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Org. Process Res. Dev., **Just Accepted Manuscript** • DOI: 10.1021/acs.oprd.8b00156 • Publication Date (Web): 09 Aug 2018

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

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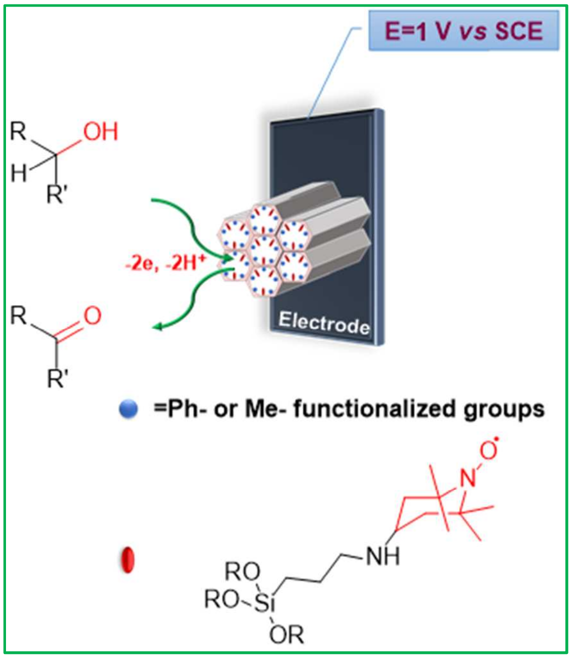


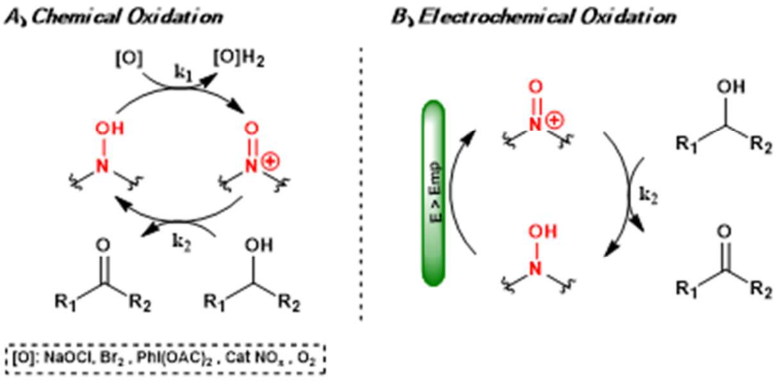
Abstract

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

Due to the fundamental role of aldehydes, ketones and carboxylic acids 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, having mostly replaced the latter and other toxic stoichiometric oxidants with a catalytic amount of TEMPO (2,2,6,6-tetramethyl-1-piperidine N-oxyl) or its nitroxyl radical derivatives thanks to their high selectivity and pronounced versatility.[2] In general, in TEMPO-like mediated oxidations, diverse primary oxidants are generally used to promote catalytic turnover, the most common of which include bleach (NaOCl), hypervalent iodine reagents, and O_2 in combination with NOx co-catalysts (Scheme 1A).[3]



Scheme 1. Chemical (A) and electrochemical (B) alcohol oxidation mediated by stable organic nitroxyl radicals.

Remarkable recent advances even include the mechanically induced oxidation of a broad set of alcohols,[4] 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. Although, several elegant and successful immobilization strategies have been developed, providing the possibility of reusing the radicals to a great extent,[6] the environmental concerns associated with the NO_X materials used in these metal-free systems is 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 in 1983 who generated the catalytically active cyclic 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 that to immobilize TEMPO motif onto a solid electrode surface, and use the modified electrode for the electrooxidation 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) 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 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, 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 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 such first catalytically active and stable electrodes.

Results and Discussion

Previous studies on the activity and stability of amorphous ORMOSIL (organically modified silica) 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, 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), TEOS and 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 was maintained for molar ratios of organosilane-to-TEOS up to 60% for methyl[17] 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 GC electrode surfaces according with organosilane (MTES + TPTES) TEOS molar ratio < 25% in the sol precursor solution. The resulting electrode (HCSTE) accessibility was then examined by voltammetric study of a dissolved redox probe. Figure 1 shows the voltammetric responses of $Fe(CN)_6^{3-}$ 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 electrode.

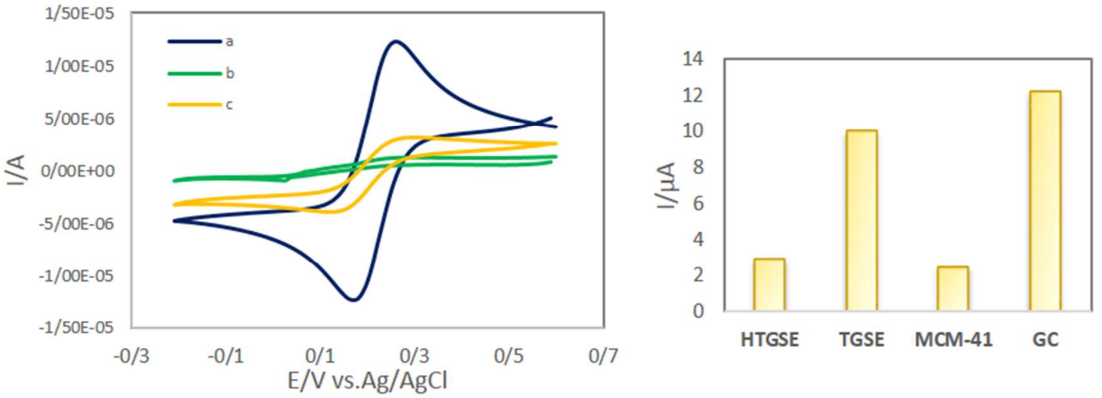


Figure 1: Left: CVs of 1.0 mM $Fe(CN)_6^{3-}$ on (a) bare GC electrode, and of HTGSE modified electrode (b) before and (c) after CTAB extraction; Supporting electrolyte 0.15 M phosphate buffer (pH=7),scan rate: 20 mV s^{-1}; Right: currents 1.0 mM $Fe(CN)_6^{3-}$ on HTGSE, TGSE, MCM-41 and bare electrode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

Now, the current is rather similar to that observed for the glassy carbon electrode coated with MCM-41 silica, which provides indirect evidence of a porous, accessible structure also for the HCSTE film. The lower voltammetric currents 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 $Fe(CN)_6^{3-}$ species.

To prove our assumption as well as to investigate the existence of TEMPO groups in the channels of HCSTE modified electrode, the electrochemical response of TEMPO groups using cyclic voltammetry was investigated (Figure 2). In the first two cycles (a and b in Figure 2) only 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 cyclic voltammetry studies of TGSE electrode, showing both anodic and cathodic peaks from the first cycle on.

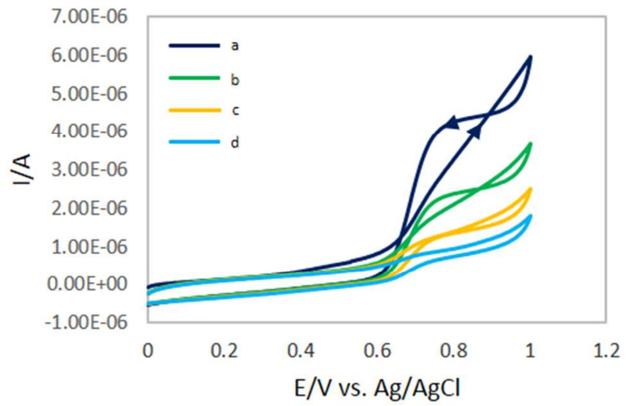


Figure 2. CVs of HTGSE after CTAB extraction (a: cycle 1, b: cycle 2, c: cycle 3 and d: cycle 4); 0.15 M phosphate buffer (pH=7) as supporting electrolyte, scan rate: 10 mV s^{-1}.

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

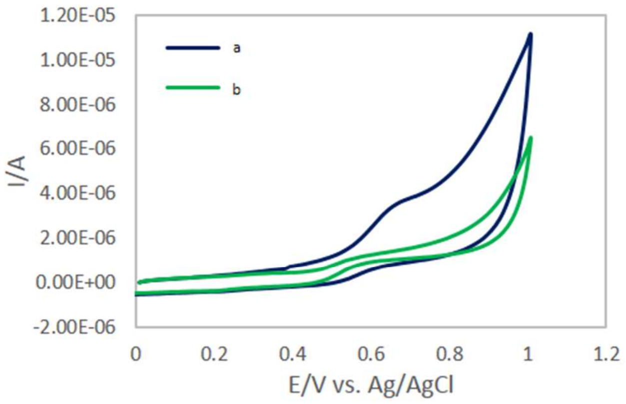


Figure 3. CVs of TGSE after CTAB extraction (a: cycle 1 and b: cycle 2) 0.15 M phosphate buffer (pH=7) as supporting electrolyte, scan rate: 10 mV s^{-1}.

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 benzyl alcohol (BA) dissolved in buffered aqueous solution.

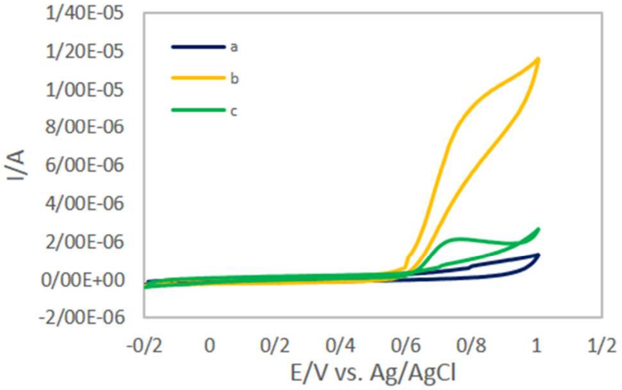


Figure 4. CVs of bare GC electrode in the presence of BA (a), and of HCSTE in the presence of 9.0 mM BA (b), and in the absence of BA (c); Supporting electrolyte 0.15 M phosphate buffer (pH = 7); scan rate: 20 mV s^{-1}.

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), 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 HCSTE electrode in the absence of BA.

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

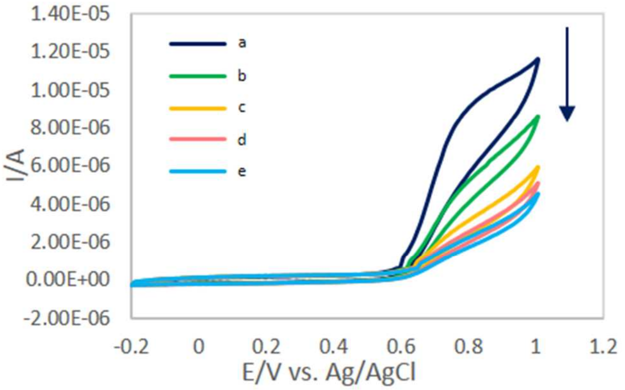


Figure 5. Multi-cyclic voltammograms of HCSTE in the presence of 9.0mM of BA (a: cycle 1, b: cycle 2, c: cycle 3, d: cycle 4 and e: cycle 5) ; Supporting electrolyte 0.15 M phosphate buffer (pH = 7); scan rate: 20 mV s^{-1}.

Consecutive recycling of potential in the presence of BA at the surface of the same HCSTE electrode shows (Figure 5) 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 electroactive HCSTE electrode encouraged us to investigate the potential of this electrode in the electrooxidation of BA and its stability and durability in aqueous media on larger scale. We therefore coated larger graphite plate electrodes (260 cm^2 geometric area) with the active ORMOSIL layer via EASA electrodeposition of organosilica (X% $MeSi(OR)_3$ + 5% TEMPO-propyltrialkoxysilane) in the presence of CTAB. After surfactant extraction, the graphite electrodes functionalized with mesoporous organosilica were named TM-X@MCM-41 (T:TEMPO, M:methyl and X:prechantage 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 TM-X@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 (C, H, N) analysis. For the purpose of comparison with previously reported electrode (TEMPO@MCM-41),[14] an electrode containing 5% TEMPO and bearing no methyl functionality was also prepared according to previously reported method for TGSE preparation, with slight modifications only.

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

Entry	Type modified electrode	N(in 100 mg)	TEMPO(mmol)
1	M-15@MCM-41	0.667	------
2	TEMPO@MCM-41(piror report)	1.970	0.50
3	TM-15@MCM-41	2.225	0.54

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 TEMPO.

The electro-oxidation of 1 mmol BA was performed in 0.15 M bicarbonate solution using TEMPO@MCM-41 and TM-15@MCM-41 electrodes at 1 V *vs.* SCE controlled-potential shows lower activity for the organically modified TM-15@MCM-41 electrode in comparison with the hydrophilic TEMPO@MCM-41 electrode (Table 2).

Table 2. Screening of electro-oxidation of BA using TEMPO@MCM-41 and TM-15@MCM-41 electrodes.

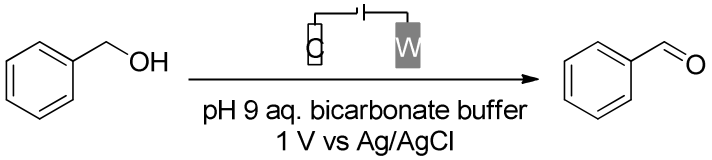
Entry	Electrode	T(h)	Conv.(%)[a]
1	TEMPO@MCM-41	2	100
2	TEMPO@MCM-41, second run	4	74
3	TM-15@MCM-41	4	64

[a]Reaction conditions: Benzyl alcohol (1.0 mmol), water (100 mL), $NaHCO_3$ (10 mmol, 0.84 g), Na_2CO_3 (1 mmol, 0.106 g), E=1.0 V vs. Ag/AgCl unless otherwise stated. The product yields were determined by gas chromatography analysis (GC) after the extraction of all aqueous phase contents using an internal standard.

Considering that 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 film on the graphite electrodes under larger scale preparation conditions. Indeed, when we attempted to prepare various type of TM-x@MCM-41 using different proportion 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 in Me/TEMPO ratios 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 non accessible (non porous) 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 satisfaction (entries 5-7 in Table 3).

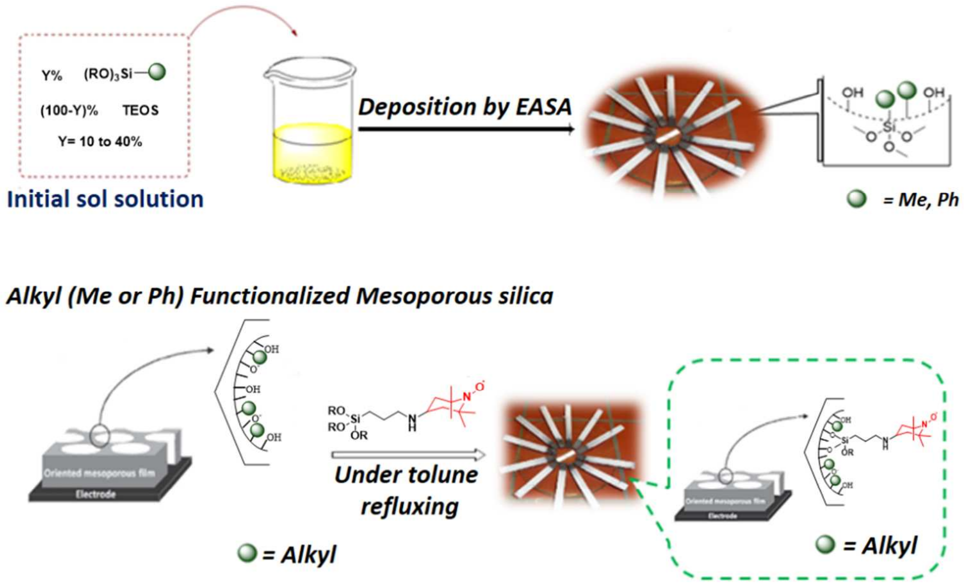
Table 3. Screening of TM-x @MCM-41 electrodes in the electro-oxidation of BA.



Entry	**Content of Sol Solution 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[a]	15% Me-TES +7.3%TEMPO-TES +78% TEOS	73
6[a]	15% Me-TES +7.3%TEMPO-TMS+78% TEOS	80
7[a]	15% Me-TMS+7.3%TEMPO-TMS+78%TEOS	78

Reaction conditions: Benzyl alcohol (1.0 mmol), water (100 mL), $NaHCO_3$ (10 mmol, 0.84 g), Na_2CO_3 (1 mmol, 0.106 g), E=1.0 V vs. Ag/AgCl unless otherwise stated. The product yields were determined by gas chromatography analysis (GC) after the extraction of all aqueous phase contents using an internal standard. [a] Deposited in the presence of S-membrane.

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, 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).



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).

Several modified electrodes using either different proportion 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 in a certain level of organo-functional group loading (i.e., up to 60% for methyl groups,[17] and 10% for amine[18]).

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]

Table 4. Abbreviation of thin films on electrode surfaces.

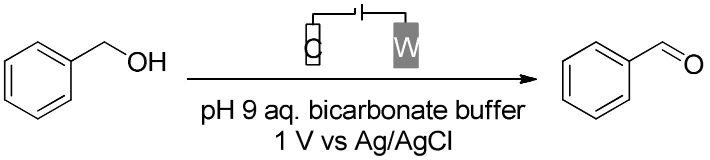
Entry	Composite of Sol-solution	Abbreviation
1	10% Me-TMS + 90% TEOS	10-Me
2	20% Me-TMS + 80% TEOS	20-Me
3	30% Me-TMS + 70% TEOS	30-Me
4	40% Me-TMS + 60% TEOS	40-Me
5	10% Ph-TMS + 90% TEOS	10-Ph
6	20% Ph-TMS + 80% TEOS	20-Ph
7	30% Ph-TMS + 70% TEOS	No deposition

Modified thin films with different proportion of Alkyl groups (Methyl and Phenyl) prepared via the EASA technique on electrode surfaces and their abbreviation.

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).

Table 5. Screening of x-A@TES electrodes in the electro-oxidation of BA



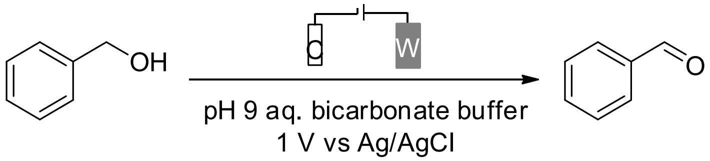
Entry	Electrode (W)	T(h)	Conv.(%) [a]
1	0-R @TES	4	79
2	10-Me@TES	4	83
3	20-Me@TES	4	88
4	30-Me@TES	4	96
5	40-Me@TES	4	90
6	10-Ph@TES	4	96
7	20-Ph@TES	4	88
8	30-Ph@TES	No active layer deposition	

[a]Reaction condition : Benzyl alcohol (1.0 mmol), water (100 mL), $NaHCO_3$ (10 mmol, 0.84 g), Na_2CO_3 (1 mmol, 0.106 g), E=1.0 V vs. Ag/AgCl unless otherwise stated. The product yields were determined by gas chromatography analysis (GC) after the extraction of all aqueous phase contents using an internal standard.

We thus checked the stability and durability of the latter electrodes that, following the first run, were washed with EtOAc and 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 **4** and **6** with 30% methyl and 10% phenyl 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).

Table 6. Screening of x-A@TES electrodes in the electro-oxidation of BA.



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

Reaction conditions in all Runs: Benzyl alcohol (1.0 mmol), water (100 mL), $NaHCO_3$ (10 mmol, 0.84 g), Na_2CO_3 (1 mmol, 0.106 g), E=1.0 V vs. Ag/AgCl unless otherwise stated. After 4 h the product yields were determined by gas chromatography analysis (GC) after the extraction of all aqueous phase contents using an internal standard.

The contact angle value of each electrode with a drop of water confirm (130°±3° for 30-Me@TES and 130°±6° for the 10-Ph@TES) 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 an hydrophobic materials.[19]

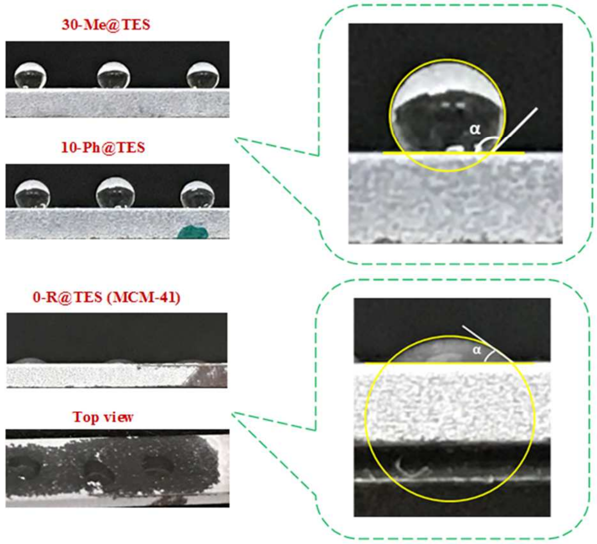


Figure 6. Contact angle measurement for 30-Me@TES, 10-Ph@TES and MCM-41 thin films.

The structure and morphology of both 30-Me@TES and 10-Ph@TES is revealed by TEM analysis showing (Figure 7) the uniform thicknes of both films and the hexagonal pattern of their channels oriented perpendicularly on the electrode surface.

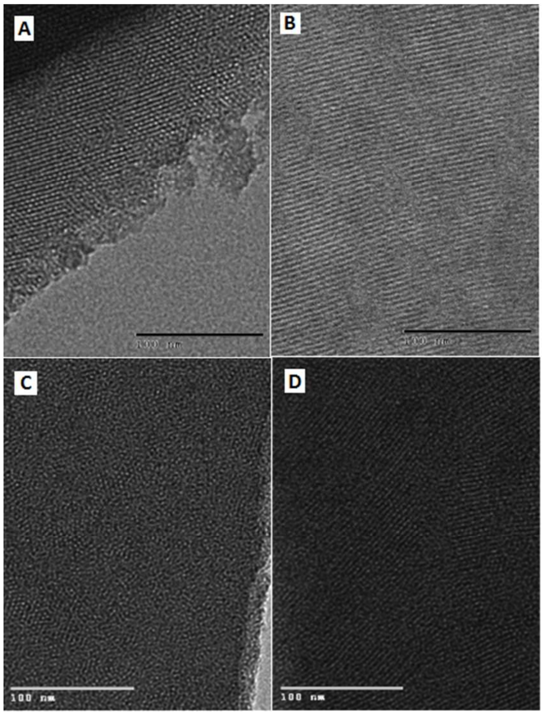
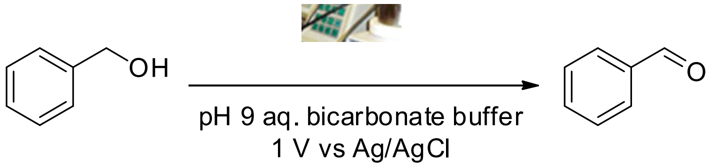


Figure 7. Top view (A, C) and side view (B, D) TEM images of 30-Me@TES and 10-Ph@TES thin films on electrode surfaces,respectively, (Scale bar: 100 nm).

To investigate the scope of these new electrocatalysts, we tested them in the consecutive electrochemical oxidation of several different benzyl alcohols under optimal conditions (1 mmol alcohol in 0.15 M hydrogencarbonate solution at room temperature electrolyzed at E=1 V *vs*. SCE). The electrocatalytic electrode efficiently mediated the waste-free electrochemical oxidation of substituted benzyl alcohols such chloro substituted benzyl alcohols (Table 7).

Table 7. Scope of the electro-oxidation of the benzyl alcohol derivatives using x-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

[a] Electrode washed with EtOAc and dried at 70 °C for 1 h , reused to oxidise 2-chlorobenzylalcohol (Run 2), [b]Electrode washed with EtOAc and dried at 70 °C for 1 h, reused to oxidise 3-chlorobenzylalcohol (Run 3), [c] Electrode washed with EtOAc and dried at 70 °C for 1 h, reused to oxidise 4-chlorobenzylalcohol (Run 4).

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

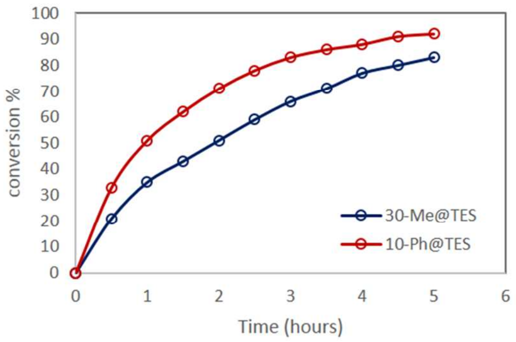


Figure 8. Comparison of the electrochemical oxidation of 0.1 M benzyl alcohol by 30-Me@TES (blue) and 10-Ph@TES (red), at 1 V/vs. Ag/AgCl, supporting electrolyte is 0.15 bicarbonate buffer at rt.

The kinetics of electro-oxidation of BA using both 30-Me@TES and 10-Ph@TES electrodes under 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 to an electrode immersed in a hydrolyzed Si alkoxide solution, to locally generate the hydroxide ions necessary to catalyze the sol-gel polycondensation of the precursors and rapid deposition on the electrode's surface of an 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 2nm in diameter, perpendicularly 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 with respect to the film plane.[14] The electrode (TGSE), alas, loses its spectacular activity after one run only.

Now we have discovered a straightforward nanochemistry route to stabilize the high 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 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(TEMPON), (3-aminopropyl)triethoxysilane 99% (APTES), (3-aminopropyl)trimethoxysilane 99% (APTMS), triethoxymethylsilane 99% (MTES), trimethoxymethylsilane 99% (MTMS) and triethoxyphenylsilane 99% (PTES) and trimthoxyphenylsilane 99% (PTMS) were purchased from Sigma-Aldrich. Analytical grade potassium hexacyanoferrate (III) ($K_3Fe(CN)_6$, Fluka) was used as redox probes for the electrochemical monitoring of the film 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 were synthesis by addition of 2.0 mmol APTAS (APTMS or APTES) to a solution of 2.0 mmol of TEMPON 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 left under stirring for 24 h, after which the excess cyanoborohydride was quenched with aqeous 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 CTAB, (10-(X+Y))mmol TEOS, Xmmol Organoalkoxysilanes (Methylalkoxysilane or Phenylalkoxysilane), Y mmol TPTAS were combined under vigorous stirring at molar ratios up to 30 mol%, further adding 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 glassy carbon 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 20s). 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 TEOS and X mmol Organoalkoxysilanes, were immersed in the ethanolic solution of TPTAS precursor and toluene (1:10) then refluxed for 24 h at 110 ^{o}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-A@TES (x: extent of alkyl group; A: methyl or phenyl; T: TEMPO)).

Typical procedure of electro-catalytic oxidation of alcohols. The oxidation of alcohols (1 to 20 mmol) was typically carried out under magnetic stirring in a 80 to 120 mL buffered solution of aqueous bicarbonate ($NaHCO_3$ 0.10 M and Na_2CO_3 0.01 M) using the Modified x-A@TES or HCSTE graphite electrodes at 1.0 V vs. Ag/AgCl as the optimum potential.

ASSOCIATED CONTENT

Supporting Information

Detailed experimental methods, Large size of TEM images, Calculation of contact angle measurements

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Acknowledgments

This article is dedicated to the memory of Professor István E Markó (1956-2016), for all he has done to advance catalysis for clean chemical productions at the School of Chemistry of Université Catholique de Louvain. The authors also acknowledge Dr. Maniya Maleki from IASBS for her generous help in measuring the contact angle of electrodes and also interpretation of the contact angle results.

List of Abbreviations

A-TES, Alkyl (methyl or phenyl) triethoxysilane

BA, benzyl alcohol

CTAB, cetyltrimethylammonium bromide

CV, cyclic voltammogram

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, Tetraethylorthosilicate

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 ;

References

(1) Sheldon, R. A. Recent advances in green catalytic oxidations of alcohols in aqueous media. *Catal. Today* **2015**, *247*, 4-13

(2) Ciriminna, R.; Pagliaro, M. Industrial oxidations with organocatalyst TEMPO and Its derivatives. *Org. Process Res. Dev*. **2010**, *14*, 245-251.

(3) (a) Cella, J. A.; Kelley, J. A.; Kenehan, E. F. Nitroxide-catalyzed oxidation of alcohols using m-chloroperbenzoic acid. New method. *J. Org. Chem*. **1975**, *40*, 1860-1862. (b) Bobbitt, J. M.; Brückner, C.; Merbouh, N. Oxoammonium- and Nitroxide-catalyzed oxidations of alcohols. *Org. React*. **2010**, *74*, 103-424; (c) Tebben, L.; Studer, A. Nitroxides: applications in synthesis and in polymer chemistry. *Angew. Chem. Int. Ed.* **2011**, *50*, 5034-5068; (d) Cao, Q.; Dornan, L. M.; Rogan, L.; Hughes, N. L.; Muldoon, M. J. Aerobic oxidation catalysis with stable radicals. *Chem. Commun*. **2014**, *50*, 4524-4543.

(4) Porcheddu, A.; Colacino, E.; Cravotto, G.; Delogu, F.; De Luca, L. Mechanically induced oxidation of alcohols to aldehydes and ketones in ambient air: revisiting TEMPO-assisted oxidations. *Beilstein J. Org. Chem*. **2017**, *13*, 2049-2055.

(5) Ryland, B.; Stahl, S. S. Practical aerobic oxidations of alcohols and amines with homogeneous Copper/TEMPO and related catalyst systems. *Angew. Chem. Int. Ed*. **2014**, *53*, 8824-8838.

(6) Megiel, E. Surface modification using TEMPO and Its derivatives. *Adv. Colloid. Interface Sci*. **2017**, *250*, 158-184

(7) (a) Lammel, G.; Cape, J. N. Nitrous acid and nitrite in the atmosphere. *Chem. Soc. Rev.* **1996**, 25, 361-369; (b) Khalafi, L.; Rafiee, M. Kinetic study of the oxidation and nitration of catechols in the presence of nitrous acid ionization equilibria. *J. Hazard. Mater.* **2010**, *174*, 801-806.

(8) Semmelhack, M. F.; Chou, C. S.; Cortes, D. A. Nitroxyl-mediated electrooxidation of alcohols to aldehydes and ketones. *J. Am. Chem. Soc*. **1983**, *105*, 4492-4494.

(9) Nutting, J. E.; Rafiee, M.; Stahl, Sh. S. Tetramethylpiperidine N-Oxyl (TEMPO), Phthalimide N-Oxyl (PINO), and related N-Oxyl species: Electrochemical properties and their use in electrocatalytic reactions, *Chem. Rev.* **2018**, *118*, 4834−4885.

(10) Rafiee, M.; Karimi, B.; Alizadeh, S. Mechanistic study of the electrocatalytic oxidation of alcohols by TEMPO and NHPI. *ChemElectroChem*. **2014**, *1*, 455-462.

(11) Cha, H. G.; Choi, K.-S. Combined biomass valorization and hydrogen production in a photoelectrochemical cell. *Nat. Chem*. **2015**, *7*, 328-333.

(12) Ciriminna, R.; Palmisano, G.; Pagliaro, M. Electrodes functionalized with the 2,2,6,6-tetramethylpiperidinyloxy radical for the waste-free oxidation of alcohols. *ChemCatChem* **2015**, *7*, 552-558.

(13) Walcarius, A. Electrochemistry of silicate-based nanomaterials. *In Encyclopedia of Nanoscience and Nanotechnology*, H. S. Nalwa (Ed.), vol 2, American Scientific Publishers, Valencia (CA): **2004**; pp. 857-893.

(14) Karimi, B.; Rafiee, M.; Alizadeh, S.; Vali, H. Eco-friendly electrocatalytic oxidation of alcohols on a novel electro-generated TEMPO- functionalized MCM-41 modified electrode. *Green Chem*. **2015**, 17, 991-1000.

(15) Palmisano, G.; Ciriminna, R.; Pagliaro, M. Waste-Free electrochemical oxidation of alcohols in water. *Adv. Synth. Catal*. **2006**, *348*, 2033-2037.

(16) Walcarius, A.; Sibottier, E.; Etienne, M.; Ghanbaja, J. Electrochemically assisted self-assembly of mesoporous silica thin films. *Nat. Mater*. **2007**, *6*, 602-608.

(17) Guillemin, Y.; Etienne, M.; Aubert, E.; Walcarius, A. Electrogeneration of highly methylated mesoporous silica thin films with vertically-aligned mesochannels and electrochemical monitoring of mass transport issues. *J. Mater Chem*. **2010**, *20*, 6799-6807.

(18) (a) Etienne, M.; Goux, A.; Sibottier, E.; Walcarius, A. Oriented mesoporous organosilica films on electrode: A new class of nanomaterials for sensing. *J. Nanosci. Nanotechnol* **2009**, *9*, 2398–2406; (b) Rafiee, M.; Karimi, B.; Abdossalami-Asl, Y.; Vali, H. Electrochemical fabrication of electroactive ordered mesoporous electrode. *Analyst* **2013**, *138*, 1740-1744.

(19) Liu, F.; Wang, L.; Sun, Q.; Zhu, L.; Meng, X.; Xiao, F. S. Transesterification catalyzed by ionic liquids on superhydrophobic mesoporous polymers: heterogeneous catalysts that are faster than homogeneous catalysts. *J. Am. Chem. Soc*. **2012**, *134*, 16948-19950.

(20) Shacham, R.; Avnir, D.; Mandler, D. Electrodeposition of methylated Sol-Gel films on conducting surfaces. *Adv. Mater*. **1999**, *11*, 384-388.

(21) Ciriminna, R.; Ghahremani, M.; Karimi, B.; Pagliaro, M. Electrochemical alcohol oxidation mediated by TEMPO like nitroxyl radicals. *ChemistryOpen*. **2017**, *6*, 5-10.