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Electrocatalysis of neurotransmitter catecholamines by 2,4,6-triphenylpyrylium ion immobilized inside zeolite Y supercages

A. Doménech,*[a] M. T. Doménech-Carbo,[b] H. García[c] and María S. Galletero[c]

[a] *Departament of Analytical Chemistry, University of Valencia, Dr. Moliner, 50, 46100 Burjasot, Valencia, Spain. E-mail: tdomenec@crbc.upv.es*

[b] *Departament of Conservation of Cultural Heritage, Polytechnical University of Valencia, Camino de Vera s/n. 46022 Valencia, Spain*

[c] *Institute of Chemical Technology CSIC-UPV, Polytechnical University of Valencia, Camino de Vera s/n. 46022 Valencia, Spain*

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2,4,6-Triphenylpyrylium ions entrapped inside the supercages of Y zeolite exert a remarkable catalytic effect toward the electrochemical oxidation of dopamine and norepinephrine (neurotrasmitter catecholamines) in neutral aqueous media.

Encapsulation of organic species inside the rigid matrix of microporous zeolites has proved to be a general methodology to control the molecular properties of the incorporated guest.[1] Zeolites are a large family of crystalline aluminosilicates whose structure defines strictly uniform channels and cavities of molecular dimensions (micropores). It is in these internal voids where a guest can be accommodated provided that its molecular size is smaller than the void dimensions. In particular, the structure of zeolite Y is formed by an array of spherical cavities (1.4 nm diameter) that are tetrahedrally interconnected through four smaller apertures (0.74 nm diameter).

We have already reported that the bulky 2,4,6-triphenylpyrylium ion (TP^+, ≈ 1.3 nm) can be prepared inside the zeolite Y supercages through a 'ship-in-a-bottle' synthesis that relies on the diffusion of much smaller synthetic precursors.[2] After the encapsulation, TP^+ remains mechanically immobilized inside the zeolite Y supercages, but it still can interact with smaller molecules through the cavity windows.

Recently one of us has shown that while the BF_4^- salt of TP^+ in water undergoes a rapid hydrolytic ring opening, when TP^+ is encapsulated within the restricted space provided by the supercages of zeolite, the host framework protects it from the nucleophilic attack of water.[3] As a result, TP^+ within Y zeolite (TPY) is completely persistent in water. This opens the opportunity for new applications of TP^+ in aqueous media, as reported herein on the catalytic effect of TPY on the electrochemical oxidation of catecholamines in aqueous solution.

The electrochemistry of pyrylium ions in solution is well understood. TP^+ undergoes one-electron reduction in protic solvents.[4] Controlled potential electrolysis produces the corresponding dipyran which in turn can be reoxidized back to TP^+. In aprotic solvents, reduction of pyrylium ions leads to the corresponding bipyranylidene together with pyrane.[5] In this case, the transient reduction wave is controlled kinetically by the irreversible dimerization of the radicals formed after the initial electron transfer.[6] Bipyranylidene and pyrane are produced by the reversible reduction of the dimer.[7] We have found that upon encapsulation in the internal voids of zeolites, owing to the impossibility to form dimers, pyrylium ions display an apparently more simple electrochemistry consisting on the quasi-reversible reduction to TP. Compartmentalization of TP^+ inside the zeolite Y impedes its diffusion and eventually that of the corresponding TP pyranyl radicals, and therefore radical coupling is inhibited.

Preliminary experiments on the electrochemistry of TP^+ incorporated within zeolite Y confirmed the inhibition of dimerization processes. Paraloid B72† and Elvacite 2044,‡ were used to obtain polymer film electrodes containing TPY as modifiers. As can be seen in Fig. 1, polymer film electrodes (PFEs) modified by zeolite Y containing TP^+, TPY-MEs, exhibit a well defined reduction process. As can be seen in Fig. 2, cyclic voltammograms show a one-electron couple at an equilibrium potential of −0.28 V *vs.* SCE in acetonitrile. The peak potential separation is about 150 mV suggesting that the electrochemical process is kinetically reversible. The morphology of voltammograms is practically identical upon immersion of the modified electrode in neutral aqueous solutions, denoting that hydrolytic ring opening is inhibited by encapsulation. The voltammetric response is enhanced on increasing the contact time of the electrode into the solution and remains stable upon repetitive cycling of the potential scan. The absence of additional peaks in repetitive cyclic voltammetry denotes that no parallel chemical reactions occur. Identical results were obtained at working electrodes with self-supported finely ground zeolite pressed onto the surface of the bare electrode. Although the internal *versus* external nature of the electrochemical response involved in zeolite-modified electrodes remains controversial,[8,9] it appears that the observed electrochemistry is essentially attributable to the population of TP^+ located at the boundary region of zeolite grains.[10,11]

The reduction process involves the incorporation of charge-balancing positive ions from the supporting electrolyte to the zeolite boundary sites and can be represented by eqn. (1).

$$TP^+_{(zeolite)} + M^+_{(sol)} + e^- = TP^\bullet_{(zeolite)} + M^+_{(zeolite)} \quad (1)$$

Encapsulation of pyrylium ions inside zeolite Y and the resulting stability in aqueous solutions has enabled us to test this material as an electrocatalyst for the oxidation of the neuro-

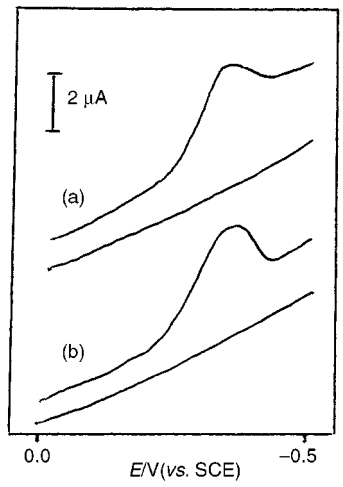


Fig. 1 Cathodic differential pulse voltammograms, including the base line, for TPY modified electrodes: (a) in MeCN (0.10 M NEt_4ClO_4) and (b) in water (0.15 M $NaClO_4$). v = 2 mV s^{-1} ΔU = 100 mV.

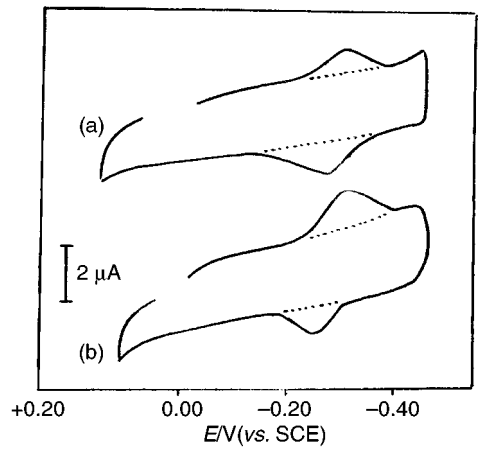


Fig. 2 Cyclic voltammograms, including the base line (dotted line), for TPY-MEs: (a) in MeCN (0.10 M NEt_4ClO_4) and (b) in water (0.15 M $NaClO_4$). v = 100 mV s^{-1}.

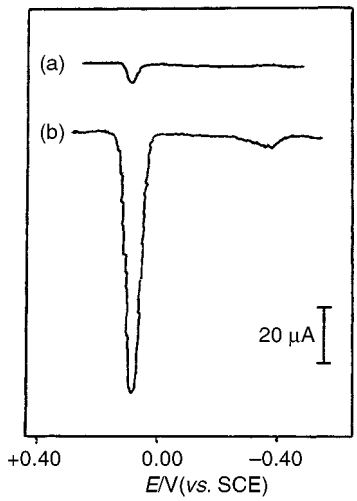
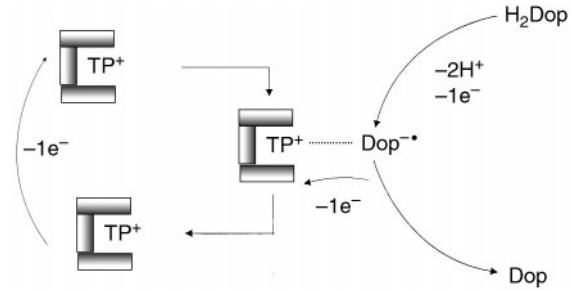


Fig. 3 Anodic DPVs for different electrodes immersed into a 1.0×10^{-4} M solution of dopamine in aqueous phosphate buffer, pH = 7.05: (a) glassy carbon electrode and (b) TPY-ME. v = 8 mV s^{-1}. ΔU = 100 mV.

transmitter catecholamines, dopamine and norepinephrine. These compounds play an essential role in neurochemistry. Since the loss of neurotransmitter-containing neurons may result in some serious diseases such as Parkinsonism,[12] the determination of such compounds in real biological systems is an obvious target in neurochemical studies.[13]

Dopamine and norepinephrine have a common dihydroxyphenethylamine moiety that is responsible for their observed electrochemistry. These species exhibit a well defined electrochemical oxidation at *ca.* +0.2 V *vs.* SCE in neutral aqueous media. The electrochemical oxidation process leads to the corresponding *o*-quinone which can be intracycled and again oxidized.[14] This electrode process has been previously used for analytical purposes by using unmodified[15] and modified electrodes.[16]

At zeolite-modified electrodes lacking encapsulated TP^+, Y-MEs, the oxidation peak of dopamine or norepinephrine is almost identical to that recorded at the basal glassy carbon electrode. In contrast, using TPY-MEs, the peak current is about 10–20 times enhanced with respect the peak obtained at the basal glassy carbon electrode. As an example, the catalytic effect of TPY on the electrochemical oxidation of dopamine is shown in Fig. 3. On scanning the potential in the anodic direction, an oxidation peak appears at −0.25 V, that corresponds to the oxidation of TP to TP^+ in the electrochemically accessible sites of the zeolite. A second prominent anodic peak is observed at *ca.* +0.20 V corresponding to the enhanced dopamine oxidation. Similar results were obtained for norepinephrine solutions. In both cases, the electrocatalytic effect was not observed at modified electrodes containing pristine Y zeolite lacking encapsulated pyrylium groups, indicating that the electrocatalytic effect must be attributed to the fraction of pyrylium ions located at the boundary sites of the zeolite particles. The electrocatalytic current increases on lowering the potential scan rate and increasing the contact time of the modified electrode with the solution prior to the electrochemical runs. All these data indicate that the net electrocatalytic effect depends on the net amount of diffusive transfer into the zeolite particles.



Scheme 1

The measured peak currents for dopamine and norepinephrine oxidations produced linear calibration graphs for 1×10^{-6} to 1×10^{-4} M concentrations of catecholamine. The sensitivity for dopamine oxidation using differential pulse voltammetry (12 A cm^{-2} M^{-1}) is similar to that for norepinephrine oxidation (10 A cm^{-2} M^{-1}), enabling the use of TPY-MEs as electrochemical sensors.

The oxidation process of dopamine and norepinephrine involves two consecutive one-electron transfer processes coupled with deprotonation reactions. The electrocatalytic effect is likely to be caused by the stabilization of the catecholamine anion radical intermediates resulting from the first electron transfer process upon adduct formation with surface-confined pyrylium, with a subsequent electron-transfer that yields the *o*-quinone and surface-confined TP, as depicted in Scheme 1.

The observation of this novel electrocatalytic effect using pyrylium ion incorporated stabilized into zeolites realizes the new opportunities that the stabilization of organic species by encapsulation inside the rigid framework of microporous materials can offer, such as for the development of new electrochemical sensors with light selectivity and increased sensitivity.

Notes and references

† Ethyl methacrylate (70%)–methyl acrylate (30%) co-polymer (P[EMA/MA]).

‡ *n*-butyl methacrylate homopolymer (PnBMA).

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