to the bare electrode. Figure 4 compares the response of an electrode modified with a physically adsorbed layer of Co-TBP over the glassy carbon or over the 4-aminopyridine-glassy carbon under N_2 and CO_2 atmosphere. These electrodes were prepared by deposition of a drop of a solution (DMF) containing the porphyrin (1 mM) on the surface over a period of 1 h. After this time, the electrodes were rinsed with ethanol and water in order to eliminate excess porphyrin. In both cases, the voltammetric response under N_2 was measured and then CO_2 was bubbled into the solution for 20 min and the reduction of CO_2 was recorded. Figure 4 shows that both electrodes have a little shoulder before a current discharge under N_2. Compared to the systems shown in Fig. 3, hydrogen evolution is catalyzed by the presence of the porphyrins. It is noticeable that with CO_2 a smaller current is observed. It is possible that the low current was due to inhibition of HER due to the presence of CO_2, or could correspond to the electroreduction of CO_2. This current wave begins at practically the same potential as the blank electrode in the presence of CO_2 (see Fig. 3), and reaches a minimum in comparison to blank electrodes. We can conclude that after the catalysis of HER, the porphyrin layers are degraded, block-

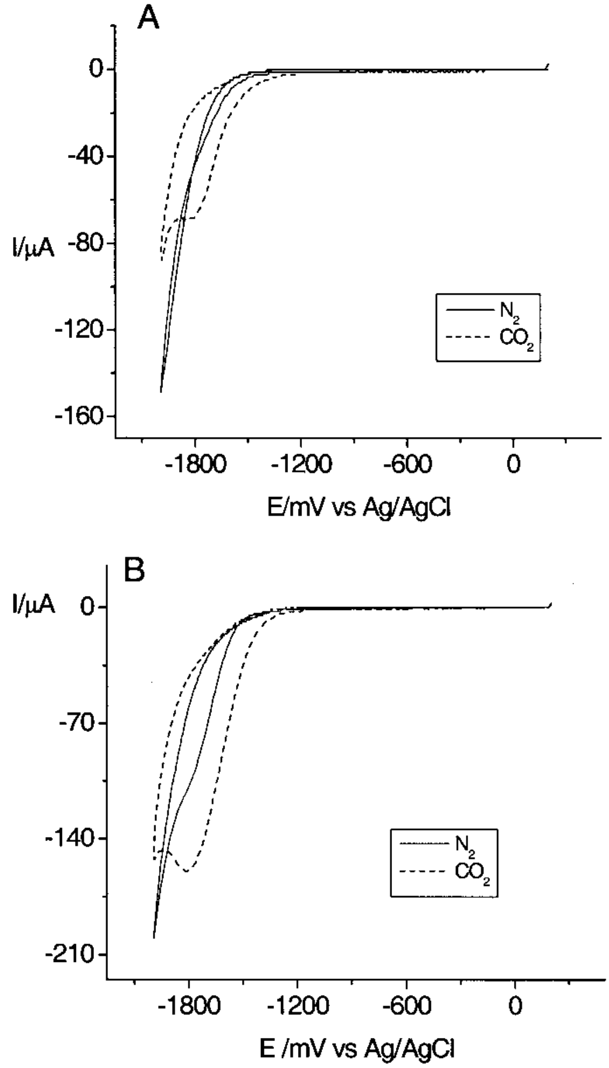


FIGURE 3 Voltammetric response of a glassy carbon (A) and 4-aminopyridine-electrode (B) under N_2 (continuous line) and CO_2 (dashed line). Scan rate: $0.05\,V\,s^{-1}$. Electrolyte: phosphate/biphosphate (pH 6.8 under N_2, pH 5.2 under CO_2) buffered aqueous solution.

ing active sites of the electrode. Consequently, the reduction of CO_2 observed corresponds to a blank (glassy) electrode with a lower quantity of active sites. Figure 5 compares the response of the supramolecular electrode under N_2 and CO_2. In this case, electrocatalysis of the reduction of CO_2 is obtained. Also, in this unique case, the electrode is stable and does not lose activity after many cycles under CO_2 or N_2. Finally, Fig. 6 compares all the systems toward the reduction of CO_2. The supramolecular electrode shows a catalytic response and a high current compared to the other systems. Both facts prove that a "different system" is formed. The higher current demonstrates that there are higher quantities of active sites compared to the other systems. It is known that in the majority of cases, when a drop of a complex is deposited on an

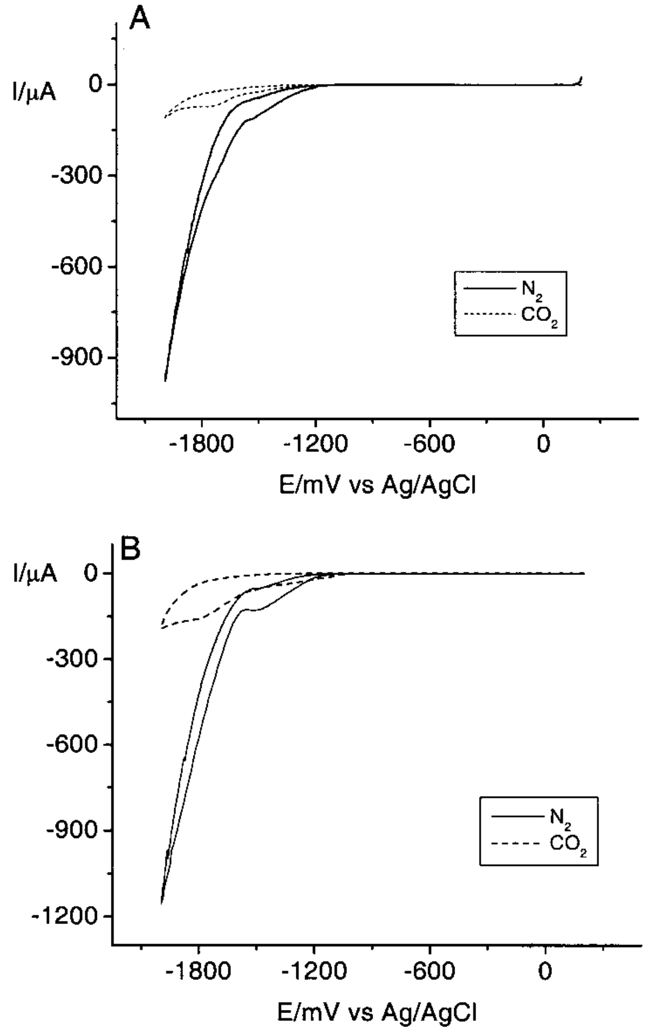


FIGURE 4 Voltammetric response of an electrode modified with a physically adsorbed layer of Co-TBP on the surface of the bare glassy carbon (A) or on the surface of the 4-aminopyridine–glassy carbon (B) under N_2 and CO_2. Scan rate: $0.05\,V\,s^{-1}$. Electrolyte: phosphate/biphosphate (pH 6.8 under N_2, pH 5.2 under CO_2) buffered aqueous solution.

electrode surface, multilayers are formed instead of a monolayer [11]. In our case, the high current shows that we have more layers than for cases of physically adsorbed porphyrins. On the other hand, these multilayers are ordered, shown by the stability and the shift in the potential toward the reduction of CO_2. Thus a truly supramolecular modified electrode is responsible for these observations. In conclusion, a supramolecular modified electrode can be obtained by the above method, and its behavior toward the reduction of CO_2 demonstrates that the system is catalytic and stable. With adsorbed layers of the same porphyrin it is not possible to catalyze the reduction of CO_2 because the system is degraded in the experimental conditions used here.

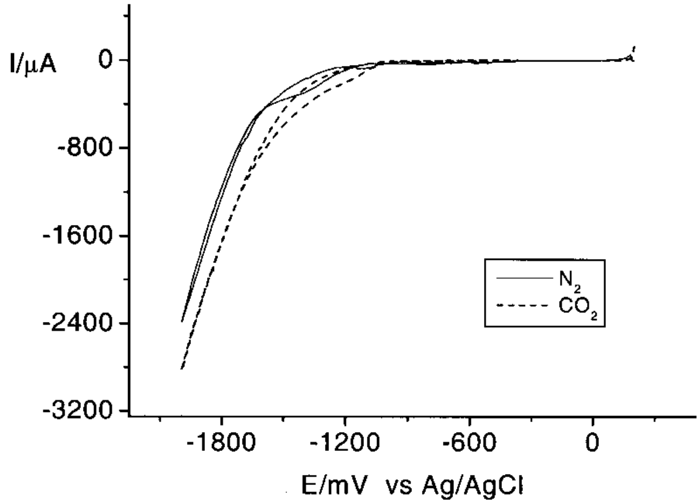


FIGURE 5 Voltammetric response of the supramolecular electrode under N_2 (continuous line) and CO_2 (dashed line). Scan rate: $0.05\,V\,s^{-1}$. Electrolyte: phosphate/biphosphate (pH 6.8 under N_2, pH 5.2 under CO_2) buffered aqueous solution.

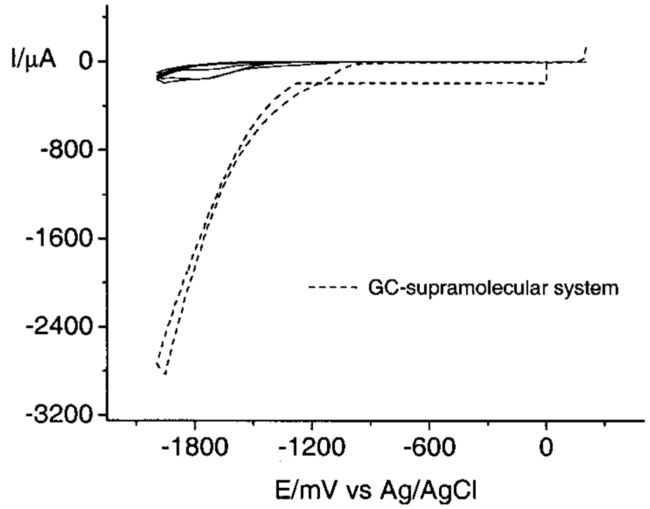


FIGURE 6 Voltammetric response of all the systems toward the reduction of CO_2. The dashed line shows the response of the supramolecular electrode. In the continuous line, the response of other systems (GC, GC–4-aminopyridine, GC-adsorbed layer and GC–4-aminopyridine–adsorbed layer). Scan rate: $0.05\,V\,s^{-1}$. Electrolyte: phosphate/biphosphate (pH 6.8 under N_2, pH 5.2 under CO_2) buffered aqueous solution.

Acknowledgments

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