

Structural insight on organosilica electrodes for waste-free alcohol oxidations

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Organic modification of sol–gel catalytic glassy electrodes made of a thin layer of organosilica doped with nitroxyl radical TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy) crucially enhances stability in the waste-free oxidation of alcohols to carbonyls in water. Structural comparison between analogous films made of organosilica and unmodified SiO₂ shows that the origin of the pronounced stable activity of the ORMOSIL film lies in high hydrophobic and also in the pronounced low degree of hydrophilicity.

KEY WORDS: sol–gel; anodic; oxidation; TEMPO; alcohols; green chemistry.

1. Introduction

Functionalized sol–gel glassy electrodes have a rich and varied electrochemistry due to their vast accessible inner porosity that allows to the oxidant and reducing reactant molecules to diffuse through the material and eventually to the surface of a conducting electrode [1]. These materials show large potential for organic synthesis. Indeed, despite being highly desirable, electroorganic syntheses traditionally have been limited by the pronounced chemical reactivity of the reactive intermediates generated at the surface of metal conductive surfaces where reactions take place [2]. On the other hand, organic reactions in (and on) water are extremely desirable as water is the most readily available and environmentally friendly solvent [3]. Stable di-tertiary-alkyl nitroxyl radicals such as TEMPO, in their turn, are increasingly finding use in industry as oxidation catalysts due to their high selectivity and pronounced versatility [4]. In these catalytic oxidations the active species is the cyclic nitrosonium ion generated *in situ* by an auxiliary oxidant. However, the same species can be generated also electrochemically by applying a relatively small electric potential (0.7 V versus Ag/AgCl) to a solution of nitroxyl radicals.

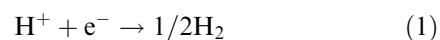
Returning to sol–gel electrodes, a major advantage of the sol–gel technique lies in the ability to prepare electrodes with the desired surface hydrophilicity-lipophilicity balance (HLB) in order to selectively control the conversion of organic substrates. Showing the potential

of this approach, we have recently introduced a molecular electrode (named TEMPO@DE) capable to afford high yields of carbonyl compounds with complete selectivity and noticeable stability by simply applying a small electric potential to a solution of the alcohol in water [5].

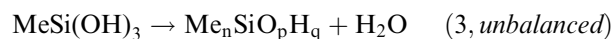
Hence, for example, whereas benzyl alcohol in water in the presence of TEMPO is rapidly oxidised to benzoic acid [6], the use of the hydrophobic electrode TEMPO@DE uniquely affords benzaldehyde by preventing diffusion of the hydrated aldehyde molecules (*gem*-diol) to the hydrophobic surface of the ORMOSIL electrode. In this paper we show how the nanostructure affects the catalytic performance of these molecular electrodes and suggest the origin of the superior performance of the organosilica electrode.

2. Experimental

The electrodes are made of a thin film of sol–gel silica doped with nitroxyl radicals deposited on the surface of an indium-tin-oxide (ITO) electrode by generation of a pH increase (Equation 1) at the electrode surface by reduction of protons near such surface [7]. Proton consumption in proximity of the electrode's surface catalyzes the sol–gel polycondensation of an organosilane such as methyltrimethoxysilane (MTMS, Equation 2) and thus ensures the electrodeposition of a thin layer of organosilica (Equation 3) at the surface of the substrate:



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By simply carrying out the electrodeposition of MTMS in the presence of aminopropyl-trimethoxysilane derivatised with the TEMPO moiety (via reductive amination with 4-oxo-TEMPO, scheme 1), a thin film of TEMPO-entrapped ORMOSIL is obtained which shows extraordinary performance in terms of both selective activity and stability.

The deposition was performed by using a CH Instruments (Austin, TX) potentiostat CHI630B Electrochemical Workstation with a standard three-electrode cell. The volume of the reaction vessel was 10 mL and an Ag/AgCl electrode in 3 M KCl was used as reference electrode. The counter electrode was a platinum-wire ($d = 0.5$ mm) whereas the working electrodes were indium-tin-oxide (ITO) plates obtained from Delta Technologies (Stillwater, MN) with a coated surface area of 0.36 cm^2 . The ITO-coated glasses were washed prior to film deposition with water, 80% (v/v) ethanol and water after which were dried at room temperature for 2 h. All chemicals were purchased from Aldrich and used without further purification. Ultrapure water (Milli-Q Millipore System) was used in all the experiments. The organosilane precursor solution (solution A) was obtained adding 5 mL of 3-aminopropyl-trimethoxysilane to a solution of 1.32 g of 4-oxo-TEMPO (4-oxo-2,2,6,6-tetramethyl-1-piperidinyloxy) and 221.2 mg of NaBH_3CN (95%) in MeOH (18 mL) in a reaction balloon kept closed under a nitrogen atmosphere. The resulting mixture was stirred for 48 h, after which the excess of sodium cyanoborohydride was quenched with 7 M HCl (50 μL).

The solution for the electrodeposition of sol-gel film consisted of 0.612 mL of MeTMS (methyltrimethoxysilane), 0.612 mL of solution A, 5 mL of ethanol and 5 mL of a solution buffered at pH 4 (Fisherbrand) and a 0.4 M in KNO_3 . Upon stirring this solution for 1 h at room temperature to promote hydrolysis in the presence of the ITO electrode, a constant negative potential of -1.1 V versus Ag/AgCl was applied to the solution for 15 min under fast stirring. The resulting coated electrode was washed with water and absolute ethanol and thus dried at r.t. for 6 h. The oxidation of the alcohol (0.5 mmol) was carried out in 10 mL of buffered water (0.2 M in NaHCO_3) although for alcohols with low water solubility (geraniol, for instance) a $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ solution 30:70 (v/v) was employed. Initial substrate concentration was 0.05 M. For all the substrates the selected potential was 1.4 V and the electrolysis was carried out under fast stirring (900 rpm). Substrate and product concentrations were assessed by a Shimadzu GC-17A gas chromatograph equipped with a Supelco-wax 10 capillary column (30 m, 0.25 mm ID) by the

internal standard method (with previously calculated response factors) using 10 μL decane as internal standard [3]. SEM images were obtained with a JEOL JSM-6400 scanning microscope. The elemental analysis of the surface was carried out with a JEOL JXA-8600 electron probe microanalyzer equipped with a NORAN Vantage automation system. DRIFT [8] and EPR [9] analyses of organosilica xerogel powders were carried out as described elsewhere.

3. Results and discussion

Figures 1 and 2 thus show the SEM pictures of the electrode surfaces obtained from copolymerization of precursors in scheme 1 with MTMS and TMOS (tetramethylorthosilicate), respectively. Both samples are relatively homogeneous and are made of small particles of the size of 10–30 nm. The particles are not identical in shape but are quite densely packed. In the silica film, however, holes are clearly distributed all over the surface. The size of these cavities is ca. 10 nm and they are likely to be macropores formed upon irregular condensation of the open, large silica particles that are typical constituents of SiO_2 xerogels obtained by alkaline sol-gel polycondensation of silicon alkoxides [10].

Surface elemental analysis (Table 1) shows that the samples are mainly composed of silicon, oxygen, and carbon. The samples are not very thick (in the order of 30 nm) as the indium signal from the ITO substrate is clearly visible in both spectra. Nitrogen from TEMPO molecules is evident in both samples, whereas sodium and fluoride are probably from the electrolyte. As typically observed with sol-gel derived silica glasses [11], for both samples the experimental carbon:silicon atom ratio is higher than the theoretical values calculated from the molar ratio of MTMS and TMOS, due to residual solvent methanol entrapped at the surface of the sol-gel cages. However, the SiO_2 xerogel shows much higher

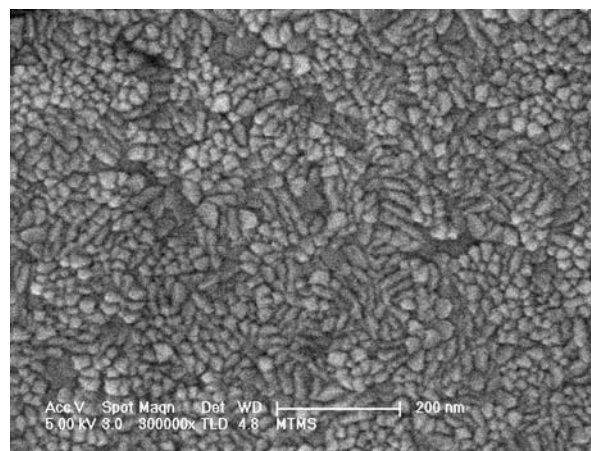


Figure 1. SEM pictures of MTMS-based organosilica film taken at two different angles.

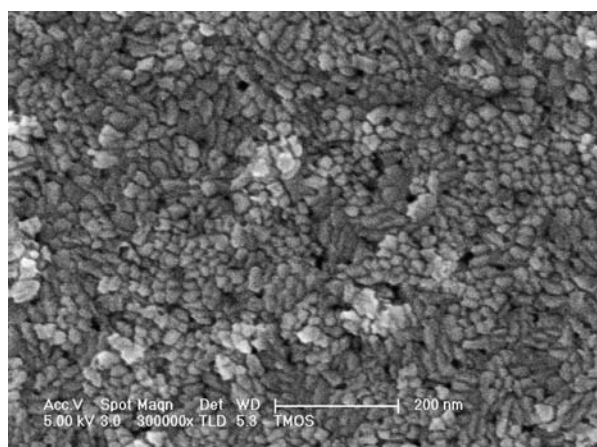
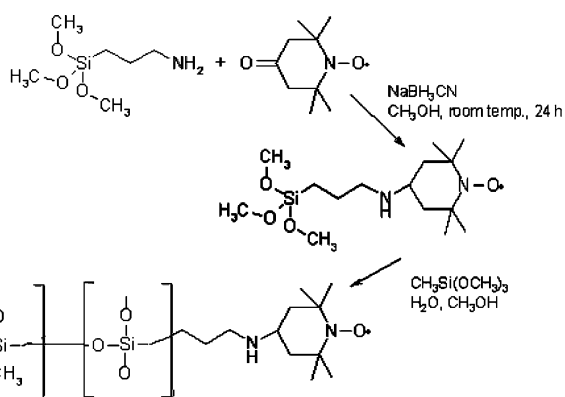


Figure 2. SEM picture of TMOS-based silica film.



Scheme 1. Synthesis of the silane precursor functionalized with TEMPO moiety.

additional carbon atom ratio compared to the ORMOSIL, due to the high polarity of the silica cage within which SiO^- groups tightly bind to the methanol hydroxyls.

Contrary to the TMOS-derived electrode which loses its activity after two runs only, the MTMS-based film shows optimal stability in catalytic activity with a practically constant activity in numerous consecutive oxidations after an 40% reduction in the catalytic activity following the first oxidative run (Figure 3) [3]. Furthermore, no appreciable variation of the electronic spectrum of the organosilica film was observed after reaction clearly pointing to its physico-chemical stability.

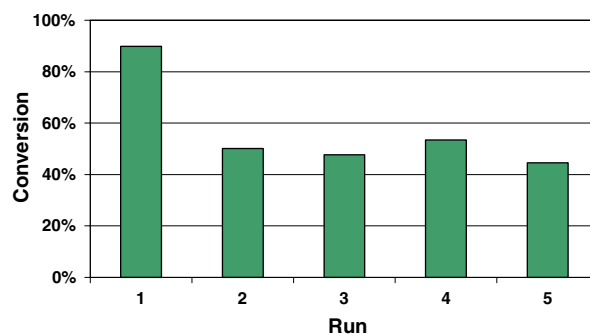
These findings are in agreement with those observed with analogous TEMPO-entrapped organosilica xerogels used in chemical oxidation [8] and show the predominant influence of the material's structure on its chemical reactivity, independently of whether the nitronium ions are generated electrochemically or by direct addition of an auxiliary oxidant.

Recent DRIFT [8] and EPR [9] spectral analyses of analogous methylsilica-entrapped TEMPO show indeed

Table 1

Atomic ratios and elemental analysis of the investigated pure silica and methylsilica electrodes

Precursor of the electrode	Theoretical atom ratio Si:O:C	Experimental atom ratio Si:O:C	Additional carbon atom ratio
TMOS	1:2:0	1: 6.11:1.5	1.5
MTMS	1:1.5:1	1:8.03:1.34	0.34
TMOS-derived electrode			
Element	At %		
C	9.21		
N	11.04		
O	37.75		
F	1.6		
Na	0.85		
Si	6.18		
In	33.37		
MTMS-derived electrode			
Element	At %		
C	6.62		
N	9.79		
O	39.69		
F	1.59		
Na	1.30		
Si	4.94		
In	36.07		

Figure 3. Conversion of 1-Phenylethanol to acetophenone mediated by the organosilica electrode TEMPO@DE after 15 h ($V = 1.4$ V).

that the surface of similar markedly alkylated ORMOSIL not only is highly hydrophobic but also shows a pronounced low degree of hydrophilicity due to depletion of silanol groups at the organosilica matrix surface. Moreover, the organosilica structure is made of larger, less tensioned six-member rings more able to accommodate the unreactive methyl groups, with the methyl groups concentrating at the cage's surface [12] largely diminishing the number of silanol groups (Si-OH) and, as a consequence, the intra-cages hydrogen bonds which limit the freedom of the dopant TEMPO molecule [13]. Organic modification of the cages, finally, imparts chemical stability to the entrapped nitroxyl catalyst, affording an electrode that can be recycled at length in alkaline environment. This is similar to what observed with analogous organosilica xerogels are used in alcohol

oxidations with bleach [10] and is due to the absence of silanol groups typical of SiO₂ xerogels that in alkaline solution are attacked by hydroxide ions leading the partial dissolution of the silica with leaching of the entrapped catalyst. Sol–gel encapsulation of the catalyst in the inner porosity of the organosilica film chemically protects the radicals from degradation which is known to be due to intermolecular quenching of the TEMPO moieties left unprotected at the material's external surface [14].

4. Conclusion

The structural features of TEMPO@DE briefly elucidated in this report explain the origin of the superior performance of organosilica-based electrodes doped with nitroxyl radicals in the electrochemical oxidation of alcohols in water affording carbonyl compounds of unprecedented purity [15]. As such it is a nice example of how materials science and organic chemistry are actually merged into a unique domain in which chemists adapt functional materials to their synthetic ends. The origins of the catalytic stability here described will be of relevance in guiding future practical applications of sol–gel organosilica electrodes to organic synthesis.

Acknowledgments

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References

- [1] A. Walcarius, D. Mandler, J.A. Cox, M. Collinson and O. Lev, *J. Mater. Chem.* 15 (2005) 3663.
- [2] H. Lund, *J. Electrochem. Soc.* 149(4) (2002) 21.
- [3] S. Narayan, J. Muldoon, M.G. Finn, V.V. Fokin, H.C. Kolb and K.B. Sharpless, *Angew. Chem. Int. Ed.* 44 (2005) 3275.
- [4] (a) A.E.J. de Nooy, A.C. Besemer and H. van Bekkum, *Synthesis* (1996) 1153. TEMPO-mediated industrial oxidations are carried out by DSM manufacturer using polyoxometalate/O₂ as primary oxidant, as described in: (b) R. Ben-Daniel, P. Alsters and R. Neumann, *J. Org. Chem.* 66 (2001) 8650.
- [5] G. Palmisano, R. Ciriminna and M. Pagliaro, *Adv. Synth. Catal.* 348 (2006) 2033.
- [6] D. Liaigre, T. Breton and E.M. Belgsir, *Electrochem. Commun.* 7 (2005) 312.
- [7] R. Shacham, D. Avnir and D. Mandler, *Adv. Mater.* 11 (1999) 384.
- [8] A. Fidalgo, R. Ciriminna, L.M. Ilharco and M. Pagliaro, *Chem. Mater.* 17 (2005) 6686.
- [9] R. Ciriminna, C. Bolm, T. Fey and M. Pagliaro, *Adv. Synth. Catal.* 344 (2002) 159.
- [10] C.J. Brinker and G.W. Scherer, *Sol–Gel Science-The Physics and Chemistry of Sol–Gel Processing* (Academic Press, San Diego, 1989).
- [11] J.D. Mackenzie and E.P. Bescher, *J. Sol–Gel Sci. Technol.* 13 (1998) 371.
- [12] B.M. De Witte, D. Commers and J.B. Uytterhoeven, *J. Non Cryst. Solids* 202 (1996) 35.
- [13] This is clearly shown by comparison of the EPR signals of TEMPO chemically entrapped in methylsilica and silica matrices, with the former spectrum resembling that of TEMPO in solution and the latter pointing to a spin molecular label severely constrained in the hydrated cages of the aminopropyl-silica matrix: A. Shames, O. Lev, B. Iosefzon-Kuyavskaya, *J. Non Cryst. Solids* 175 (1994) 14.
- [14] T. Fey, H. Fischer, S. Bachmann, K. Albert and C. Bolm, *J. Org. Chem.* 66 (2001) 8254.
- [15] An extremely desirable requirement for the fragrance and pharmaceutical industries where these chemicals are employed in large amounts.