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pH-modulated ion transport and amplified redox response of Keggin-type polyoxometalates through vertically-oriented mesoporous silica nanochannels

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ABSTRACT. Cyclic voltammetry has been applied to characterize mass transport of a Keggin-type polyoxometalates ($[\text{SiW}_{12}\text{O}_{40}]^{4-}$) through vertically-aligned mesoporous silica thin films in aqueous media. The results indicate a drastic influence of pH and the ionic strength which may be rationalized in terms of electrostatic interactions and confinement effects. Diffusion of such bulky anionic electroactive species is considerably restricted at pH values higher than the point of zero charge of the silica for which the walls of the nanochannels are negatively charged. On the other hand, the positive charge density generated in more acidic solutions favors the ingress of $[\text{SiW}_{12}\text{O}_{40}]^{4-}$ species through the mesochannels, enhancing considerably the electrochemical response, except at high ionic strength due to competition for the binding sites. The accumulation

of POM anions into the silica films can be even promoted by functionalization of the silica surface with propylammonium groups. In summary, pH tuning induced gating of the ionic flux through the silica nanopores, which can be somewhat modulated by the ionic strength by varying the thickness of the electrical double layer generated at the silica walls surface.

1. INTRODUCTION

Silica (SiO_2) is one of the most abundant amphoteric oxide materials and the speciation of surface hydroxyl groups (silanol groups, $\equiv\text{SiOH}$) is controlled by the pH of the medium. It is amphoteric because it carries either positive, negative or zero net charge depending on the pH of the surrounding solution and its ionic concentration.¹ Depending upon different manufacturing processes, the point of zero charge for silica ranges from 2 to 3.5.^{2,3} At pH below the point of zero charge, defined as the pH at which the positive and negative charges of a zwitterionic surface are balanced, protons can adsorb from solution to the oxide surface and generate protonated sites ($\equiv\text{SiOH}_2^+$) that result in an overall net positive charge at the interface. At pH values above the point of zero charge, protons desorb from hydroxyl groups into solution to create deprotonated sites ($\equiv\text{SiO}^-$) and an overall negative surface charge. Across the entire pH range, the charged surface groups of the oxide material remain in equilibrium with neutral sites.

2D hexagonal silica-based mesostructures with pores uniformly packed in an orthogonal orientation to the underlying support can be prepared by means of an electro-assisted self-assembly (EASA)⁴ method. They represent an attractive model to evidence transport features at the mesoscale and constitute an ideal configuration ensuring good accessibility towards the electrode surface. The EASA method can afford vertically-oriented silica-based thin films with small pore size varying from 2 to 3 nm that can be slightly modulated as a result of the choice of the cationic

surfactant employed either cetyltrimethylammonium bromide (CTAB) or octadecyltrimethylammonium bromide (OTAB) as template respectively.⁵ Functionalization of such vertically-oriented films can be basically achieved by three different methods: post-synthesis grafting (yet leading often to pore blocking effects), co-condensation processes essentially based on the use of an alkoxy silane and organosilanes (which is however limited to the use of simple organic functions^{6,7}) and via more versatile click chemistry approaches (likely to generate a wide range of organic-inorganic hybrid films).^{8,9}

Recent advances in nanofabrication techniques^{10,11,12} and growing interest in sensing particular molecules by nanofluidic devices^{3,13,14,15} have stimulated the research in the field of controlled ion transport through synthetic nanochannels. Nanochannels with charged surfaces having pore dimensions within the Debye length range are known to display selective transport properties which depend on the surface charge.^{16,17} When a charged surface is immersed into an electrolyte solution, ions of opposite charge are attracted to it, thereby forming an electrical double layer (EDL). The thickness of this double layer is dictated by the Debye length of the solution, which characterizes the length scale of the electrostatic screening between the charged species due to the finite concentration in the solution. Ion transport in nanoscale channels is thus expected to be strongly influenced by the effective partial charge inside channels of so small diameter, which can alter transport properties of electrolytes in confined geometries.^{18,19,20} Electrochemical techniques are good tools to study the mass transport of electroactive species through mesoporous silica films exhibiting such nanochannels.²¹ The diffusion of such redox probes is strongly dependent on the mesostructure type^{22,23} and pore orientation.³ To date, however, the investigations made on vertically-oriented mesoporous silica nanochannels have been restricted to the diffusion of small

molecules/ions or to evidencing size exclusion features (molecular sieving).⁵ Here we wish to extend it to bulkier species such as Keggin-type polyoxometalates.

PolyOxoMetalates (POMs) constitute a family of discrete chemical entities which are often considered as analogous to soluble molecular oxides. They form upon the polycondensation of similar or different oxometalate ions. The number of metallic centres associated in a single structure may vary from a few units up to several hundreds. The most convenient chemical elements for the reactions of formation of POMs are tungsten, molybdenum and vanadium, which will be found in their highest oxidation states (+VI or +V).^{24,25,26} POMs exhibit an enormous potential in the sense that their composition can be specially tailored according to particular multi-step and stereospecific syntheses. The latter allow to specifically incorporate in the scaffold different metallic cations, organic compounds or organometallic complexes.^{27,28,29} POMs may also be grafted on nano-structured materials such as graphene,³⁰ carbon nanotubes, mesoporous silica and metal nanoparticles.^{31,32,33,34,35} This grafting may rely on the formation of chemical bonds or be just a simple physisorption phenomenon. Among the great diversity of POMs described in the literature, we are interested in the Keggin-type structure,³⁶ which seems to be the most known of all by far. We have chosen the $[\text{SiW}_{12}\text{O}_{40}]^{4-}$ polyoxoanion, which results from the condensation of twelve $\{\text{WO}_6\}$ octahedra around a $\{\text{SiO}_4\}$ tetrahedron (Figure 1A), as a good model for the present study as its electrochemical behaviour, both in solution and in the solid state, is known from previous reports.^{37,38,39}

In this paper, we have carefully studied the effect of selected experimental parameters (i.e., pH of the surrounding solution and ionic strength) on the permeability properties of vertically-aligned mesoporous silica thin films (see top and cross-section TEM views on Figure 1B&C) by using an anionic redox probe from Keggin-type POMs family, $[\text{SiW}_{12}\text{O}_{40}]^{4-}$. Compared to smaller redox

probes (e.g., $\text{Fe}(\text{CN})_6^{3-/4-}$),⁴⁰ more restricted mass transport through the mesochannels might be expected. In addition, tuning the transport of ionic species through silica nanochannels by varying the ionic strength and pH of the solution has been underexplored. These two experimental parameters are of importance as pH will affect the surface charge density of silica and consequently the electrostatic interactions with the anionic species, $[\text{SiW}_{12}\text{O}_{40}]^{4-}$, and the ionic strength will define the EDL thickness likely to influence the transport of charged species through the small channels. Studying the optimal conditions favoring the mass transport of polyoxometalates through the nanochannels is a prerequisite to succeed in their confinement inside these silica matrices, with possible applications in the field of (electro)catalysis or molecular electronics for instance.

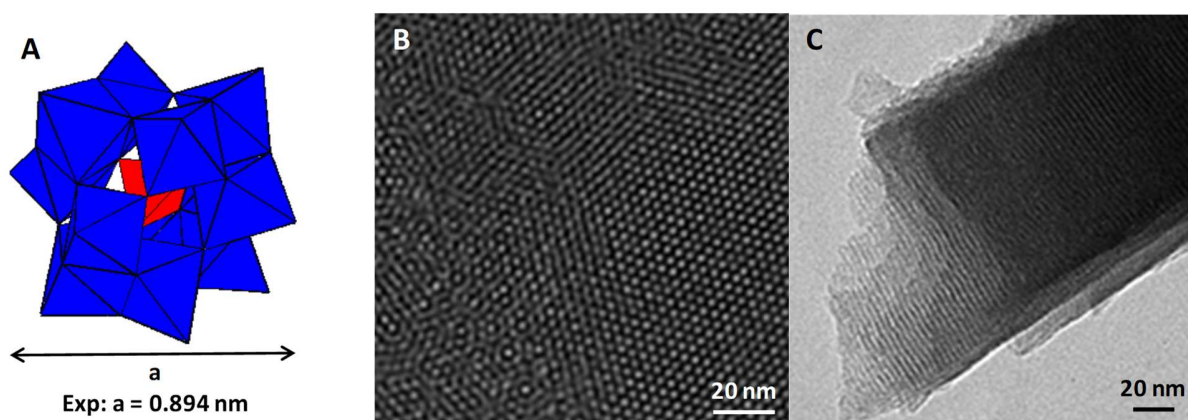


Figure 1. A) Representative structure of the heteropolyanion studied: $[\text{SiW}_{12}\text{O}_{40}]^{4-}$. B, C) Transmission electron micrographs of the vertically-oriented silica thin films: top-view (B) and cross-section (C).

2. EXPERIMENTAL

2.1. Chemicals and reagents

Tetraethoxysilane (TEOS, 98%, Alfa Aesar), (3-aminopropyl)triethoxysilane (APTES, 99%, Aldrich), ethanol (95-96%, Merck), NaNO₃ (98%, Prolabo), HCl (37% Riedel de Haen), cetyltrimethylammonium bromide (CTAB, 99%, Acros), have been used as received. Pure samples of K₄[SiW₁₂O₄₀].17H₂O were obtained by following a synthetic procedure previously reported.⁴¹ They were dissolved at the desired concentration in aqueous solutions containing H₂SO₄ and/or Na₂SO₄ as supporting electrolyte.

2.2. Preparation and functionalization of vertically-aligned mesoporous silica thin films

The vertically-oriented silica thin films have been electrochemically generated on indium-tin oxide (ITO) electrodes according to the previously reported EASA procedure.^{5,42} A hydroalcoholic solution (10 mL H₂O/10 mL ethanol) containing 100 mM of the silica precursor (TEOS), 32 mM of CTAB as template and 0.1 M NaNO₃ was prepared. The pH was adjusted to 3 by adding 0.1 M HCl. After a first step of hydrolysis for 2.5h, a cathodic potential of -1.3 V was applied for 20 s to the ITO working electrode with subsequent deposition of the silica layer. The electrode surface was thoroughly rinsed with water and aged overnight at 130°C. Template extraction was performed by immersing the film electrode in an ethanol solution containing 0.1 M HCl for 15 min.

EASA was also used to afford the generation of amino-functionalized mesoporous silica thin films under potentiostatic conditions on ITO plates but the procedure has to be somewhat adapted due to the intrinsic basic properties of (3-aminopropyl)triethoxysilane (APTES).⁶ 0.2 mmol of APTES were added to a solution made of 10 mL ethanol and 10 mL aqueous solution of 0.1 M NaNO₃, and its pH was adjusted to 3 by adding 1.0 M HCl. Then, 1.8 mmol of TEOS and 0.64 mmol of CTAB were added to the solution. The sol was aged for 2.5 h under stirring before use. A cathodic

potential of -1.3 V was applied for 20 s. The electrode was rinsed quickly with deionized water. The silica film obtained was aged overnight in an oven at 130°C. Prior to use, template extraction was made as above.

2.3. Apparatus

Electrochemical data were obtained using an EG & G 273 A driven by a PC with the M270 software. A one-compartment cell with a standard three-electrode configuration was used for cyclic voltammetry (CV) experiments. The reference electrode was a saturated calomel electrode (SCE) separated from the bulk electrolyte solution via fritted compartments filled with the same electrolyte; the counter electrode was a platinum gauze of large surface area. The working electrode was an indium-tin oxide plate. Cyclic voltammograms have been recorded at 20 mV s⁻¹ (unless specified otherwise) from aqueous solutions of the POM at selected pH values and ionic strengths adjusted using H₂SO₄ and/or Na₂SO₄.

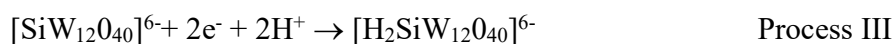
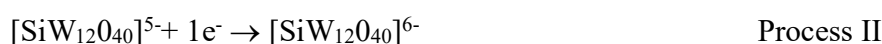
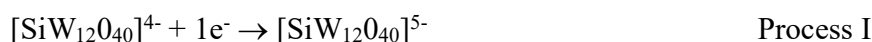
3. Results and discussion

3.1. Preliminary considerations

The electrochemical behavior of a Keggin-type heteropolyanion, [SiW₁₂O₄₀]⁴⁻ has been first checked on bare indium-tin oxide (ITO) electrode (Figure 2). The measurements have been carried out in acidic media, within a pH range that will be investigated later on with the silica film modified electrodes.

A series of electrochemical experiments have been performed concerning the reduction of [SiW₁₂O₄₀]⁴⁻ in an aqueous electrolyte solution consisting of different compositions of H₂SO₄ +

Na₂SO₄ in the pH range from 1 to 3 (Figure 2). Cyclic voltammograms of [SiW₁₂O₄₀]⁴⁻ recorded on bare ITO involve three reversible processes corresponding to the reduction of W centers: two initial reversible single-electron processes (I and II) followed by an overall two-electron step (process III).



The half-wave potentials $E_{1/2}$ for I and II are essentially independent of pH. In contrast, $E_{1/2}$ for the third process shifted to more negative values with increasing pH. Such electrochemical behavior is analogous to the one previously described using glassy carbon as a working electrode.³⁸

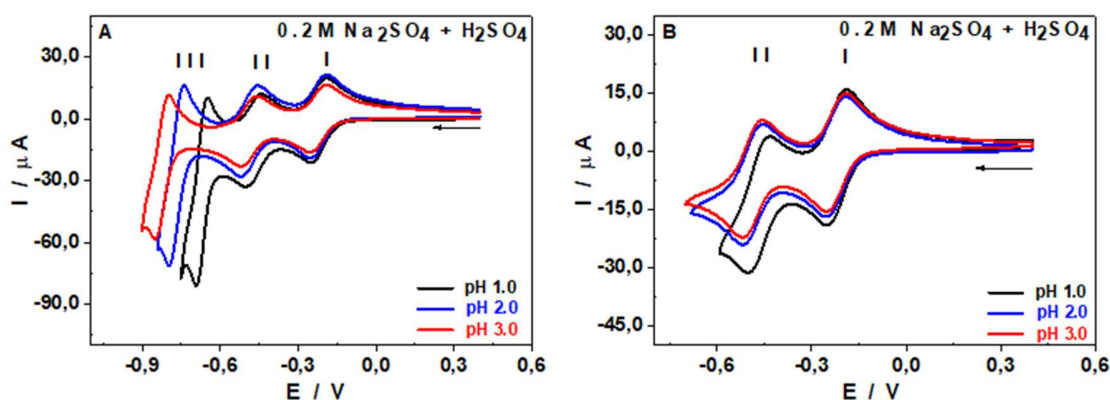


Figure 2. Cyclic voltammograms recorded on bare ITO electrode in a solution containing 5.0×10^{-4} M [SiW₁₂O₄₀]⁴⁻ and 0.2 M Na₂SO₄ + H₂SO₄ at different concentrations adjusted to fix pH values at 0.3 (black line), 1.0 (red line), 2.0 (blue line) and 3.0 (green line). Part A represents the whole potential window while part B is restricted to that of the two first redox processes.

The vertically-aligned silica films prepared are characterized by their mesoporous channels network uniformly and densely packed in a hexagonal arrangement (Figure 1B). The pore diameter when using CTAB as surfactant is of 2.1 nm and the thickness of the silica thin film is close to 100 nm (Figure 1C). Their presence onto the ITO electrode surface is likely to affect the above voltammetric processes. Indeed, the electrochemical behavior of ionic compounds on silica films is strongly influenced by their own charge and size, and the charge density of the silica walls.^{35,43} To our knowledge most of the work previously reported in the study of the mass transport of charged species through mesoporous channels has been performed at pH higher than the isoelectronic point of silica. Typically in these conditions, cationic redox probes such as Ru(NH)₆³⁺ exhibit an accumulation phenomenon due to electrostatic attractions with negatively charged silica walls at pH higher than 3, whereas some repulsion effects were observed in more acidic media (detailed analysis of the electrochemical response of this redox probe as a function of pH is presented in Fig. S3, see SI). One can thus expect an opposite behavior for the [SiW₁₂O₄₀]⁴⁻ anion.

In the context of a charged surface in an electrolytic solution, the thickness of the double layer that forms at the charged surface is called the Debye length (λ_D). It is known as the shielding distance as it represents the distance over which the charged surface is shielded from the bulk and can be

expressed as
$$\lambda_D = \sqrt{\frac{\epsilon_0 \epsilon_r K_B T}{2 N_A q^2 I}}$$
 Equation 1

Where ϵ_0 is the vacuum permittivity ($8.85 \times 10^{-12} \text{ .m}^{-1}$), ϵ_r is the relative permittivity of water ($7.84 \times 10^{-10} \text{ F.m}^{-1}$ at 25°C) also called dielectric constant, K_B is the Boltzmann constant ($1.38 \times 10^{-23} \text{ J.K}^{-1}$), T is the temperature in K, q is the charge of an electron, I is the ionic strength and N_A is the

Avogadro number ($6.02 \times 10^{23} \text{ mol}^{-1}$). I is referred to as the ionic strength. The Debye length is proportional to the reciprocal of the ionic strength. The larger the concentration of ions, the more they "shield" the charged surface and the thinner the Debye length is. This is represented in figure 1 above by the dotted green line. As the ionic strength increases, the potential drops off faster and the effects of the charged surface are negated quicker (as a function of distance). As can be deduced from equation 1, the thickness of the double layer is dependent on the electrolyte concentration and can be estimated from the Debye-Hückel length (i.e., respectively 10 nm, 3 nm, 1 nm and 0.3 nm for electrolyte concentrations of 1 mM, 10 mM, 100 mM and 1 M).⁴⁴

3.2. Electrochemical behavior of $[\text{SiW}_{12}\text{O}_{40}]^{4-}$ on mesoporous silica film modified ITO electrode in highly acidic media

3.2.1. Cyclic voltammetry (CV) at pH 0.3 to 1.0

Figure 3 shows typical CV curves recorded at pH 0.3 (Fig. 3A) and pH 1 (Fig. 3B). Compared to bare ITO, the two successive monoelectronic processes (located at -0.26 V and -0.49 V) and the bielectronic step (at -0.65 V) occur at approximately the same potential values on the surfactant-free mesoporous silica film electrode (prior to CTAB extraction, no signal can be seen (red curve on Fig. 3A), confirming that the silica film is free of holes/defects). At pH 0.3, the modified electrode exhibits much larger peak currents compared to the ones obtained on bare ITO in 0.5 M H_2SO_4 (compare blue and black lines in Fig. 3A). This significant increase of the peak currents up to $I_{\text{film}}/I_{\text{ITO}} = 2.2$ (for the first signal) is attributed to an accumulation phenomenon due to favorable interactions between $[\text{SiW}_{12}\text{O}_{40}]^{4-}$ species and the silica walls that are positively charged in 0.5 M H_2SO_4 . The situation is different at pH 1 where a small decrease in the CV signals with respect to

bare ITO is observed (Fig. 3B). Although the silica walls are still positively charged at pH 1.0, one can expect a lower charge density than at pH 0.3, leading to a smaller accumulation power. It is also noteworthy that the ionic strength is different in these cases (0.1 M or 0.5 M H₂SO₄), inducing a thicker electrical double layer (EDL) in more diluted H₂SO₄ (i.e., larger Debye length), resulting in more restricted mass transport through the film at pH 1 and thus less intense CV peaks.

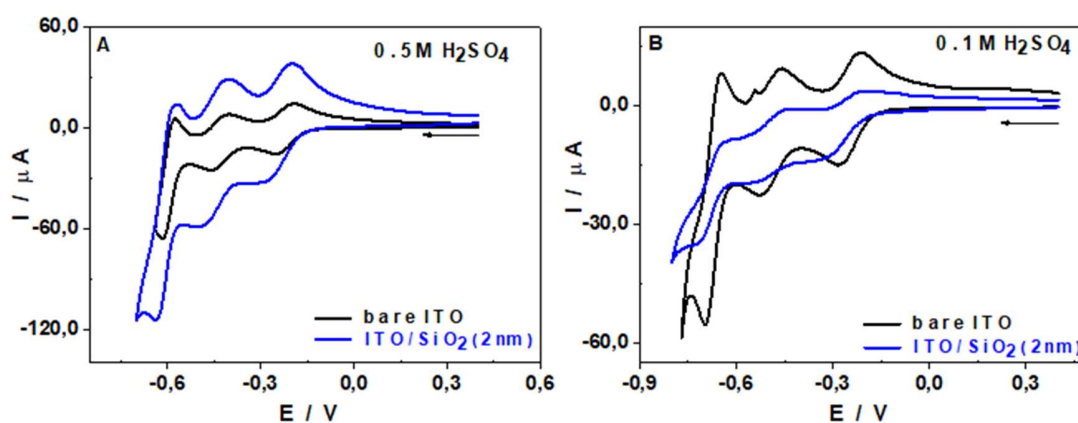


Figure 3. Cyclic voltammograms recorded in a solution containing 5.0×10^{-4} M $[\text{SiW}_{12}\text{O}_{40}]^{4-}$ and H₂SO₄ at concentrations adjusted to fix pH values at 0.3 (A) or 1.0 (B) using bare ITO electrode (black) and ITO covered with a mesoporous silica film after surfactant extraction (blue); a control experiment performed prior to surfactant extraction is also shown in red on part A of the figure.

3.2.2. Effect of ionic strength at pH 0.3 to 1.0

Effect of the ionic strength of the solution has been investigated by adding Na₂SO₄ to the above media and typical results are illustrated in Figure 4, showing the variation in intensity of the first voltammetric signal when passing from bare ITO to the film electrode. No significant changes in terms of peak current and peak potential values are observed on the electrochemical response of

$[\text{SiW}_{12}\text{O}_{40}]^{4-}$ on bare ITO when increasing the ionic strength of the electrolyte (see black lines in Figure 4). In contrast, noticeable changes of the CV signals is observed when adding Na_2SO_4 to the H_2SO_4 solutions. At pH 0.3, one can see an important decrease in peak intensity when adding increasing amounts of Na_2SO_4 in the medium (compare parts A-C in Figure 4), which can be assigned to a competition between the anionic electroactive species and the increasing amounts of SO_4^{2-} provided by both H_2SO_4 and Na_2SO_4 in the electrolyte solution. The effect is more drastic in $0.5 \text{ M } \text{H}_2\text{SO}_4 + 0.3 \text{ M } \text{Na}_2\text{SO}_4$ which corresponds to an ionic strength of 1.4 M. Media with ionic strength lower than 0.5 M cannot be checked at this pH value since 0.5 M H_2SO_4 solution is the minimum concentration required to reach this pH.

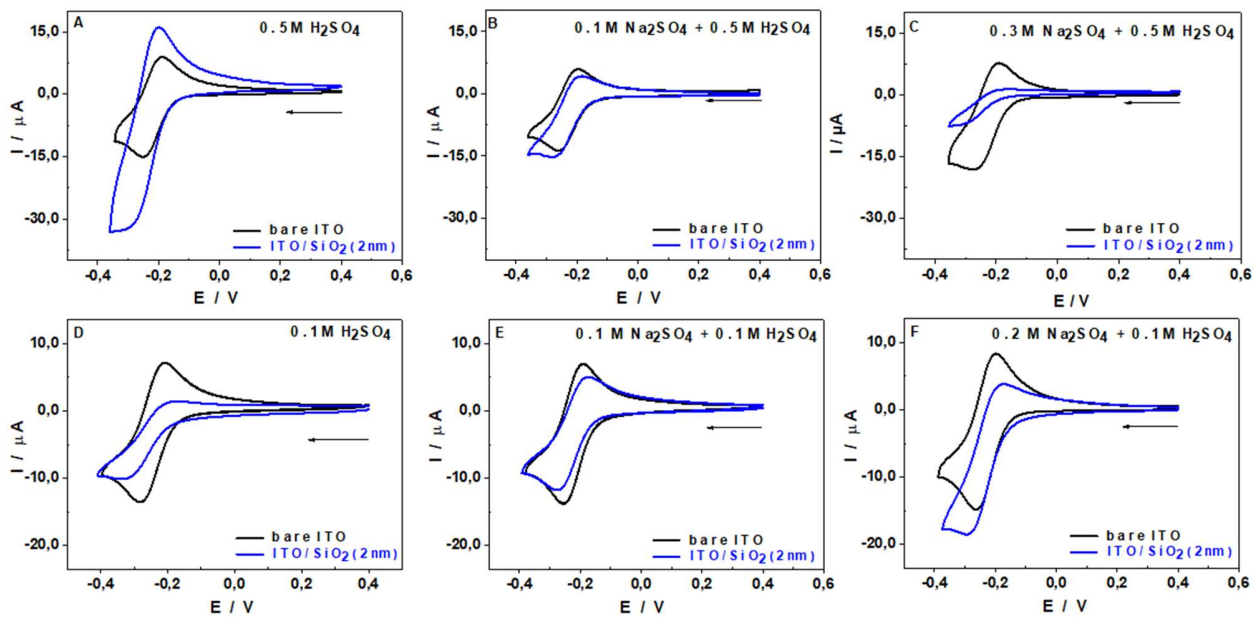
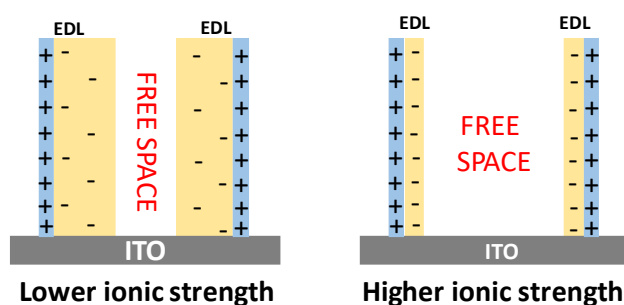


Figure 4. Cyclic voltammograms recorded in a solution containing $5.0 \times 10^{-4} \text{ M } [\text{SiW}_{12}\text{O}_{40}]^{4-}$ and H_2SO_4 at concentrations adjusted to fix pH values at 0.3 (A-C) or 1.0 (D-F) and Na_2SO_4 at selected concentrations (see on plots) to get various ionic strengths, using bare ITO electrode (black) and ITO covered with a mesoporous silica film after surfactant extraction (blue). Electrolyte media

composition: 0.5 M H₂SO₄ (A); 0.5 M H₂SO₄ + 0.1 M Na₂SO₄ (B); 0.5 M H₂SO₄ + 0.3 M Na₂SO₄ (C); 0.1M H₂SO₄ (D), 0.1M H₂SO₄ + 0.10 M Na₂SO₄ (E); 0.1 M H₂SO₄ + 0.2 M Na₂SO₄ (F).

At pH 1.0, the silica walls are still positive but the charge density is expected to be smaller than at pH 0.3 (resulting in lower response of [SiW₁₂O₄₀]⁴⁻, as discussed above), and the ionic strength of the starting solution (i.e., before adding Na₂SO₄) is also smaller. In that case (pH 1.0), small amounts of added Na₂SO₄ result first in some increase of peak currents (up to 0.2 M Na₂SO₄, see parts D-F in Figure 4) and then lead to some decrease at higher ionic strengths (see Table 1). Starting from a $I_{\text{film}}/I_{\text{ITO}}$ ratio of 0.70 in 0.1 M H₂SO₄ alone, it raises to 0.95 and 1.25 when adding 0.1 and 0.2 M Na₂SO₄, respectively, and then decreases down to 0.60 in 0.3 M Na₂SO₄. One can interpret these results on the basis of two parameters that are likely to affect the accumulation and transport of [SiW₁₂O₄₀]⁴⁻ species in the nanochannels. First, an increase of the ionic strength leads to a decrease in the thickness of the electrical double layer (EDL), contributing to facilitate free diffusion in the region outside the EDL generated adjacent to the positively charged silica walls⁴⁵ (to counterbalance the surface charge, see illustration on scheme 1), and thereby to more intense voltammetric signals for [SiW₁₂O₄₀]⁴⁻. The extent of the EDL can be approximately predicted by the Debye length λ_D , which depends on the molar concentration of the electrolyte and its thickness λ_D can be estimated by means of the Debye-Hückel parameter κ (Equation 1). When passing from an ionic strength of 0.1 M to 1.0 M, λ_D decreases from 1 nm to 0.3 nm; on the basis of a mesopore diameter of 2.1 nm, it is therefore necessary to increase the ionic strength above 0.1 M to open a free diffusion zone in the nanochannels. However, increasing too much the electrolyte concentration in the medium (e.g., above 0.1 M Na₂SO₄) contributes to enhance the competition between [SiW₁₂O₄₀]⁴⁻ and SO₄²⁻ anions for the positive sites in the film, resulting in a decrease in the voltammetric signals, as already discussed for pH 0.3 (Table 1). The best ionic strength has

thus to be found as a compromise between a value high enough to keep the EDL as thin as possible (and the free diffusion zone as large as possible in the nanochannels) but not too high to avoid competition of the electrolyte anions on the accumulation of $[\text{SiW}_{12}\text{O}_{40}]^{4-}$ species in the film.



Scheme 1. Schematic representation of the nanochannels in highly acidic medium (where the low pH induces positive charges on the silica walls) as a function of the ionic strength.

Note that the enhanced electrochemical response reaches a maximum in 0.1 M H_2SO_4 /0.2 M Na_2SO_4 solution for which an accumulation of the anionic electroactive species is observed on a silica thin film compared to ITO in a similar way as previously described at pH 0.3. Both media has a similar ionic strength, however in this case the ratio $I_{\text{film}}/I_{\text{ITO}}$ is about 1.3 which is quite smaller than the 2.2 observed at pH 0.3. The difference can be attributed to the lower positive charge density at pH 1 compared to pH 0.3.

3.2.3. Behavior of an amino-functionalized mesoporous silica film

Attempts to enhance the accumulation process have been also made by using an amino-functionalized silica film (i.e., containing ammonium moieties inside the mesochannels of the silica layer as the amine groups are protonated at pH 0.3 and 1.0). Such increase in the positive

charge density could favor even more the electrostatic interactions with the anionic POMs and contribute to enhance the amplification of their electrochemical response. However, the voltammetric peaks assigned to the electrochemical reduction of the $[\text{SiW}_{12}\text{O}_{40}]^{4-}$ became lower than observed on a non-modified silica thin film without any enhancement with respect to the bare electrode ($I_{\text{film}}/I_{\text{ITO}} = 0.7$ in the best cases, see Table 1). This can be explained by stronger resistance to mass transport of the electroactive species through the nanochannels (as otherwise reported for organically-functionalized mesoporous silica films^{8,9}), which is not compensated here by the larger number of positive sites.

3.2.4. Desorption of the $[\text{SiW}_{12}\text{O}_{40}]^{4-}$

Multiple successive cyclic voltammetry measurements have been performed using a $[\text{SiW}_{12}\text{O}_{40}]^{4-}$ loaded film electrode immersed in POM-free solutions of different compositions of electrolyte in order to determine the dependence of the desorption of $[\text{SiW}_{12}\text{O}_{40}]^{4-}$ as a function of pH and ionic strength of the medium. To this aim, the experiments have been carried out in conditions leading to the most important accumulation phenomenon of $[\text{SiW}_{12}\text{O}_{40}]^{4-}$ (i.e., pH 0.3, 0.5 M H_2SO_4), as obtained from recording up to 50 successive voltammetric scans (at 100 mV s^{-1}) with the mesoporous silica film electrode in 0.5 mM $[\text{SiW}_{12}\text{O}_{40}]^{4-}$. Subsequent desorption has been monitored by multisweep cyclic voltammetry after transferring the electrode into the various POM-free electrolytic solutions, and variations of the first cathodic peak currents with the number of CV scans have been plotted (Figure 5).

Depending on the solution composition (0.5 M H_2SO_4 (pH = 0.3); 0.1 M H_2SO_4 (pH = 1); 0.1 M H_2SO_4 + 0.1 M Na_2SO_4 (pH = 1); 0.1 M H_2SO_4 + 0.2 M Na_2SO_4 (pH = 1)), distinct variations can be seen. At pH 0.3, which corresponds to the solution of lowest pH and quite high ionic strength,

an extremely fast decrease in cathodic peak currents (I_{pc}) is observed, and I_{pc} values rapidly reach a steady-state value at ca. 15% of its initial intensity, suggesting that most $[\text{SiW}_{12}\text{O}_{40}]^{4-}$ species have been removed from the film. Such fast desorption process is explained by the ion exchange of $[\text{SiW}_{12}\text{O}_{40}]^{4-}$ for SO_4^{2-} anions from the electrolyte. The situation is significantly different at pH 1, which corresponds to the solution of lowest ionic strength, where desorption of $[\text{SiW}_{12}\text{O}_{40}]^{4-}$ is much less (steady-state I_{pc} values around 85% of their initial intensity). This is due to the lesser amount of competing SO_4^{2-} anions, and to the rather strong affinity of the bulky $[\text{SiW}_{12}\text{O}_{40}]^{4-}$ anions for the positively charged nanochannels. Intermediate behavior is observed when adding Na_2SO_4 to the pH 1 solution, with lower steady-state I_{pc} values for higher ionic strengths, as a result of increasing the amount of competing SO_4^{2-} anions into the solution. By controlling the ionic strength, it is therefore possible to tune the amount of $[\text{SiW}_{12}\text{O}_{40}]^{4-}$ keeping adsorbed into the film and exhibiting a stable CV response upon multiple potential scans.

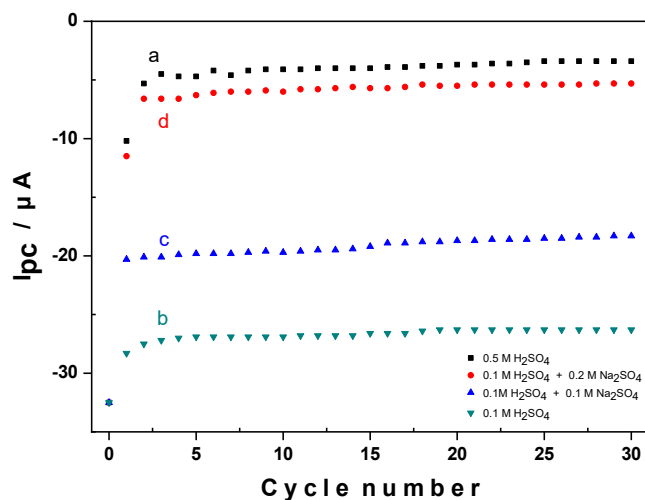


Figure 5. Variation of the intensity of the first cathodic peak currents obtained after transferring an electrode pretreated for 50 successive CV scans in 0.5 mM $[\text{SiW}_{12}\text{O}_{40}]^{4-}$ to a POM-free solution,

expressed as a function of the number of voltammetric scans recorded in electrolyte media of various compositions: 0.5 M H₂SO₄ (a); 0.1 M H₂SO₄ (b); 0.1 M H₂SO₄ + 0.1 M Na₂SO₄ (c); 0.1 M H₂SO₄ + 0.2 M Na₂SO₄ (d).

3.3. Electrochemical behavior of [SiW₁₂O₄₀]⁴⁻ on mesoporous silica film modified ITO electrode in slightly acidic media

3.3.1. CV and effect of ionic strength at pH 2 and 3

The electrochemical behavior of [SiW₁₂O₄₀]⁴⁻ has been subsequently studied at pH 2 and 3, where the silica walls contain less silanolate groups and might be neutral or slightly negatively charged. In these conditions, less pronounced electrostatic interactions are expected to affect the transport of POM species through the film. Figure 6 shows typical CV curves for [SiW₁₂O₄₀]⁴⁻ at pH 2. The ionic strength of the media has been varied by addition of Na₂SO₄. In the absence of Na₂SO₄ (Fig. 6A), no noticeable voltammetric signal is observed for [SiW₁₂O₄₀]⁴⁻ on the silica film electrode at pH 2 (0.01 M H₂SO₄). This absence of the cathodic processes is assigned to the very low ionic strength of the medium at pH 2 in the presence of only H₂SO₄ which is associated with an increase of the EDL thickness that can even be larger than the mesopore radius (leading to possible overlapping; a Debye length of the order of ~1 nm can be estimated from equation 1 for an ionic strength of 100 mM). By contrast, well-defined voltammetric signals for [SiW₁₂O₄₀]⁴⁻ progressively grow when adding 0.05 M or 0.1 M Na₂SO₄ in the medium (see respectively parts B&C in Figure 6), but the peak currents fail to reach the intensity obtained on bare ITO. This is again due to lowering the EDL thickness and thus enlarging the free diffusion zone in the nanochannels (scheme 1), but the effect is less pronounced than that observed above at pH 1 due

to few or no accumulation of $[\text{SiW}_{12}\text{O}_{40}]^{4-}$ on the silica walls. And the situation is even worse at pH 3 where the silica surface is neutral and starts even to become slightly negatively-charged, for which the voltammetric signals reach only ca. 2/3 of their intensity observed on bare ITO (Figure 7). In that case, no favorable interaction is expected between the POM and the silica surface and thus no accumulation of $[\text{SiW}_{12}\text{O}_{40}]^{4-}$ species into the film, the electrochemical response being essentially controlled by their diffusion through the nanochannels from the solution to the electrode surface.

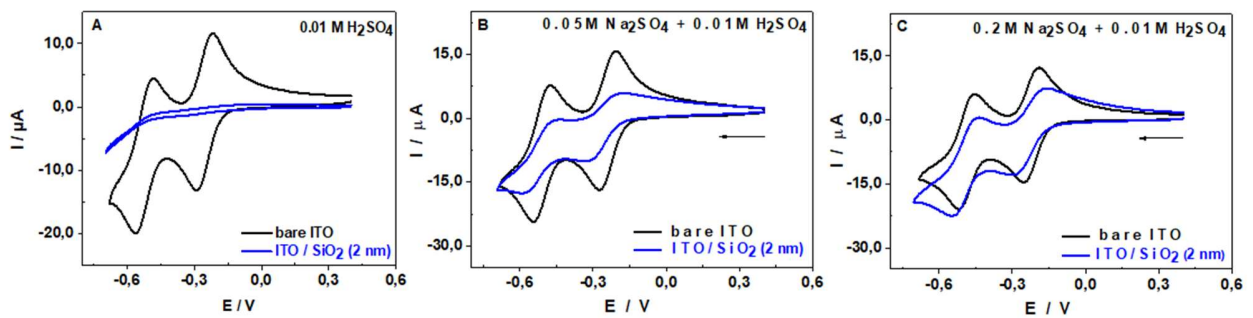


Figure 6. Cyclic voltammograms recorded in a solution containing 5.0×10^{-4} M $[\text{SiW}_{12}\text{O}_{40}]^{4-}$ at pH 2 (0.01 M H_2SO_4 , A) to which increasing amounts of Na_2SO_4 have been added (0.05 M (B) and 0.2 M (C)), using bare ITO electrode (black) and ITO covered with a mesoporous silica film after surfactant extraction (blue).

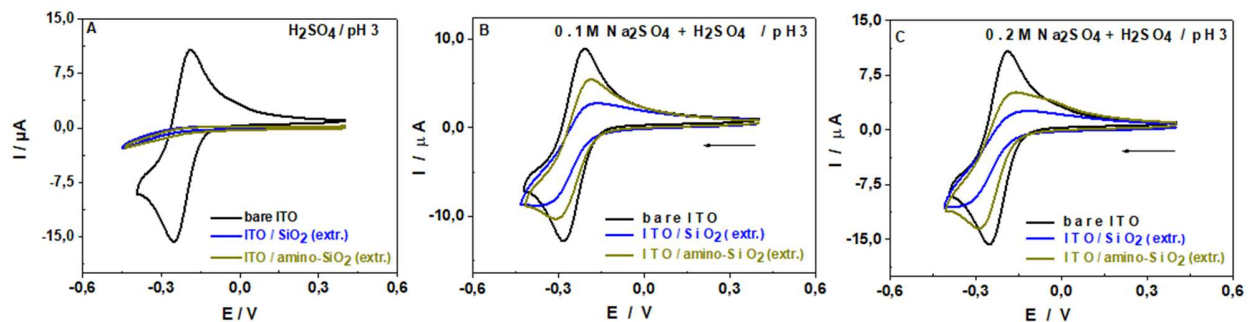


Figure 7. Cyclic voltammograms recorded in a solution containing 5.0×10^{-4} M $[\text{SiW}_{12}\text{O}_{40}]^{4-}$ and 0.001 M H_2SO_4 alone (A), or with 0.1 M Na_2SO_4 (B) or 0.2 M Na_2SO_4 (C), using bare ITO electrode (black), ITO covered with a mesoporous silica film after surfactant extraction (blue), and an amino-functionalized silica film on ITO (dark green).

A way to improve somewhat the voltammetric response of $[\text{SiW}_{12}\text{O}_{40}]^{4-}$ is via the introduction of amino functionalities in the silica films, which are positively charged in acidic media. As shown on Figure 7 (dark green curves), this contributes to slightly larger peak currents, suggesting some accumulation behavior arising from the presence of quaternary ammonium groups at pH 3. The effect is however not so overwhelming as these groups attached to the mesopore walls can also lead to steric hindrance that makes more complicated the diffusion of electroactive probes through the nanochannels. In the best case, $I_{\text{NH}_2\text{-film}}/I_{\text{ITO}}$ ratios of about 0.7 – 0.9 can be achieved in the presence of added Na_2SO_4 in the 0.1 – 0.3 M concentration range (Table 1).

Table 1. Summary of the ratios of peak current values observed at the film electrodes relative to bare ITO (I_{rel}), respectively for the three cathodic signals observed for 0.5 mM $[\text{SiW}_{12}\text{O}_{40}]^{4-}$ at a various pH and ionic strengths. The mesoporous films were respectively made of only silica (TEOS) or functionalized with amino groups (T/ NH_2). The ionic strength has been estimated considering only the first dissociation of H_2SO_4 .

Table 1.

[SiW ₁₂ O ₄₀] ⁴⁻						
pH = 0.3				I _{rel} = I _{film} / I _{ITO}		
[Na ₂ SO ₄]	[H ₂ SO ₄]	I		1 st wave	2 nd wave	3 rd wave
0	0.5	0.5	TEOS	2.20	2.00	1.35
			T/NH ₂	0.71	0.57	0.75
0.1	0.5	0.8	TEOS	1.00	1.00	0.70
0.3	0.5	1.4	TEOS	0.38	0.40	0.46
pH = 1.0				I _{rel} = I _{film} / I _{ITO}		
[Na ₂ SO ₄]	[H ₂ SO ₄]	I		1 st wave	2 nd wave	3 rd wave
0	0.1	0.1	TEOS	0.70	0.40	0.40
0.1	0.1	0.4	TEOS	0.95	1.00	1.00
0.2	0.1	0.7	TEOS	1.25	1.50	0.80
			T/NH ₂	0.74	0.56	0.70
0.3	0.1	1.0	TEOS	0.60	0.57	0.64
			T/NH ₂	0.57	0.50	0.42
pH = 2.0				I _{rel} = I _{film} / I _{ITO}		
[Na ₂ SO ₄]	[H ₂ SO ₄]	I		1 st wave	2 nd wave	3 rd wave
0.05	0.01	0.16	TEOS	0.60	0.50	0.56
0.2	0.01	0.61	TEOS	0.83	0.83	0.93
			T/NH ₂	0.91	1.00	1.00
pH = 3.0				I _{rel} = I _{film} / I _{ITO}		
[Na ₂ SO ₄]	[H ₂ SO ₄]	I		1 st wave	2 nd wave	3 rd wave
0.1	0.001	0.30	TEOS	0.72	1.02	0.94
0.2	0.001	0.61	TEOS	0.81	1.00	0.72
			T/NH ₂	0.91	0.90	0.88

3.3.2. Film behavior at pH 4

The electrochemical response of $[\text{SiW}_{12}\text{O}_{40}]^{4-}$ has been also investigated at pH 4.0 in acetate buffer. At pH 4 the silica films have an important density of negative charges that would make stronger the electrostatic repulsion with $[\text{SiW}_{12}\text{O}_{40}]^{4-}$. As expected, quasi non-existent and poorly defined signals are observed (Figure 8) as a result of hindered mass transport of these electroactive species through the mesochannels and therefore suppressed electrochemical response. No real effect of the ionic strength is observed. Again, the presence of quaternary ammonium cations onto the silica walls enhances the electrochemical response of $[\text{SiW}_{12}\text{O}_{40}]^{4-}$ compared to the non-modified silica film. However, even in the case of the amino-functionalized silica film the $I_{\text{film}}/I_{\text{ITO}}$ ratio does not reach the value close to the unity. Two reasons could contribute to explain this rather low $I_{\text{film}}/I_{\text{ITO}}$ ratio: a first one is that the quaternary ammonium cations are not numerous enough to compensate the negative charge present on the silica walls due to the silanolate groups, and a second one involves steric hindrance for mass transport of $[\text{SiW}_{12}\text{O}_{40}]^{4-}$ inside the mesopores (partially occupied by the protonated amine groups); probably both phenomena co-exist and it remains difficult to make clear distinction.

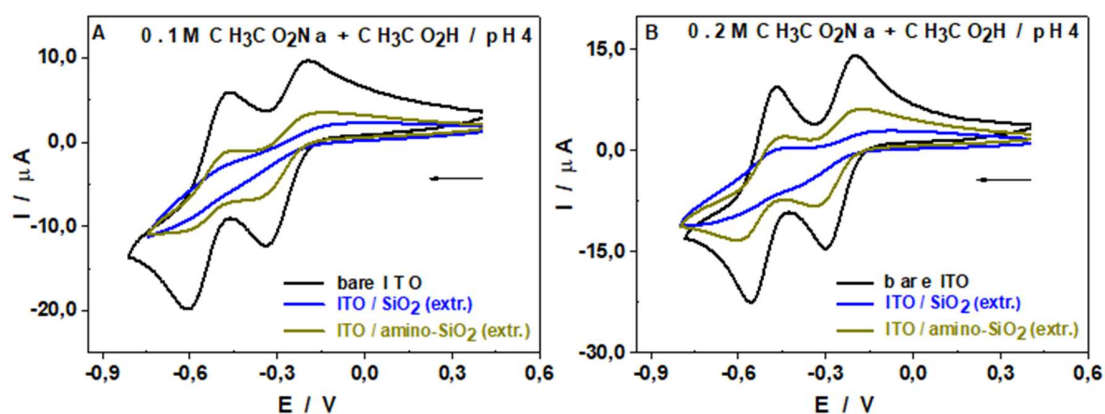
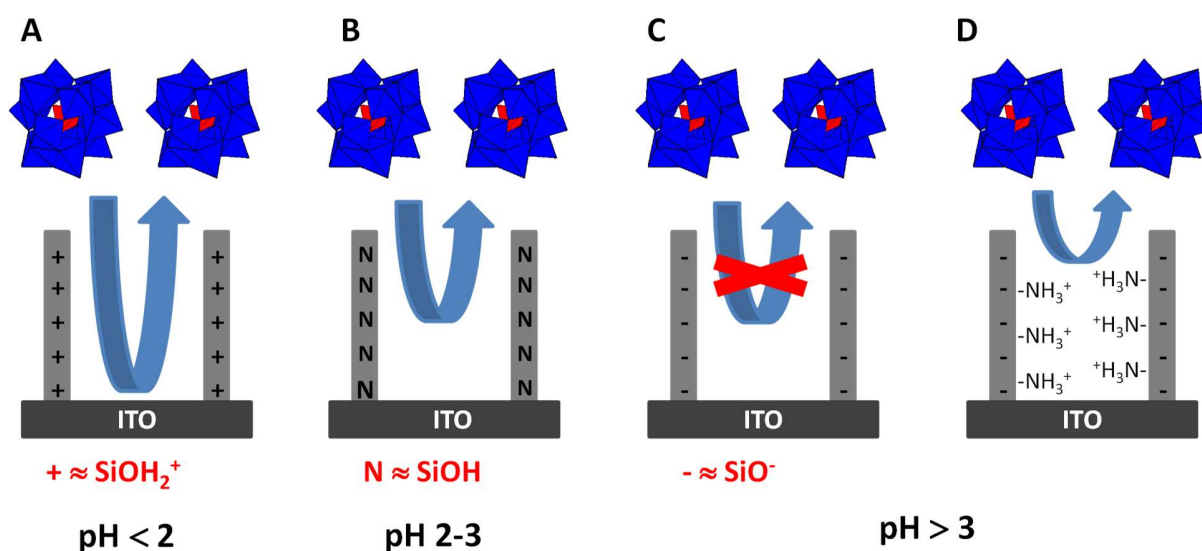


Figure 7. Cyclic voltammograms of 5.0×10^{-4} M $[\text{SiW}_{12}\text{O}_{40}]^{4-}$ in acetate buffer at pH 4.0 (0.1 M (A) or 0.2 M (B)), using bare ITO electrode (black) and ITO covered with a mesoporous silica film after surfactant extraction (blue).

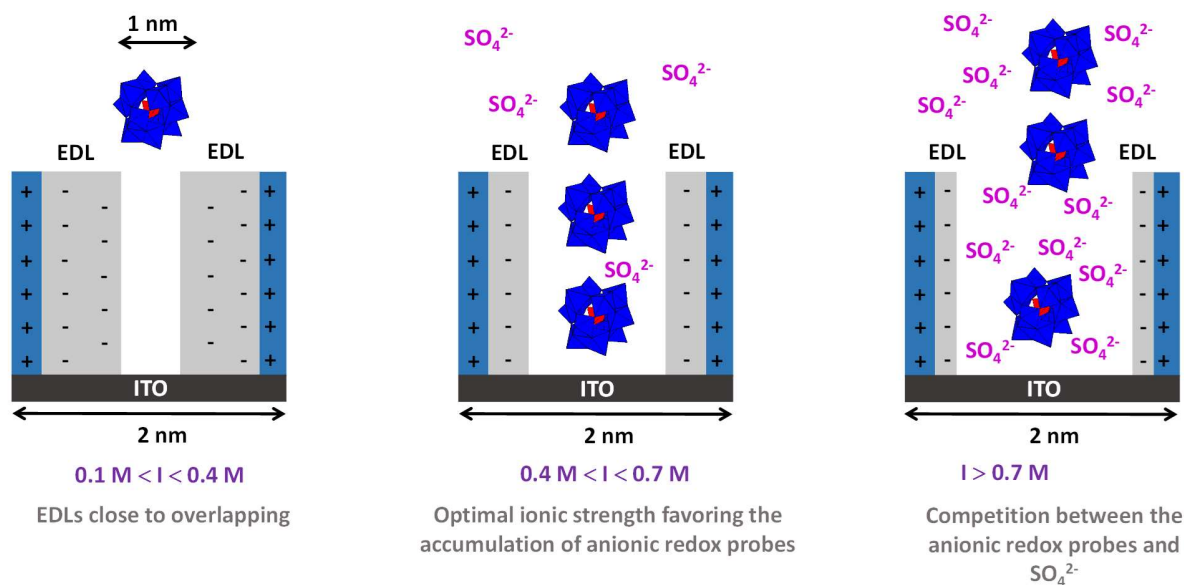
4. Concluding remarks

The voltammetric response of $[\text{SiW}_{12}\text{O}_{40}]^{4-}$ has been studied using ITO electrodes covered with vertically-oriented mesoporous silica films. The results have demonstrated on one hand, the possibility to get well-defined electrochemical signals for such a bulky anion and, on the other hand, a significant influence of pH and ionic strength of the medium on these processes. The effect of pH is illustrated on Scheme 2. Taking into account the amphoteric character of silica, the surface of mesopore walls can be either positive (due to $\equiv\text{SiOH}_2^+$ functions, prominent at $\text{pH} < 2$), neutral (mainly $\equiv\text{SiOH}$ groups at $\text{pH} 2\text{-}3$), or negative (due to $\equiv\text{SiO}^-$ at $\text{pH} > 3$). As a consequence, POM anions were likely to be accumulated only in very acidic media, leading to large CV peaks (as large as low was the pH), whereas the electrochemical responses were suppressed at pH above 3 due to electrostatic repulsions from the negatively charged mesopore channels (it is possible to

circumvent somewhat this limitation by introducing positive charges by functionalization with propylammonium moieties but their presence in the small channels contributed to induce some resistance to mass transport and thus moderately intense peak currents). An intermediate behavior was observed on neutral films (pH 2-3) for which $[\text{SiW}_{12}\text{O}_{40}]^{4-}$ species were able to cross the film without noticeable accumulation/rejection phenomena. Ionic strength also played an important role. As illustrated on Scheme 3, it has to be high enough to enable the existence of a free diffusion zone in the small channels (thanks to narrow EDL layers), and thus large voltammetric signals, but not too high to avoid competition of the electrolyte anions with the $[\text{SiW}_{12}\text{O}_{40}]^{4-}$ probes for the binding sites (which resulted in lower current intensities).



Scheme 2. Schematic illustration of the surface charge of silica nanochannels as a function of pH and their effect on the film permeability to the anionic redox probes. A) pH < pI: Positive charge density. B) pH = pI: Neutral silica. C) pH > pI: Negative charge density. D) Amino-functionalized silica film at pH > pI (protonated at pH lower than the pK_a of ~10).



Scheme 3. Schematic representation of the influence of ionic strength on the ingress of POM anions through positively charged nanochannels (acidic media) as a result of variations in EDL thickness, and competitive effects in concentrated sulfate solutions.

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