

New Stable Catalytic Electrodes Functionalized with TEMPO for the Waste-Free Oxidation of Alcohol

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Supporting Information

ABSTRACT: We report the first catalytically active and stable sol–gel electrode functionalized with the TEMPO moiety for the highly selective oxidation of alcohols with an electric current only. The method shows broad applicability to different substrates, opening the route to the widespread adoption of this eminently clean technology by the fine chemical and pharmaceutical industries.

KEYWORDS: alcohol oxidation, electrocatalytic activity, EASA, TEMPO, hydrophobicity, thin films

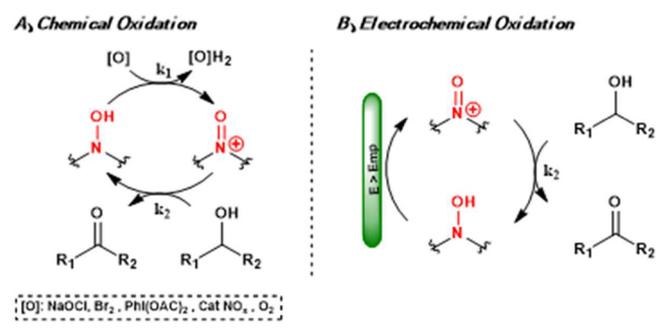
INTRODUCTION

Because aldehydes, ketones, and carboxylic acids play a fundamental role in the chemical industry as well as in several other industrial fields, the catalytic oxidation of alcohols to carbonyl compounds or carboxylic acids using environmentally benign oxidants, catalysts, and reaction media continues to attract a great deal of research.¹ Gone are the days in which industry used highly toxic chromium(VI) reactants; they and other toxic stoichiometric oxidants have mostly been replaced with catalytic amounts of 2,2,6,6-tetramethyl-1-piperidine *N*-oxyl (TEMPO) and its nitroxyl radical derivatives thanks to their high selectivity and pronounced versatility.² In general, in TEMPO-like mediated oxidations, diverse primary oxidants are used to promote catalytic turnover, the most common of which include bleach (NaOCl), hypervalent iodine reagents, and O₂ in combination with NO_x co-catalysts (Scheme 1A).³

Remarkable recent advances even include the mechanically induced oxidation of a broad set of alcohols⁴ via ball-milling the substrates under air in the presence of Stahl's catalyst.⁵ However, there are some limitations associated with these protocols, such as the use of toxic NO_x sources and/or halogen-based co-oxidants and the employment of costly and barely recoverable TEMPO in homogeneous form. Nonetheless, several elegant and successful immobilization strategies have been developed, providing the possibility of reusing the radicals to a great extent,⁶ yet the environmental concerns associated with the NO_x materials used in these metal-free systems are still an important issue that remains to be addressed.⁷

A promising approach avoiding the use of toxic electron carriers or co-oxidant was first proposed by Semmelhack and co-workers, who in 1983 generated the catalytically active cyclic

Scheme 1. (A) Chemical and (B) Electrochemical Alcohol Oxidation Mediated by Stable Organic Nitroxyl Radicals



nitrosonium ion by applying a relatively small electric potential (0.7 V vs Ag/AgCl) to nitroxyl radicals dissolved in solution (Scheme 1B).⁸ The method remained relatively unexplored until recently,⁹ when it was used for the electrocatalytic synthesis of some carbonyls on preparative scale,¹⁰ as well as for the solar-driven oxidation of 5-hydroxymethylfurfural into 2,5-furandicarboxylic acid at the anode of a photoelectrochemical cell.¹¹

In this research context, then, the last issue to be addressed to make the oxidation entirely clean and waste-free is to immobilize the TEMPO motif onto a solid electrode surface and use the modified electrode for the electro-oxidation of alcohols.¹² Among the various electrode modifiers, periodic mesoporous organosilicas (PMOs) offer uniquely attractive properties (i.e., ion exchange capacity, size and/or charge selectivity, hosting capabilities, catalytic or redox activity, and selective recognition or permselective properties) that are widely exploited, most notably for electroanalytical applications.¹³ Indeed, a most promising progress was reported in 2015, when a highly ordered TEMPO-functionalized mesoporous hybrid silica electrode (TGSE) film with perpendicular mesochannels was found to be remarkably active and selective in the oxidation of primary benzylic, allylic, and aliphatic alcohols in aqueous bicarbonate solution at room temperature without the need of any co-catalyst.¹⁴

Interestingly, the modified electrode could be conveniently employed also on preparative scale, and the catalytic process,

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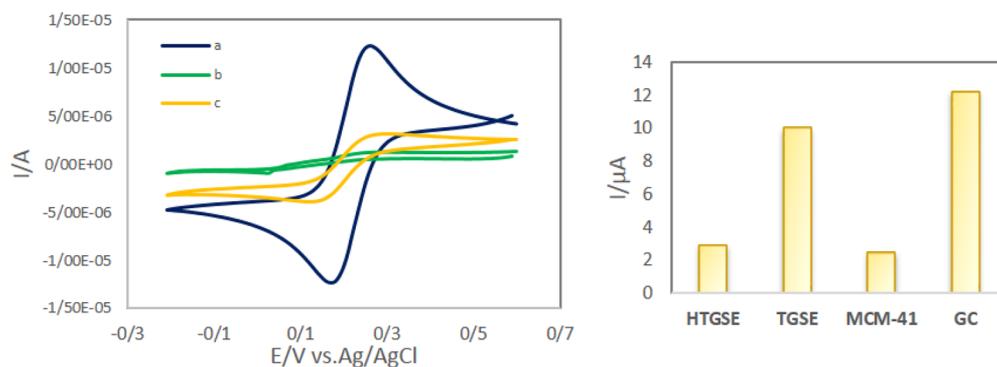


Figure 1. Left: Cyclic voltammograms of 1.0 mM $\text{Fe}(\text{CN})_6^{3-}$ on (a) bare GC electrode, and of HTGSE-modified electrode (b) before and (c) after CTAB extraction. Supporting electrolyte, 0.15 M phosphate buffer (pH = 7); scan rate, 20 mV s^{-1} . Right: Currents of 1.0 mM $\text{Fe}(\text{CN})_6^{3-}$ on HTGSE, TGSE, MCM-41, and bare electrode (GC).

with a TON of up to 3070 h^{-1} , became the fastest ever reported for TEMPO-mediated alcohol oxidations under chemical, electrochemical, or aerobic conditions. However, in the alkaline solution buffered at pH 9, in which the reaction is performed, the TGSE electrode rapidly degrades due to the known chemical instability of purely inorganic silica comprising the MCM-41 scaffold.

In addition to good selective activity and broad applicability to different substrates, the electrode's stability is perhaps the most important factor that will drive the adoption of this eminently clean technology by the fine chemical and pharmaceutical industry.

Now, we report the development of the first such catalytically active and stable electrodes.

RESULTS AND DISCUSSION

Previous studies on the activity and stability of amorphous organically modified silica (ORMOSIL) and SiO_2 electrodes functionalized with TEMPO employed at pH 9.3, clearly showed that the latter electrode lost its activity completely after only two runs in the electro-oxidation of benzyl alcohol (BA), whereas the ORMOSIL electrode retained its modest activity.¹⁵ Hence, a first attempt to stabilize the periodic mesoporous silica-based electrodes was based on extending the electro-assisted self-assembly (EASA)¹⁶ method to the generation of oriented mesoporous thin films bearing both organic groups and TEMPO groups covalently attached to the mesopore channels.

Such organic groups were introduced into the film by direct co-condensation of alkyltriethoxysilane (A-TES), tetraethyl-orthosilicate (TEOS), and the precursor of organosilane-bearing TEMPO group, whose loading was varied to achieve the maximal possible functionalization level without losing the oriented hexagonal mesostructure. Considering that sol-gel co-condensation in electrochemical interfacial surfactant templating is only possible up to a certain level of organo functional group loading for hybrid ordered films prepared by EASA, the ordered mesostructure and pore orientation were maintained for molar ratios of organosilane to TEOS up to 60% for methyl¹⁷ and 10% for propylamine groups.¹⁸

A preliminary study was thus necessary to optimize the different experimental protocols. We focused initially on the preparation of mesoporous films onto glassy carbon (GC) electrode surfaces accordingly with organosilane (MTES + TPTES)–TEOS molar ratio <25% in the sol precursor solution. The accessibility of the resulting electrode (HCSTE) was then examined by voltammetric study of a dissolved redox probe.

Figure 1 shows the voltammetric responses of $\text{Fe}(\text{CN})_6^{3-}$ on bare GC electrode as well as on the modified electrode before and after extraction of the templating surfactant. A significant current decrease is observed for the HCSTE electrode organically modified with both methyl and TEMPO moieties in comparison to both previously reported TGSE electrodes.

Now, the current is rather similar to that observed for the GC electrode coated with MCM-41 silica, which provides indirect evidence of a porous, accessible structure also for the HCSTE film. The lower voltammetric current for the HCSTE compared with the TGSE is likely due to the absence of positively charged amine groups in the channels. Also, we postulate that the presence of methyl groups inside the HCSTE channels is responsible for the extraordinary decline in the diffusion of ionic $\text{Fe}(\text{CN})_6^{3-}$ species.

To prove our assumption as well as to investigate the existence of TEMPO groups in the channels of the HCSTE-modified electrode, the electrochemical response of TEMPO groups using cyclic voltammetry (CV) was investigated (Figure 2). In the first two cycles (a and b in Figure 2) only

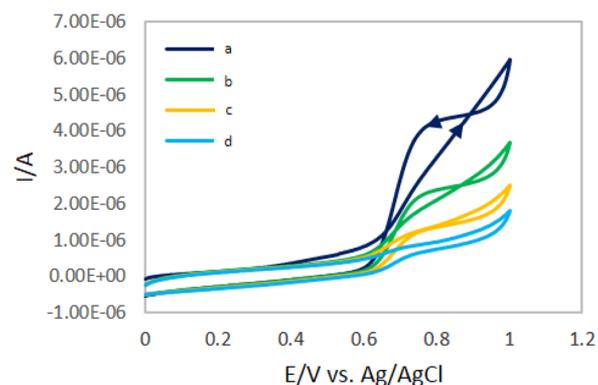


Figure 2. Cyclic voltammograms of HTGSE electrode after CTAB extraction (a, cycle 1; b, cycle 2; c, cycle 3; and d, cycle 4). Supporting electrolyte, 0.15 M phosphate buffer (pH = 7); scan rate, 10 mV s^{-1} .

cathodic peaks were observed at 0.65 V vs SCE, whereas in the subsequent cycles (cycles c, d, etc.) both anodic and cathodic peaks were observed. This observation is in contrast to the results of CV studies of the TGSE electrode, showing both anodic and cathodic peaks from the first cycle on.

Moreover, whereas the TGSE electrode shows a remarkable drop in the height of anodic current already in the second cycle (b in Figure 3), the HCSTE electrode displays only a slight

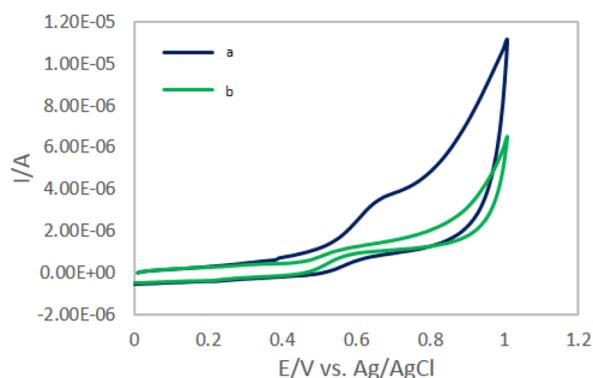


Figure 3. Cyclic voltammograms of TGSE electrode after CTAB extraction (a, cycle 1; and b, cycle 2). Supporting electrolyte, 0.15 M phosphate buffer (pH = 7); scan rate, 10 mV s^{-1} .

decrease in the second run (Figure 2), which points to remarkable higher stability of the latter electrode.

The reduction in the anodic current, indeed, can be safely attributed to more pronounced leaching (or quenching) of the TEMPO groups at the TGSE electrode's surface due to the low stability of its silica backbone in alkaline reaction medium. On the other hand, the presence of methyl groups inside the channels of HCSTE results in higher stability of this electrode in the same basic aqueous medium, leading to a lower drop in electrode currents in comparison to those observed with the hydrophilic TGSE electrode.

To investigate the electrocatalytic activity of the HCSTE electrode, we attempted the electrochemical oxidation of BA dissolved in buffered aqueous solution.

The cyclic voltammograms of bare GC and HCSTE electrodes immersed in a 9.0 mM solution of BA show a high anodic current peak at 0.7 V for the HCSTE electrode (Figure 4a),

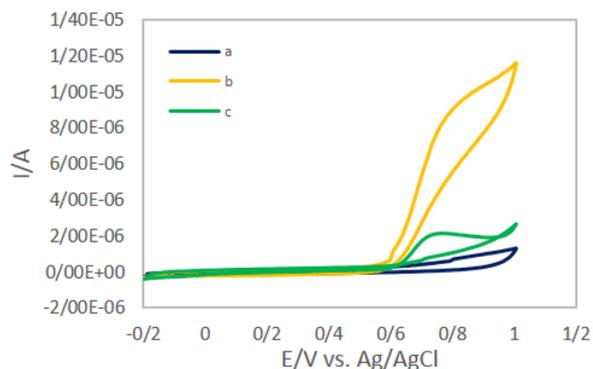


Figure 4. Cyclic voltammograms of bare GC electrode in the presence of BA (a), and of HCSTE electrode in the presence of 9.0 mM BA (b) and in the absence of BA (c). Supporting electrolyte, 0.15 M phosphate buffer (pH = 7); scan rate, 20 mV s^{-1} .

while the corresponding cathodic peak disappeared (Figure 4b). Furthermore, a low anodic current peak (Figure 4c) at the same point appeared in the voltammogram of the HCSTE electrode in the absence of BA.

These observations clearly demonstrate the catalytic activity of HCSTE electrode electro-oxidation as BA is oxidized inside the accessible ordered mesoporosity of the organically modified HCSTE electrode wherein the TEMPO moieties are located.

Consecutive recycling of potential in the presence of BA at the surface of the same HCSTE electrode shows (Figure 5)

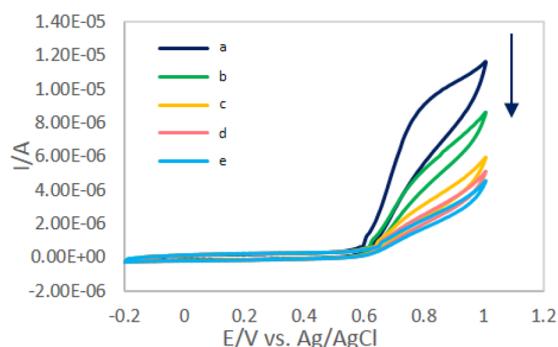


Figure 5. Multicyclic voltammograms of HCSTE in the presence of 9.0 mM of BA (a, cycle 1; b, cycle 2; c, cycle 3; d, cycle 4; and e, cycle 5). Supporting electrolyte, 0.15 M phosphate buffer (pH = 7); scan rate, 20 mV s^{-1} .

that the height of anodic current peaks decreases and shifts to the higher voltages, pointing to progressive inhibition of the electrocatalytic oxidative process.

These preliminary results in the study of an electroactive HCSTE electrode encouraged us to investigate the potential of this electrode in the electro-oxidation of BA and its stability and durability in aqueous media on a larger scale. We therefore coated larger graphite plate electrodes (260 cm^2 geometric area) with the active ORMOSIL layer via EASA electro-deposition of organosilica ($X\% \text{MeSi(OR)}_3 + 5\% \text{TEMPO-propyltrialkoxysilane}$) in the presence of CTAB. After surfactant extraction, the graphite electrodes functionalized with mesoporous organosilica were named $\text{TM-}x\text{@MCM-41}$ ($T = \text{TEMPO}$; $M = \text{methyl}$; and $x = \text{percentage of methyl-modified silane in sol-gel precursor solution}$).

A number of graphite electrodes with and without TEMPO moieties were deposited using various sol-gel precursor solutions, including $\text{TM-}x\text{@MCM-41}$ containing 15% methyl precursor and 5% TEMPO precursor (TM-15@MCM-41), and another incorporating 15% methyl and no TEMPO moieties (M-15@MCM-41).

The nitrogen content of the scratched films of these electrodes was determined by elemental (CHN) analysis. For the purpose of comparison with a previously reported electrode (TEMPO@MCM-41),¹⁴ an electrode containing 5% TEMPO and bearing no methyl functionality was also prepared according to the previously reported method for TGSE preparation, with only slight modifications.

Table 1 displays that both the nitrogen content and the TEMPO loading in the TEMPO@MCM-41 and TM-15@MCM-41 electrodes are in good agreement with each other.

Table 1. Elemental (CHN) Analyses of the Nitrogen Content in Blank (M-15@MCM-41) and TEMPO-Functionalized Thin Films (TEMPO@MCM-41 and TM-15@MCM-41 Electrode Surfaces) and Calculated for TEMPO

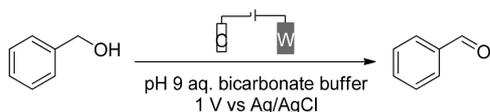
| entry | modified electrode | N (in 100 mg) | TEMPO (mmol) |
|-------|--------------------------------------|---------------|--------------|
| 1 | M-15@MCM-41 | 0.667 | – |
| 2 | TEMPO@MCM-41 (prior report) | 1.970 | 0.50 |
| 3 | TM-15@MCM-41 | 2.225 | 0.54 |

The electro-oxidation of 1 mmol of BA, performed in 0.15 M bicarbonate solution using TEMPO@MCM-41 and TM-15@MCM-41 electrodes at 1 V vs SCE controlled potential, showed lower activity for the organically modified

Table 2. Screening of Electro-oxidation of BA Using TEMPO@MCM-41 and TM-15@MCM-41 Electrodes^a

| entry | electrode | T (h) | conv (%) |
|-------|--------------------------|-------|----------|
| 1 | TEMPO@MCM-41 | 2 | 100 |
| 2 | TEMPO@MCM-41, second run | 4 | 74 |
| 3 | TM-15@MCM-41 | 4 | 64 |

^aReaction conditions: benzyl alcohol (1.0 mmol), water (100 mL), NaHCO₃ (10 mmol, 0.84 g), Na₂CO₃ (1 mmol, 0.106 g), *E* = 1.0 V vs Ag/AgCl unless stated otherwise. The product yields were determined by gas chromatography analysis after the extraction of all aqueous-phase contents using an internal standard.

Table 3. Screening of TM-*x*@MCM-41 Electrodes in the Electro-oxidation of BA^a

| entry | sol solution contents for thin film on W | conv (%) |
|----------------|--|----------|
| 1 | TEMPO@MCM-41 | 74 |
| 2 | 15% Me-TES + 5% TEMPO-TES + 80% TEOS | 64 |
| 3 | 15% Me-TES + 7.3% TEMPO-TES + 78% TEOS | 69 |
| 4 | 15% Me-TES + 10% TEMPO-TES + 75% TEOS | 54 |
| 5 ^b | 15% Me-TES + 7.3% TEMPO-TES + 78% TEOS | 73 |
| 6 ^b | 15% Me-TES + 7.3% TEMPO-TMS + 78% TEOS | 80 |
| 7 ^b | 15% Me-TMS + 7.3% TEMPO-TMS + 78% TEOS | 78 |

^aReaction conditions: benzyl alcohol (1.0 mmol), water (100 mL), NaHCO₃ (10 mmol, 0.84 g), Na₂CO₃ (1 mmol, 0.106 g), *E* = 1.0 V vs Ag/AgCl unless stated otherwise. The product yields were determined by gas chromatography analysis after the extraction of all aqueous-phase contents using an internal standard. ^bDeposited in the presence of S-membrane.

TM-15@MCM-41 electrode in comparison with the hydrophilic TEMPO@MCM-41 electrode (Table 2).

Considering the comparable loadings of TEMPO in both electrodes (TM-15@MCM-41 and TEMPO@MCM-41 supported on graphite plates), this outcome seems to point to inhomogeneous formation of thin mesoporous films on the graphite electrodes under larger scale preparation conditions. Indeed, when we attempted to prepare various types of TM-*x*@MCM-41 using different proportions of MeSi(OMe)₃, TEOS, and TEMPO precursor under the same EASA condition (Table 3, entries 2–4 vs entry 1), we found that changing the Me/TEMPO ratio as well as increasing the TEMPO loading had no significant effect in improving the catalytic performance of the electrode.

Such inhomogeneous formation of the mesoporous thin film on the graphite electrodes may arise from the different rate of hydrolysis and co-condensation of Si precursors, resulting in the burying of TEMPO functionalities in nonaccessible (nonporous) parts of the organosilica layer. Indeed, when in order to balance the rate of hydrolysis/condensation of Si precursors we managed to prepare the TM-*x*@MCM-41 electrodes by employing TEMPO-TMS instead of TEMPO-TES (and using a new cell-divided technique having home-designed S-membrane), we obtained slight improvements in the electrocatalytic activity, though still far from satisfactory (entries 5–7 in Table 3).

To overcome this problem, we decided to investigate the grafting method for functionalization of thin film with the TEMPO moiety, fully retaining the oriented hexagonal mesostructure. In this way, a thin layer of periodic mesoporous

organosilica bearing alkyl groups at the surface of well oriented channels was constructed on the electrode surface by direct co-condensation using the EASA technique. The TEMPO functionality was subsequently attached to the surface of the organically modified periodic mesoporous film by direct grafting of TEMPO-TMS (Scheme 2).

Several modified electrodes using different proportions of methyl (Me, 0–40%) or phenyl (Ph, 0–20%) were constructed using again the EASA technique (Table 4). When employing 30% PhSi(OMe)₃, though, no significant deposition was observed (Table 4, entry 7). We remind here that organic modification of periodic mesoporous organosilica with organo functional groups is only possible to a certain level of organo functional group loading (i.e., up to 60% for methyl groups,¹⁷ and 10% for amine¹⁸).

Above these threshold values, formation of the transient surfactant hemimicelle assemblies on the electrode surface under potential control is disturbed and cannot properly induce the growth of an ordered and oriented mesostructure. After extraction of the surfactant by acidic ethanol solutions under moderate stirring for 20 min, the organically modified MCM-41 thin films were treated under reflux in toluene for 24 h with an ethanol solution containing the previously synthesized TEMPO-functionalized organosilane for direct grafting.¹⁴

After 24 h, the resulting functionalized and organically modified electrodes were rinsed in ethanol for 45 min under moderate stirring. After drying at room temperature, the electrodes ready for use were denoted as *x*-A@TES (*x* = extent of alkyl group; A = methyl or phenyl; T = TEMPO).

We used the resulting modified electrodes in the electro-oxidation of several alcohols to investigate their catalytic activity, scope, and durability. First, controlled-potential coulometry was performed with each modified electrodes in 0.15 M bicarbonate solution containing 1 mmol of BA at 1 V vs SCE (Table 5). Electrodes 4 and 6, with respectively 30% methyl and 10% phenyl degree of organic modification, exhibited the highest activity in the electrochemical oxidation BA (Table 5, entries 4 and 6).

We thus checked the stability and durability of the latter electrodes that, following the first run, were washed with EtOAc, dried in an oven at 70 °C for 1 h, and immersed again in a solution containing 0.15 M bicarbonate and 1 mmol of BA to repeat the electrolysis at 1 V vs SCE (run 2).

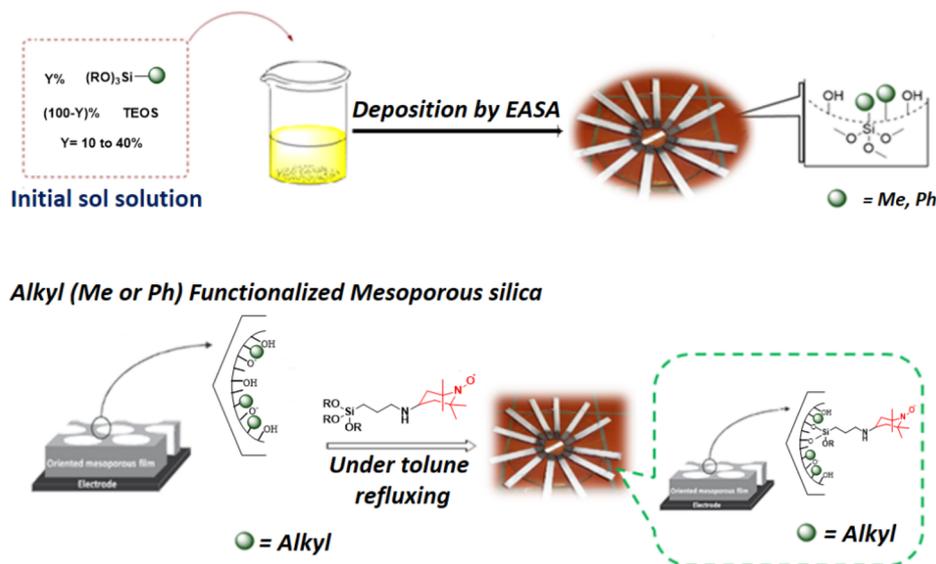
Both electrodes in entries 4 and 6, with 30% methyl and 10% phenyl, respectively, demonstrated much higher stability and durability as compared to the electrode with no auxiliary organic moieties (0-R@TES), showing evidence that such groups at the outer surface of the ORMOSIL channels significantly enhance the stability of the electrocatalytic thin film in the alkaline aqueous media during the electro-oxidation (Table 6).

The contact angle value of each electrode with a drop of water (130° ± 3° for 30-Me@TES and 130° ± 6° for the 10-Ph@TES) confirms their good hydrophobic character in comparison with 0-R@TES (MCM-41) having a 28° ± 4° contact angle (Figure 6). A contact angle >90°, indeed, is characteristic of hydrophobic materials.¹⁹

The structure and morphology of both 30-Me@TES and 10-Ph@TES are revealed by transmission electron microscopy (TEM) analysis (Figure 7), showing the uniform thickness of both films and the hexagonal pattern of their channels oriented perpendicular on the electrode surface.

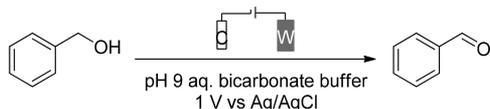
To investigate the scope of these new electrocatalysts, we tested them in the consecutive electrochemical oxidation of

Scheme 2. Preliminary Formation of the Periodic Mesoporous Organosilica Thin Film (Top), Followed by Grafting of TEMPO-TMS on the Accessible Inner Channel Surface (Bottom)

Table 4. Thin Films^a on Electrode Surfaces

| entry | composition of sol-solution | abbreviation |
|-------|-----------------------------|---------------|
| 1 | 10% Me-TMS + 90% TEOS | 10-Me |
| 2 | 20% Me-TMS + 80% TEOS | 20-Me |
| 3 | 30% Me-TMS + 70% TEOS | 30-Me |
| 4 | 40% Me-TMS + 60% TEOS | 40-Me |
| 5 | 10% Ph-TMS + 90% TEOS | 10-Ph |
| 6 | 20% Ph-TMS + 80% TEOS | 20-Ph |
| 7 | 30% Ph-TMS + 70% TEOS | no deposition |

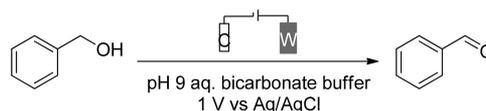
^aModified thin films with different proportions of alkyl groups (methyl and phenyl) prepared via the EASA technique on electrode surfaces.

Table 5. Screening of *x*-A@TES Electrodes in the Electro-oxidation of BA^a

| entry | electrode W | T (h) | conv (%) |
|-------|-------------|----------------------------|----------|
| 1 | 0-R@TES | 4 | 79 |
| 2 | 10-Me@TES | 4 | 83 |
| 3 | 20-Me@TES | 4 | 88 |
| 4 | 30-Me@TES | 4 | 96 |
| 5 | 40-Me@TES | 4 | 90 |
| 6 | 10-Ph@TES | 4 | 96 |
| 7 | 20-Ph@TES | 4 | 88 |
| 8 | 30-Ph@TES | no active layer deposition | |

^aReaction conditions: benzyl alcohol (1.0 mmol), water (100 mL), NaHCO₃ (10 mmol, 0.84 g), Na₂CO₃ (1 mmol, 0.106 g), E = 1.0 V vs Ag/AgCl unless stated otherwise. The product yields were determined by gas chromatography analysis after the extraction of all aqueous-phase contents using an internal standard.

several different BAs under optimal conditions (1 mmol of alcohol in 0.15 M hydrogen carbonate solution at room temperature electrolyzed at E = 1 V vs SCE). The electrocatalytic electrode efficiently mediated the waste-free electrochemical oxidation of substituted BAs such as chloro-substituted BAs (Table 7).

Table 6. Screening of *x*-A@TES Electrodes in the Electro-oxidation of BA^a

| entry | electrode, W | conv (%) | | |
|-------|--------------|----------|-------|-------|
| | | run 1 | run 2 | run 3 |
| 1 | 0-R@TES | 79 | 62 | 63 |
| 2 | 10-Me@TES | 83 | 76 | 63 |
| 3 | 20-Me@TES | 88 | 76 | 65 |
| 4 | 30-Me@TES | 96 | 93 | 87 |
| 5 | 40-Me@TES | 90 | 80 | 79 |
| 6 | 10-Ph@TES | 96 | 97 | 88 |
| 7 | 20-Ph@TES | 88 | 72 | 63 |

^aReaction conditions in all runs: benzyl alcohol (1.0 mmol), water (100 mL), NaHCO₃ (10 mmol, 0.84 g), Na₂CO₃ (1 mmol, 0.106 g), E = 1.0 V vs Ag/AgCl unless stated otherwise. After 4 h the product yields were determined by gas chromatography analysis after the extraction of all aqueous-phase contents using an internal standard.

Again, after each run the electrodes were washed with EtOAc and dried for 1 h at 70 °C. Prior to reuse the electrodes were immersed in solution containing 0.15 M bicarbonate and 1 mmol of another chlorobenzyl alcohol derivative, carrying out the electrolysis at 1 V vs SCE. Entries 3–6 in Table 6 show that the activity of the electrocatalyst was fully retained even after four consecutive runs.

The kinetics of electro-oxidation of BA using both 30-Me@TES and 10-Ph@TES electrodes under the described optimal electro-oxidation conditions show (Figure 8) higher activity for the 10-Ph@TES electrode, which may not be surprising, given the affinity between the phenyl group in the supported thin film and the diffusing BA molecules.

CONCLUSION

In 1999, Schacham, Mandler, and Avnir reported a surprising discovery that inaugurated the field of sol-gel electrochemistry:²⁰ it is enough to apply a suitable negative potential

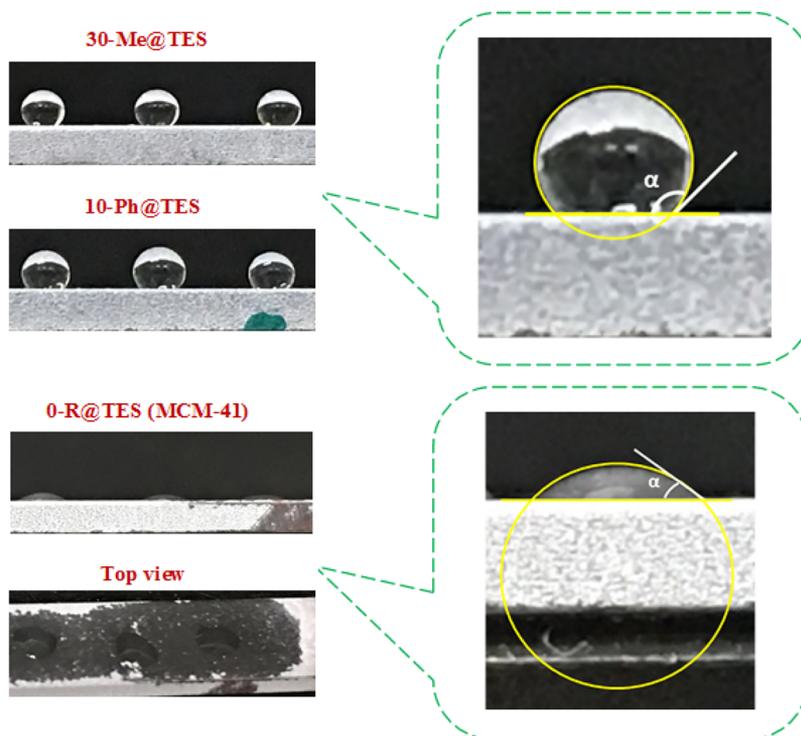


Figure 6. Contact angle measurement for 30-Me@TES, 10-Ph@TES, and MCM-41 thin films.

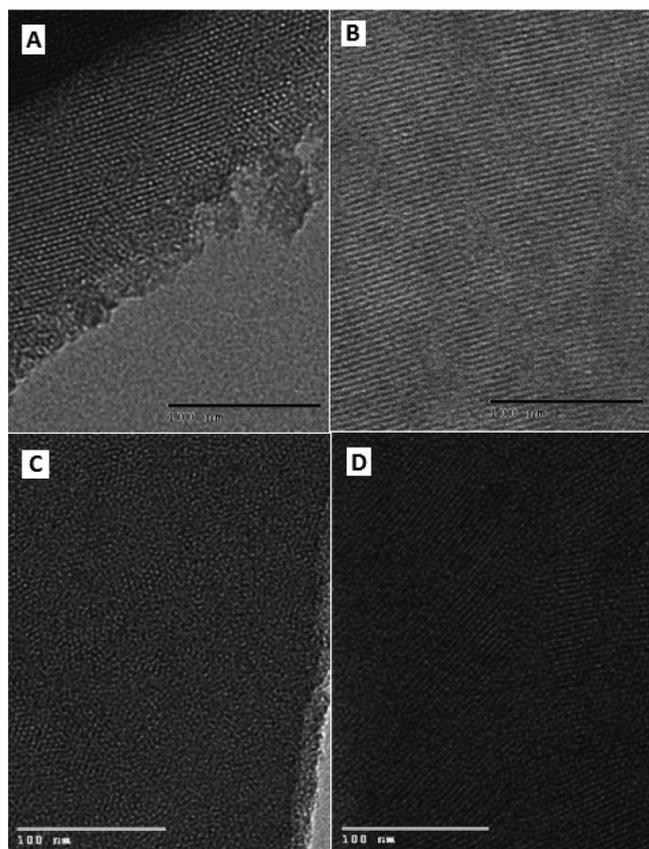


Figure 7. Top view (A,C) and side view (B,D) TEM images of (A,B) 30-Me@TES and (C,D) 10-Ph@TES thin films on electrode surfaces. Scale bar: 100 nm.

to an electrode immersed in a hydrolyzed Si alkoxide solution to locally generate the hydroxide ions necessary to catalyze the

Table 7. Scope of the Electro-oxidation of the BA Derivatives Using α -A@TES Electrodes



| entry | electrode, W | 30-Me@TES | | 10-Ph@TES | |
|-------|---------------------------|-----------|----------|-----------|----------|
| | | T (h) | conv (%) | T (h) | conv (%) |
| 1 | H | 4 | 96 | 4 | 96 |
| 2 | 4-methoxy | 6 | 84 | 6 | 66 |
| 3 | 4-chloro | 3 | 99 | 3 | 97 |
| 4 | 2-chloro ^a | 4 | 97 | 4 | 96 |
| 5 | 3-chloro ^b | 8 | 96 | 8 | 96 |
| 6 | 2,4-dichloro ^c | 8 | 97 | 8 | 97 |

^aElectrode washed with EtOAc and dried at 70 °C for 1 h, reused to oxidize 2-chlorobenzyl alcohol (run 2). ^bElectrode washed with EtOAc and dried at 70 °C for 1 h, reused to oxidize 3-chlorobenzyl alcohol (run 3). ^cElectrode washed with EtOAc and dried at 70 °C for 1 h, reused to oxidize 4-chlorobenzyl alcohol (run 4).

sol-gel polycondensation of the precursors and rapid deposition on the electrode's surface of a highly porous and accessible uniform silica (or organosilica) layer. In 2007, Walcarius extended the method to prepare periodic mesoporous silica by carrying out the process in the presence of a templating surfactant.¹⁶ Now, formation of a transient surfactant hemimicelle induces the growth of hexagonally packed one-dimensional channels of about 2 nm in diameter, perpendicular to the electrode surface. The latter method will lead to the introduction of the most active TEMPO-based alcohol oxidation catalyst comprised of highly ordered, hexagonally packed mesopore channels with perfect orthogonal orientation

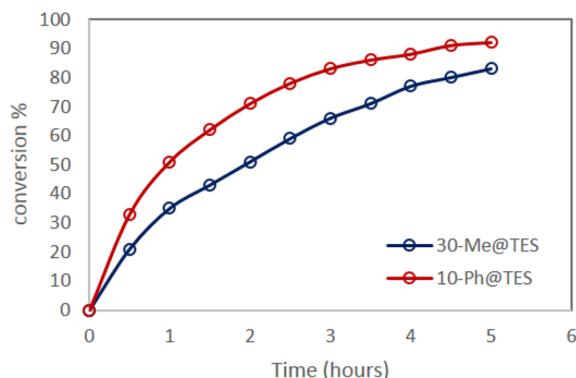


Figure 8. Comparison of the electrochemical oxidation of 0.1 M benzyl alcohol by 30-Me@TES (blue) and 10-Ph@TES (red) at 1 V vs Ag/AgCl. Supporting electrolyte is 0.15 bicarbonate buffer at room temperature.

with respect to the film plane.¹⁴ The TGSE electrode, alas, loses its spectacular activity after one run only.

Now we have discovered a straightforward nanochemistry route to stabilize the highly selective activity of periodic mesoporous sol–gel electrodes functionalized with the TEMPO moiety, via deposition of an organically modified thin film on the surface of an electrode via the EASA method, followed by functionalization of the channels of the resulting organosilica via direct grafting with a TEMPO-bearing silicon alkoxide solution. Alkylation degrees consisting of 10% phenyl modification and 30% methylation are particularly stable and active. The new thin films do not suffer from mass transfer and diffusion limitations of amorphous ORMOSIL electrodes,¹⁵ ensuring quick substrate diffusion and electro-oxidation. Yet, owing to better surface hydrophilic–lipophilic balance, now the electrodes retain both accessibility to the active sites and exquisite stability, opening the route to the entirely waste-free conversion of alcohols into carbonyls or carboxylic acid on an industrial scale in the fine chemical and pharmaceutical industries.²¹

EXPERIMENTAL SECTION

Materials. Tetraethylorthosilicate 99% (TEOS), cetyltrimethylammonium bromide 98% (CTAB), sodium nitrate, sodium bicarbonate, sodium acetate, sodium cyanoborohydride 95%, acetic acid, hydrochloric acid 37%, and all alcohol substrates were purchased from Merck. 4-Oxo-2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO), (3-aminopropyl)triethoxysilane 99% (APTES), (3-aminopropyl)trimethoxysilane 99% (APTMS), triethoxymethylsilane 99% (MTES), trimethoxymethylsilane 99% (MTMS), triethoxyphenylsilane 99% (PTES), and trimethoxyphenylsilane 99% (PTMS) were purchased from Sigma-Aldrich. Analytical-grade potassium hexacyanoferrate(III) ($K_3Fe(CN)_6$, Fluka) was used as redox probe for the electrochemical monitoring of the film's mass transport properties. All purchased chemicals were used without further purification.

Typical Precursor Synthetic Procedure. For the preparation of the precursor 2,2,6,6-tetramethyl-4-(3-(trialkoxysilyl)propylamino)piperidin-1-ol (TPTAS), the Si alkoxide precursor bearing the nitroxyl radical was synthesized by addition of 2.0 mmol of APTAS (APTMS or APTES) to a solution of 2.0 mmol of TEMPO in dried EtOH (20 mL) in a tightly closed reaction flask under a N_2 atmosphere. After 3 h stirring, $NaBH_3CN$ (2.2 mmol) was added to the reaction mixture, and the resulting mixture was left under stirring for 24 h,

after which the excess cyanoborohydride was quenched with aqueous HCl (4.0 M, 1.5 mL). The ethanol-based solution of the precursor thereby obtained was used without further purification.

General Procedure for Construction of Electro-assisted Self-Assembly Generated and Organically Modified Electrodes Functionalized with TEMPO. (a) *Initial Sol Preparation.* Various mixtures consisting of 3.26 mmol of CTAB, $(10 - (x + y))$ mmol of TEOS, x mmol of organoalkoxysilanes (methylalkoxysilane or phenylalkoxysilane), and y mmol of TPTAS were combined under vigorous stirring at molar ratios up to 30 mol%, with further addition of ethanol (15 mL) and 15 mL of an aqueous solution 0.1 M in $NaNO_3$ and 3.0 mM in HCl. The sol mixtures were allowed to hydrolyze for 2.5 h at pH 3 under stirring at room temperature.

(b) *Thin Film Formation.* Graphite or GC electrodes were immersed in the above-mentioned sol precursor mixtures. Electrodeposition of the sol–gel hybrid silica film was achieved by applying a suitable cathodic current (-1.9 mA cm^{-2}) for a defined period of time (typically 20 s). The electrodes were rapidly removed from the solution and immediately rinsed with distilled water. The electrodeposited surfactant-templated film was then dried overnight in an oven at 130 °C. Extraction of the surfactant template was carried out in acidic ethanol solutions under moderate stirring for 10 min affording the organically modified periodically mesoporous electrode functionalized with both organic and TEMPO moieties (HCSTE).

Typical Procedure for the Grafting of 2,2,6,6-Tetramethyl-4-(3-(trialkoxysilyl)propylamino)piperidin-1-ol (TPTAS) on (Modified) Hydrophobic Electrodes. The modified electrodes obtained by the initial sol containing Si source of $(10 - x)$ mmol of TEOS and x mmol of organoalkoxysilanes were immersed in the ethanolic solution of TPTAS precursor and toluene (1:10) and then refluxed for 24 h at 110 °C. The resulting functionalized electrodes were rinsed under mild stirring in ethanol for 45 min. After drying at room temperature modified electrodes bearing both alkyl and TEMPO functionalities were obtained and denoted as $x\text{-A@TES}$ (x = extent of alkyl group; A = methyl or phenyl; T = TEMPO).

Typical Procedure for the Electrocatalytic Oxidation of Alcohols. The oxidation of alcohols (1–20 mmol) was typically carried out under magnetic stirring in a 80–120 mL buffered solution of aqueous bicarbonate (0.10 M $NaHCO_3$, 0.01 M Na_2CO_3) using the modified $x\text{-A@TES}$ or HCSTE graphite electrodes at 1.0 V vs Ag/AgCl as the optimum potential.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.oprd.8b00156.

Detailed experimental methods, large view of TEM images, calculation of contact angle measurements (PDF)

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Notes

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ABBREVIATIONS

A-TES, alkyl (methyl or phenyl) triethoxysilane; BA, benzyl alcohol; CTAB, cetyltrimethylammonium bromide; CV, cyclic voltammetry; GC, glassy carbon; EASA, electro-assisted self-assembly; MTES, methyltriethoxysilane; Me-TMS, methyltrimethoxysilane; ORMOSIL, organically modified silicate; PMO, periodic mesoporous organosilicas; TEMPO, 2,2,6,6-tetramethyl-1-piperidine N-oxyl; TGSE, TEMPO-functionalized mesoporous hybrid silica electrode; TEOS, tetraethyl-orthosilicate; TPTES, 2,2,6,6-tetramethyl-4-(3-(triethoxysilyl)propylamino)piperidin-1-ol; TEMPO-TMS, 2,2,6,6-tetramethyl-4-(3-(trimethoxysilyl)propylamino)piperidin-1-ol; TEMPO-TES, 2,2,6,6-tetramethyl-4-(3-(triethoxysilyl)propylamino)piperidin-1-ol

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