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Orientation dependent electrocatalysis using self-assembled molecular films

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Received (in Cambridge, UK) 6th March 2002, Accepted 17th April 2002
First published as an Advance Article on the web 13th May 2002

Surface orientation of self-assembled molecular films of 2,9,6,23-tetraamino cobalt phthalocyanine on gold and silver is shown to determine the nature and the products of the electrocatalytic reduction of oxygen.

Phthalocyanines have been shown to have very interesting properties coupled with excellent stability to heat, light and harsh chemical environments. Their optical and electronic properties have been exploited in various applications.[1] Most of the applications require the use of phthalocyanines in the form of oriented, well-packed and ordered thin films. Chemisorption of molecules on to metal substrates is one the methods of forming thin films that offer the flexibility of molecular ordering and orientation.[2] The study of self assembled molecular films of phthalocyanines include the work of Cook, Russell and co-workers[3] who reported on the preparation of phthalocyanines with one or two trichlorosilyl alkyl chains and subsequently formed self assembled monolayers (SAMs) on glass and silicon. The studies on the SAM formation of the thiol and disulfide derivatized phthalocyanines on gold surfaces suggest that the orientation of the phthalocyanine ring of the molecule depends on the length of the spacer between the ring and the gold surface. Li and co-workers[4] designed a strategy to orient two different phthalocyanine molecules on to gold substrates by having one or eight linker arms. Porter and co-workers[5] have reported on similar studies using porphyrins with a different number of linker arms. These studies were aimed at having adsorption of molecules on the same metal surface with a different number of linkers arms to manipulate the orientation.

The self-assembly technique may constrain a macromolecule to adopt a packing preference on a surface that it would not otherwise adopt. This capability will be very useful for orienting anisotropic molecules for electrocatalysis and device applications. A number of studies in the literature have dealt with films of phthalocyanines on conducting substrates like carbon, gold *etc*.[6] These films were formed either by dip coating or spin coating procedures and they result in random orientation of phthalocyanines on to the surfaces. This paper demonstrates the differences in the surface architecture of a phthalocyanine molecule playing a role in determining the products and the kinetics of electrocatalysis reactions.

2,9,16,23-Tetraamino Co(II) phthalocyanine [TACo(II)Pc] was prepared using a reported procedure.[7] Self-assembled molecular films were formed on gold and silver electrodes by immersing clean gold and silver substrates in a saturated solution of phthalocyanine in n-butanol for 48 h. Subsequently, the coated surfaces were washed well to remove the physisorbed molecules. Cyclic voltammetric studies on the TACo(II)Pc covered substrates have been carried out in deaerated buffer solutions, to understand their electrochemical behaviour. Two well-defined, redox peaks are observed with formal potentials at -0.24 V and -0.66 V, at a scan rate of 200 mV s^{-1} on an Ag surface covered with TACo(II)Pc. The redox peaks close to -0.66V are associated with Co(II)/Co(I) couple. The peak currents for both the anodic and cathodic processes vary linearly with the scan rate, as expected for a surface confined species. The film is very stable and the peak currents stay constant with repeated cycling in the potential range between 0.05 and -0.9 V. The relationship between the full width at half maximum of the peak at -0.66 V and the number of electrons involved in the process follows a one electron reversible reaction. Considering the peak as a one-electron redox couple, a surface concentration of $(0.35 \pm 0.05) \times 10^{-10}$ mol cm^{-2} has been calculated for the real surface area after correcting for the roughness factor. A similar calculation leads to a coverage of $(2.53 \pm 0.07) \times 10^{-10}$ mol cm^{-2} for gold electrodes after correcting for the roughness factor. A difference of approximately 8 times in the coverage leads us to believe that the orientation of the phthalocyanine molecules is different on the two surfaces.

FT-Raman spectroscopy with an excitation wavelength of 1064 nm using a Nd:YAG laser has the advantage of being a 'fluorescence-free' Raman technique. Fig. 1 shows the active frequency region of the TACo(II)Pc films on silver (A) and gold (B) respectively. Table 1 gives the various bands and the corresponding assignments. The spectra are dominated by strong in-plane stretching and breathing modes of the macrocycle and are assigned based on the reported literature.[4,8] The self-assembly process leads to an interaction of the metal with the nitrogen of the amino group and this would give rise to a metal–nitrogen stretch that is observed at 235 cm^{-1}. This is absent in the case of neat as well as solution spectra.

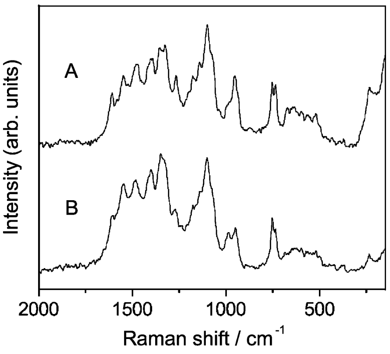


Fig. 1 FT-Raman spectra of TACo(II)Pc covered (A) Ag;(B) Au.

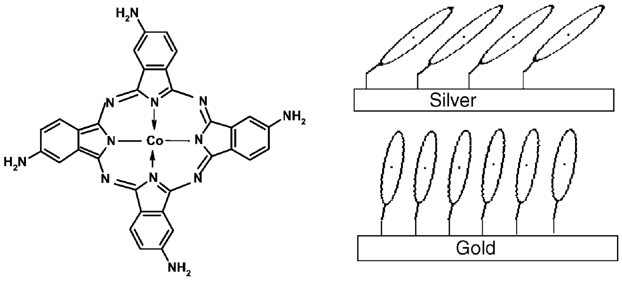
Table 1 FT-Raman spectral bands of TACo(II)Pc films on Ag and Au. Relative intensities are given in brackets

Silver	$I/I_{\gamma Ag-N}$	Gold	$I/I_{\gamma Au-N}$	Assignments
1608(26)		1605(46)		δNH_2
1553(44)	1.83	1549(75)	5.00	$\gamma C\alpha N\alpha$
1469(56)	2.36	1484(77)	5.13	Isoindole ring stretch
1396(67)		1401(86)		$\gamma C\alpha N\beta$, $\gamma C\beta C\beta$
1349(80)	3.33	1349(100)	6.66	$\gamma C\beta C\beta$, $\gamma C\alpha N\alpha$
1328(80)		1331(96)		Pyrrole stretch
952(39)		951(37)		Benzene breathing
754(34)	1.42	754(46)	3.06	In-plane macrocycle stretch
736(42)		736(36)		Pyrrole ring out-of- plane bending
236(24)		235(15)		γAg–N and γAu–N

γ Stretching; δ, Bending.

DOI: 10.1039/b202254k

The pattern of changes in peak intensities on the two metal surfaces shows that the same molecule adopts different orientations. According to surface selection rules of Raman scattering measurements, only the vibrations that have scattering tensor components perpendicular to the surface will be strongly enhanced. Hence, it is expected that the characteristic in-plane vibrational modes of the macrocycle will be enhanced when the phthalocyanine ring is oriented perpendicular to the surface as opposed to the orientation at an inclined angle or to an orientation having the phthalocyanine ring parallel to the surface. To arrive at this comparison, one requires a band that is out-of plane and common to both surfaces. The metal–nitrogen (of the amino group anchored on to the surface) stretching vibration that has a large component perpendicular to the surface can serve as an out-of plane reference. The ratios obtained from the peak heights using a linear baseline correction are given in Table 1. The ratio of the in-plane phthalocyanine stretch at 1550 cm^{-1} to the metal–nitrogen stretch is 1.8 for silver while it is 5 in the case of gold. The ratio observed in the case of 1350 cm^{-1} stretch is 3.3 for silver and 6.6 for gold while it is 1.4 for silver and 3.06 for gold for the 754 cm^{-1} band. This leads to the conclusion that the orientation of the molecule on the gold surface is close to being perpendicular while on silver it is at an angle lower than on the gold. It should, however, be pointed out that the phthalocyanine ring orientation on silver is not flat since there is some enhancement seen in the Raman signals and the ratios are smaller than on the gold surface. Based on the coverage and the Raman data, we propose a schematic model of the orientation of the phthalocyanine molecules on the two surfaces as given in Scheme 1.



Scheme 1

The implications of the two different orientations are revealed in the electrocatalysis of oxygen reduction. Fig. 2 shows the cyclic voltammograms of a bare and TACo(II)Pc covered Ag electrodes in 0.1 M phosphate buffer at pH 7. The bare electrode results in a single reduction peak for dissolved oxygen at −0.4 V. The self-assembled TACo(II)Pc film leads to a two-step reduction process, the first one corresponding to the reduction of oxygen to hydrogen peroxide and the second one corresponding to the reduction of hydrogen peroxide to products. The currents for the first step of O_2 reduction vary linearly with the square root of scan rate (not shown) confirming the process to be diffusion limited. The second peak is assigned to the reduction of peroxide formed in the first step based on the increase in currents when hydrogen peroxide is intentionally spiked in to the solution (Fig. 2B (iii)). The kinetic parameter, αn_a calculated based on the E_p^c – log (scan rate) plots are 0.17 for the bare surface while the values are 0.27 and 0.20 for the first and second reduction peaks respectively for the TACo(II)Pc covered surface. Repeated cycling of the modified electrodes does not result in any change in the voltammograms revealing that the stability of the phthalocyanine monolayer is very good.

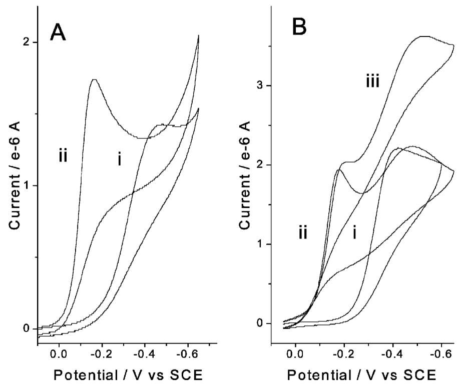


Fig. 2 Cyclic voltammograms showing O_2 reduction on (i) bare; (ii) TACo(II)Pc covered (A) Au and (B) Ag. Curve (iii) is with added H_2O_2 in the solution.

The cyclic voltammograms corresponding to the bare and tetraamino cobalt phthalocyanine covered gold electrode is also shown in Fig. 2. The bare surface shows a single irreversible peak. The TACo(II)Pc coated gold electrode also leads to an only one step reduction process unlike the two-step catalysis observed on the coated silver surface. The reaction does not seem to proceed beyond the formation of hydrogen peroxide to a considerable extent. Addition of hydrogen peroxide to the electrolyte does not result in any change in the voltammetric behaviour. The αn_a calculated for bare gold surface is 0.15 while the phthalocyanine covered surface leads to a value of 0.20.

Macrocycles such as porphyrins and phthalocyanines are known to be good electrocatalysts for oxygen reduction. Murray *et al*[9] have reported on the catalysis using a cofacial diporphyrin adsorbed on graphite and gold electrodes. According to the authors, the catalysis on an edge plane pyrolitic graphite is not well understood. As for the catalysis using tetraamino cobalt phthalocyanine, the active material reported is a polymerized film[6] physically adsorbed on a graphite electrode. The monomer was found to be very unstable and repeated cycling led to the removal of the monomer from the electrode surface. Moreover, the physisorbed films would generally give rise to random orientations of the molecules on the surface.

In the present study, the catalysis being different may result from the orientation differences leading to a difference in the accessibility of the analyte and the by-product towards the two metal surfaces. Secondly, the proposed mechanism of oxygen reduction using cobalt phthalocyanine macrocycle involves the formation of oxygen adducts which subsequently form other intermediates towards the formation of the products.[10] In the present study, the orientation difference on the two surfaces may lead to differences in the formation of adducts and intermediates that probably give rise to different products. This aspect is being investigated further.

Financial support from the DST and the CSIR, New Delhi, India are gratefully acknowledged.

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