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# Electro-induced surfactant self-assembly driven to vertical growth of oriented mesoporous films

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## CONSPECTUS

Supramolecular soft-templating approaches to mesoporous materials have revolutionized the generation of regular nanoarchitectures exhibiting unique features such as uniform pore structure with tuneable dimensions, large surface area and high pore volume, variability of composition and/or ease of functionalization with a wide range of organo-functional groups, or good hosts for the *in situ* synthesis of nanoobjects. One appealing concept in this field is the development of ordered mesoporous thin films as such a configuration has proven to be essential for various applications including separation, sensing, catalysis (electro and photo), energy conversion and storage, photonics, solar cells, photo- and electrochromism, low- $k$  dielectric coatings for microelectronics, bio and nanobio devices or biomimetic surfaces. Supported or free-standing mesoporous films are mostly prepared by evaporation induced self-assembly methods, thanks to their good processing capability and flexibility to manufacture mesostructured oxides and organic-inorganic hybrids films with periodically organized porosity.

One important challenge is the control of pore orientation, especially in one-dimensional nanostructures, which is not straightforward from the above evaporation induced self-assembly methods. Accessibility of the pores represents another critical issue, which can be basically ensured in the event of effective interconnections between the pores, but the vertical alignment of mesopore channels will definitely offer the best configuration to secure the most efficient transfer processes through the mesoporous membranes. The orthogonal growth of mesochannels is however not thermodynamically favored, requiring the development of methods enabling self-organization through non-equilibrium states. We found that electrochemistry afforded a real boon to tackle this problem via the electrochemically assisted self-assembly (EASA) method, which not only provides a fast and versatile way to generate highly ordered and hexagonally packed mesopore channels, but also constitutes a real platform for the development of functionalized oriented films carrying a wide range of organo-functional groups of adjustable composition and properties.

This account introduces the EASA concept and discusses its development along with the significant progress made from its discovery, notably in view of recent advances on the functionalization of oriented mesoporous silica films, which expand their fields of application. EASA is based on the *in situ* combination of electrochemically-triggered pH-induced polycondensation of silica precursors with electrochemical interfacial surfactant templating, leading to the very fast (few seconds) growth of vertically aligned silica walls through self-assembly around surfactant hemi-micelles transiently formed onto the underlying support. This method benefits from the possibility to deposit uniform thin films onto surfaces of different nature and complex morphologies including at the microscale. From this discovery, our research expanded to cover domains beyond the simple production of bare silica films, turning to the

challenge of incorporation and exploitation of organo-functional groups or nanofilaments. So far, the great majority of methods developed for the functionalization of mesoporous silica is based on post-synthesis grafting or co-condensation approaches, which suffer from serious limitations with oriented films (pore blocking, lack of ordering). We demonstrated the uniqueness of EASA combined with click chemistry to afford a versatile and universal route to oriented mesoporous films bearing organo-functional groups of multiple composition. This opened perspectives for future developments and applications, some of which (sensing, permselective coatings, energy storage, electrocatalysis, electrochromism) are also considered in this account.

#### KEY REFERENCES

- Goux, A.; Etienne, M.; Aubert, E.; Lecomte, C.; Ghanbaja, J.; Walcarius, A. Oriented Mesoporous Silica Films Obtained by Electro-Assisted Self-Assembly (EASA). *Chem. Mater.* **2009**, *21*, 731–741.<sup>1</sup> *This work describes the basics of EASA and the main parameters governing the process; it establishes the conditions required to form aggregate-free mesoporous thin films.*
- Vilà, N.; Ghanbaja, J.; Aubert, E.; Walcarius, A. Electrochemically Assisted Generation of Highly Ordered Azide-Functionalized Mesoporous Silica for Oriented Hybrid Films. *Angew. Chem. Int. Ed.* **2014**, *53*, 2945–2950.<sup>2</sup> *This study reports a universal route for the generation of highly functionalized mesoporous silica films with vertically aligned nanochannels.*
- Nasir, T.; Herzog, G.; Liu, L.; Hébrant, M.; Despas, C.; Walcarius, A. Mesoporous Silica Thin Films for Improved Electrochemical Detection of Paraquat. *ACS Sensors* **2018**, *3*, 484–493.<sup>3</sup> *This work investigates the exploitation of charge selectivity in oriented mesoporous silica thin films for rapid and sensitive detection of a pesticide in real medium.*

• Wang, J.; Vilà, N.; Walcarius, A. Redox-Active Vertically-Aligned Mesoporous Silica Thin Films as Transparent Surfaces for Energy Storage Applications. *ACS Appl. Mater. Interfaces* **2020**, *12*, 24262–24270.<sup>4</sup> *This study was the first to demonstrate the ability of EASA to prepare novel pseudocapacitive hybrid materials based on electron hopping electron transfer mechanism.*

## 1. INTRODUCTION

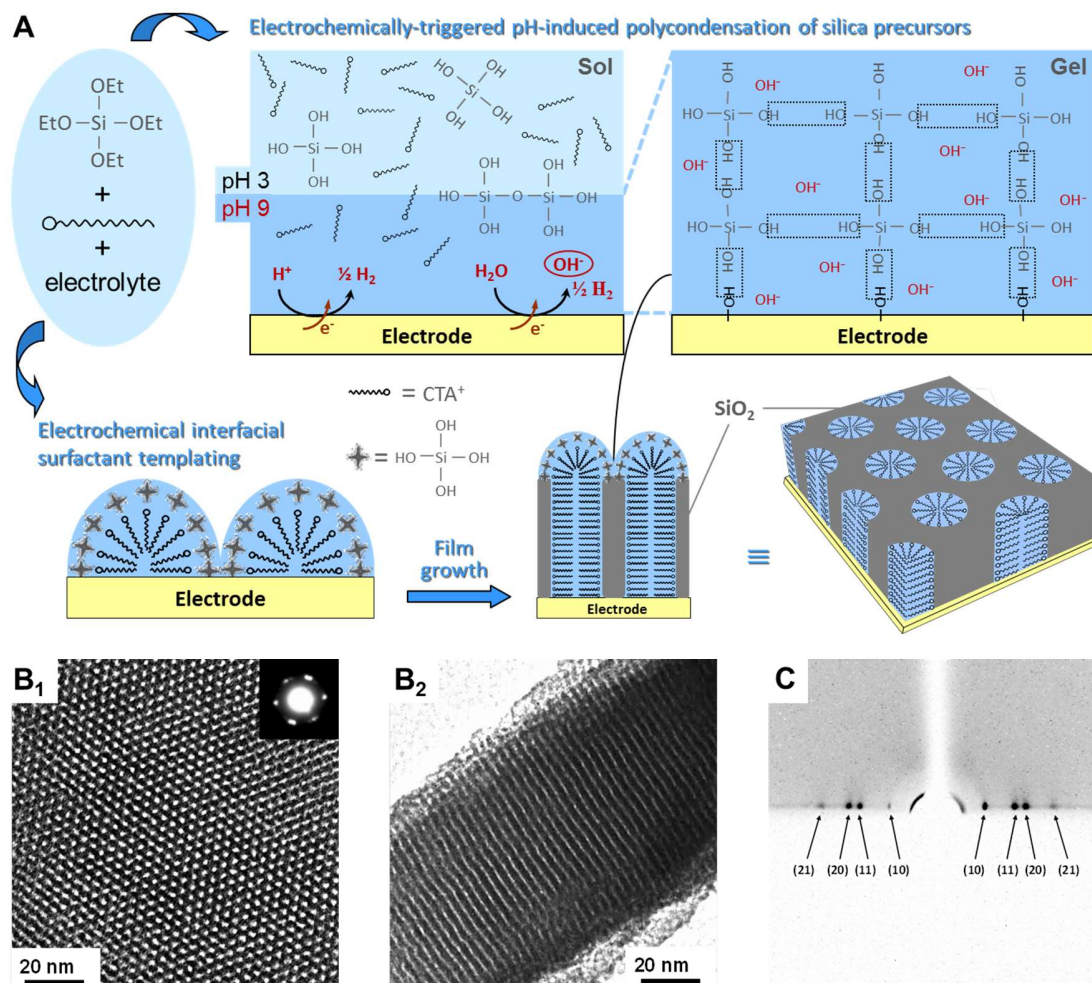
Supramolecular soft-templating approaches promote the development of ordered mesoporous materials with multilevel nanoarchitectures.<sup>5-7</sup> Their unique features (uniform pore structure with tuneable dimensions, large surface area and pore volume, variability of composition and/or ease of functionalization with a wide range of organo-functional groups, hosts for the *in situ* synthesis of nanoobjects) make them very attractive in various fields. They are of particular interest for electrochemical purposes (sensors, energy storage), by exploiting the fast transport processes ensured by such regular nanostructures.<sup>8,9</sup> On the other hand, the fabrication of ordered mesoporous thin films is growingly appealing as such a configuration has proven to be essential for various applications including separation, sensing, catalysis (electro and photo), energy conversion and storage, photonics, solar cells, photo- and electrochromism, low-*k* dielectric coatings for microelectronics, bio and nanobio devices or biomimetic surfaces.<sup>10</sup> So far, mesostructured oxides and organic-inorganic hybrids films with periodically organized porosity are mostly prepared by evaporation induced self-assembly (EISA), a sol-gel method in which solvent evaporation leads to increased surfactant concentration promoting the self-assembly of silica-surfactant micelles and their deposition as lyotropic liquid crystalline mesophases onto a solid support.<sup>11,12</sup> The control of pore orientation, especially in one-dimensional nanostructures,<sup>13</sup>

represents important challenge as it is not straightforward from the EISA methods, even if some progress emerged from attempting to control the alignment of mesochannels with respect to the underlying support.<sup>14</sup> Substrate patterning, epitaxial growth, or external field orientation, are usually required to get preferential vertical orientation of mesopores instead of the thermodynamically favoured in-plane orientation.<sup>13,14</sup> Accessibility of the pores represents another critical issue, which can be basically ensured in the event of effective interconnections between the pores,<sup>15,16</sup> (really effective in 3D mesophases generated by EISA<sup>17</sup>) but the vertical alignment of mesopore channels will offer an ideal configuration to secure efficient transfer processes through the mesoporous membranes. We discovered that electrochemistry is likely to tackle the above problems via a subtle combination of electrochemically induced surfactant self-assembly and sol-gel electrodeposition.<sup>18</sup> This led to the development of the so-called electro-assisted self-assembly (EASA) method,<sup>1</sup> which not only provides a fast and versatile way to generate highly ordered and hexagonally packed mesopore channels, but also constitutes a real platform for the development of functionalized oriented films carrying a wide range of organo-functional groups of adjustable composition and properties.<sup>2,19</sup> Actually, electrochemical deposition has been widely used for the preparation of electroactive and/or conducting materials, and it can be also applied as an advanced approach for the synthesis of nanoporous metal or alloy architectures,<sup>20,21</sup> but it is less common for generating non-redox and insulating metal oxides or hydroxides for which indirect electrochemical synthesis methods should be considered.<sup>22</sup>

This account describes the EASA concept from its discovery,<sup>18</sup> development and optimization,<sup>1</sup> to the emerging applications,<sup>3,4</sup> through discussions on the intrinsic properties of the oriented silica nanochannel membranes and their modulation, as well as the original strategies reported for their functionalization,<sup>2</sup> by focusing primarily on the main advances made in our group.

## 2. THE EASA CONCEPT

The sol-gel process is widely exploited for the preparation of silica-based materials. It involves two reactions, the hydrolysis and condensation of silica precursors, which occur simultaneously or successively. Their rates are strongly pH-dependent (Figure S1), the hydrolysis being fast at pH 3-4 while condensation accelerated when increasing pH above 4 (or in ultra-acidic media (pH<1)). Based on this knowledge, starting from a stable sol at pH 3, one can electrochemically trigger a pH increase at the electrode/solution interface by the application of a suitable cathodic potential leading to polycondensation of the silica precursors and film deposition onto the electrode surface (Figure 1A). The applied potential not only plays the role of generating the hydroxyl catalyst but also contributes to electrochemical interfacial surfactant templating to induce the growth of the mesopore channels orthogonally to the underlying electrode support. Thanks to the transient formation of cationic hemimicelles onto the electrode surface under potential control,<sup>23</sup> their favourable electrostatic interactions with the negatively charged silica subunits (as nanobuilding blocks<sup>24</sup>) likely to form at pH 9-10, an oriented mesostructure is formed within few seconds under kinetic control (the final material being heated at 130°C in order to complete the formation of siloxane bonds in the silica walls).<sup>18</sup> This mechanism is conceptually different from the evaporation techniques, for which material formation starts at the solution/air interface and then the film deposits onto the solid support, as EASA enables the film growth from the electrode surface thus ensuring its unique vertical orientation. Microscopic examination confirms both the highly ordered hexagonal packing of mesopore channels and their vertical alignment through the membrane (Figure 1B), a structure being confirmed by grazing incidence X-ray diffraction (Figure 1C), demonstrating the ability of EASA to generate uniform deposits over wide areas.<sup>1,18</sup> The structure is kept integrally after surfactant removal.



**Figure 1.** (A) Schematic illustration of the EASA process. (B) TEM images of the ordered and oriented mesoporous silica film (B<sub>1</sub> top view with electron diffraction pattern as inset; B<sub>2</sub> cross-section). Reproduced with permission from ref. 18. Copyright 2007 Nature Publishing Group. (C) Typical GI-XD pattern confirming the hexagonal packing of vertically aligned mesopore channels. Reproduced with permission from ref. 1. Copyright 2009 American Chemical Society.

This concept can be extended to the synthesis of mesoporous metal films with perpendicular nanochannels,<sup>21,25</sup> for which driving forces are also the potential-controlled surface aggregation of surfactants and the favourable surfactant-precursors interactions, but the metal nanostructure is built by direct electrochemical reduction of the metal precursors (contrary to the above indirect electrodeposition where electrochemistry is used for generating OH<sup>-</sup> species likely to induce film

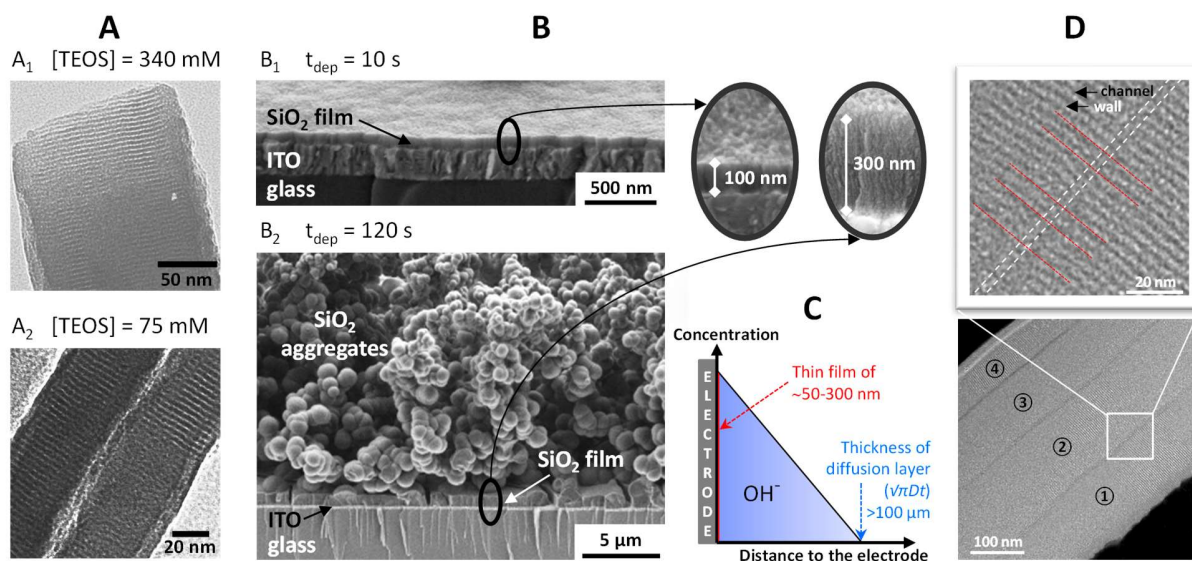


growth). The electrochemical synthesis of oriented mesostructures of metal oxides via potential-triggered surfactant assembly onto a solid support is also possible, by exploiting the ability of anionic hemi-micelles to form on electrodes and to interact with metal cations which are then precipitated in the form of metal oxides or hydroxides upon the generation of  $\text{OH}^-$  species, leading to the vertical growth of the material.<sup>26</sup> This demonstrates that electro-induced surfactant self-assembly is indeed a versatile approach to drive the vertical growth of a wide range of oriented mesoporous films (in principle to any material that can be electrochemically deposited, directly or indirectly, whose precursors are likely to interact favourably with interfacial amphiphilic structures).

### 3. DEVELOPMENT AND INTEREST OF THE METHOD

Three main parameters are affecting the EASA process: the precursor concentration, the electrodeposition time and the applied potential. Tuning the concentration of silica precursor (e.g., TEOS, tetraethoxysilane) influences the polycondensation rate and therefore the film thickness (Figure 2A), which can be easily adjusted between typically 40 and 150 nm (for [TEOS] ranging between 75 and 340 mM). The amount of surfactant (e.g., CTAB, cetyltrimethylammonium bromide) in the synthesis medium does not affect the film growth rates and ordered/oriented mesostructures can be formed in a rather wide window around the critical micellar concentration, providing the CTAB/TEOS molar ratio is maintained in the 0.16-0.64 range.<sup>1</sup> Increasing the deposition time evidently leads to thicker deposits, however associated to the formation of (usually unwanted) aggregates (Figure 2B). This is explained by the presence of the electrogenerated  $\text{OH}^-$  catalysts in a much wider domain ( $\sim 100 \mu\text{m}$  range, corresponding to the diffusion layer) than the film thickness ( $\sim 100 \text{nm}$  range) (Figure 2C), in which ‘bulk’

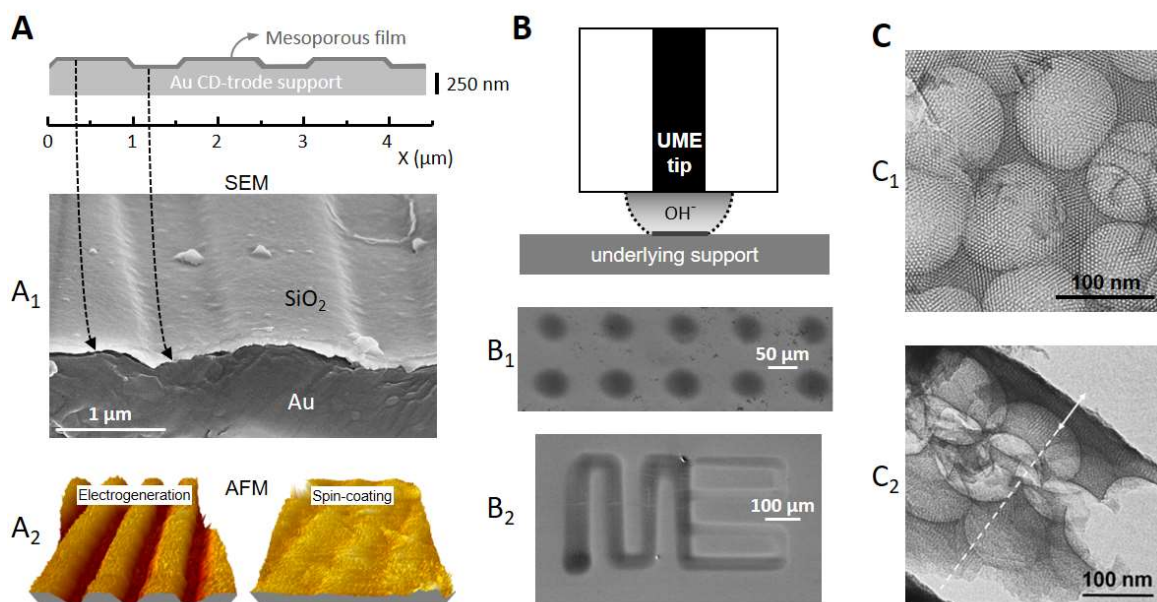
precipitation of mesoporous silica particles/aggregates can occur, especially at long deposition times (>30s) and very cathodic potentials (huge amounts of generated OH<sup>-</sup> species).<sup>1,18</sup> If wishing to get only the aggregate-free mesoporous films, it is thus important to control these parameters with using diluted solutions ([TEOS]<125 mM) and short deposition times (<10 s) at an appropriately low potential value (depending on the nature of the electrode).<sup>1</sup> For reaching thicker aggregate-free films, one has to apply a sequential deposition approach to multilayered films, which is easily accessible by EASA,<sup>27</sup> while keeping interconnections open between each layer (Figure 2D). Finally, using alkylammonium surfactants of distinct alkyl chain lengths (C<sub>14</sub> to C<sub>18</sub>), it is possible to vary somewhat the mesopore diameters from 1.3 to 3.3 nm, with lattice parameters d(10) ranging from 2.9 to 3.5 nm (Table S1).<sup>22</sup>



**Figure 2.** (A) Effect of precursor concentration on the mesoporous silica film thickness (cross-section TEM images obtained for films prepared by EASA at -1.3 V for 20 s on ITO electrode using TEOS concentrations of respectively 340 mM (A<sub>1</sub>) and 75 mM (A<sub>2</sub>) with  $n\text{CTAB}/n\text{TEOS} = 0.32$ ). Reproduced with permission from ref. 1. Copyright 2009 American Chemical Society. (B) Effect of deposition time ( $t_{\text{dep}}$ ) on the film morphology (cross-section FE-SEM images obtained for samples prepared as in (A) for  $t_{\text{dep}} = 10$  s (B<sub>1</sub>) and 120 s (B<sub>2</sub>), with enlargements to see the

uniform film thickness). (C) Scheme representing the catalyst ( $\text{OH}^-$ ) concentration profile at the electrode/solution interface. (D) Cross-section TEM images of a multilayer film generated by four successive EASA steps performed as in (B<sub>1</sub>), obtained from vertical slices of the film cut by ionic abrasion by focused ion beam (top image is a magnified view at the intersection between the two first electrodeposited layers). Adapted with permission from ref. 27. Copyright 2017 Elsevier.

Concurrent to our EASA method are some more recent approaches to hexagonal mesostructures perpendicular to the substrate surface, such as the Stöber-solution growth method (involving the cross-linking of silica precursors by an ammonia catalysts),<sup>28</sup> or an oil-induced co-assembly strategy,<sup>29</sup> which offer the advantage of being applicable to film formation on nonconductive supports, but require much longer synthesis times (from hours to days). A real interest of EASA is its suitability for uniform deposition onto substrates of complex morphology or at the local (micrometric) scale. For example, we demonstrated successful electrodeposition of an oriented mesoporous film of a uniform thickness of 80 nm onto a streaked gold electrode originating from a recordable CD (Au CD-trode, with base bands of 1- $\mu\text{m}$  width separated by stripes of 0.5- $\mu\text{m}$  width and 100 nm height),<sup>18</sup> fitting exactly the substrate morphology at the nanometric scale contrary to similar film prepared by classical spin-coating for which the streaked geometry is almost invisible after deposition (Figure 3A). This can be also applied to other supports of various size and shape, such as microfibers, microporous inverse Opal-like substrates, or even exfoliated graphite supports.<sup>30,31</sup> Another attractive feature of EASA is the possibility to form patterned mesoporous silica thin films at the microscale (using an ultramicroelectrode to generate locally the hydroxyl catalyst, see Figure 3B),<sup>32</sup> offering an alternative to the use of lithographical techniques (otherwise applied to patterning of oriented mesoporous metal films, for instance).<sup>33</sup> Hierarchical macro-mesoporous films can be also prepared by EASA through polystyrene bead assemblies while maintaining the vertical orientation throughout the membrane (Figure 3C).<sup>34</sup>



**Figure 3.** (A) Illustration of the possibility of EASA to generate a uniform mesoporous silica film onto a support of streaked morphology at the microscale: (A<sub>1</sub>) cross-section SEM view; (A<sub>2</sub>) AFM images comparing the deposits obtained by EASA (electrogeneration) and the classical evaporation technique (spin-coating). Adapted with permission from ref. 18. Copyright 2007 Nature Publishing Group. (B) Illustration of possible patterning by local EASA using an ultramicroelectrode tip (UME,  $\varnothing = 25 \mu\text{m}$ ) generating the OH<sup>-</sup> catalyst close to the support: SEM images of (B<sub>1</sub>) 10 dots and (B<sub>2</sub>) a pattern obtained by moving the tip (at  $15 \mu\text{m s}^{-1}$ ) in the  $x$ - $y$  plane. Reproduced with permission from ref. 32. Copyright 2011 American Chemical Society. (C) TEM images of fragments of mesoporous silica generated by EASA through polystyrene beads assembly on ITO electrode (C<sub>1</sub> top view and C<sub>2</sub> cross-section). Reproduced with permission from ref. 34. Copyright 2010 American Chemical Society.

EASA can be applied to oriented film deposition, either potentiostatically or galvanostatically,<sup>1</sup> on various conducting surfaces of different nature (Au, Pt, Cu, several C materials, indium or fluoride-doped tin oxide electrodes (ITO, FTO), or Si wafers). However, good adhesion to the substrate is only achieved for hydroxylated surfaces (ITO, FTO), whereas other electrodes need to be adequately activated (as carbon)<sup>35</sup> or pretreated (electrografting of aminosilane on C,<sup>36</sup> or attachment of mercaptosilane on Au,<sup>37</sup> for instance) to get films durably attached to the support.

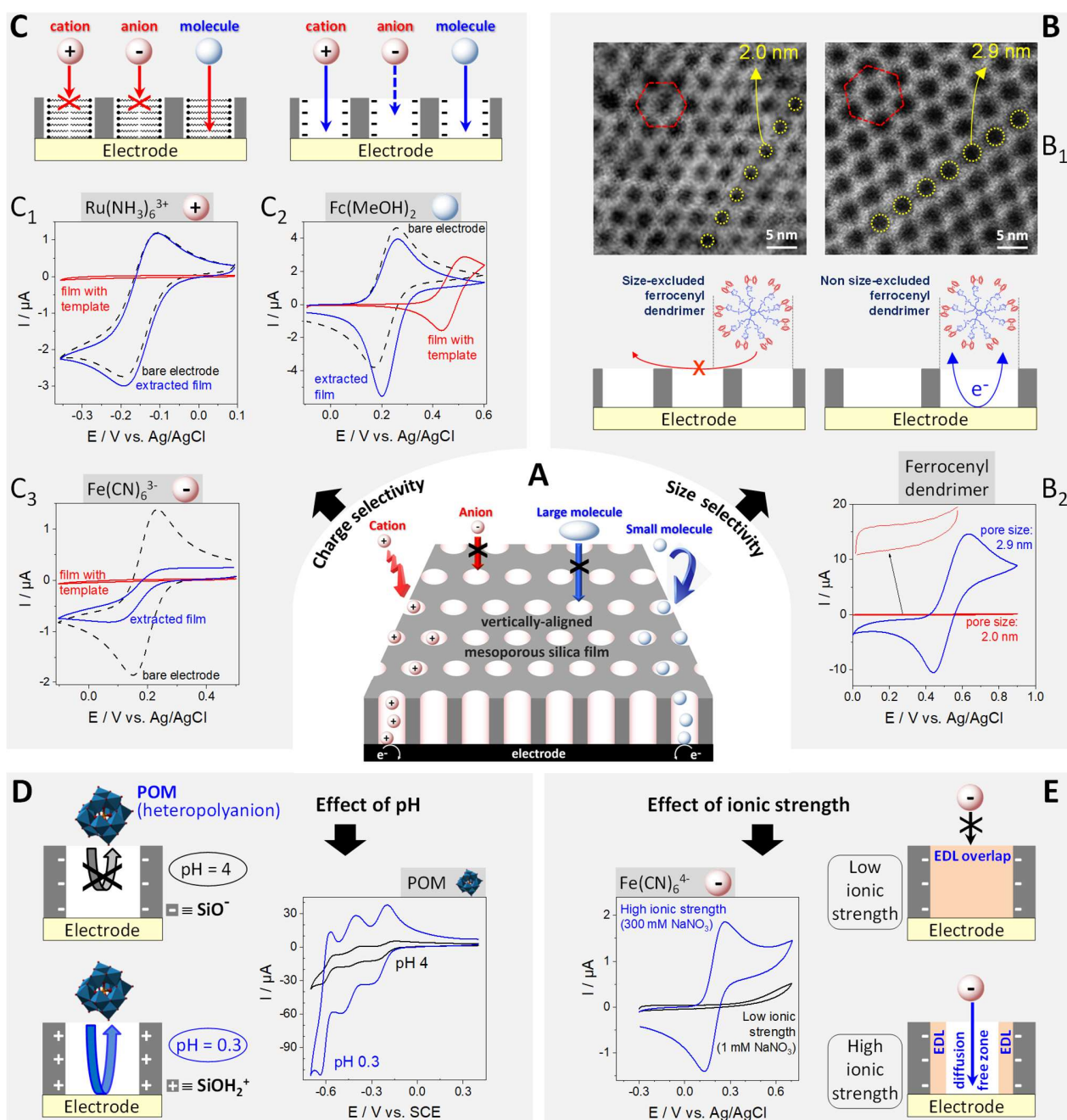
#### 4. INTRINSIC FILM PROPERTIES AND THEIR MODULATION

Vertically aligned silica nanochannel membranes exhibit both size and charge selectivity (Figure 4A). Redox-active molecules that are too large to enter the mesopores (e.g., haemoglobin) are not likely to reach the electrode surface and are therefore not detectable.<sup>38</sup> This is especially impressive when using two films of quite distinct pore diameters but rather close to each other (2.0&2.9 nm) and a redox probe of size ranging in-between (i.e.,  $1.9 \times 2.4 \times 2.7 \text{ nm}^3$  for the nonaferrocenyl dendrimer),<sup>39</sup> demonstrating a perfect molecular sieving effect at the nanometric scale (Figure 4B). Although transport phenomena of non size-excluded species through the film are usually very fast thanks to the vertical alignment of 1D channels<sup>1</sup> (i.e., diffusion rates of the same order of magnitude as in interconnected 3D cubic phases<sup>16,22</sup>), they can be temporally trapped in the mesochannels, resulting in hindered molecular diffusion and opening the door to investigating single redox events by fluorescence.<sup>36</sup>

Using redox probes of different charge (cationic  $\text{Ru}(\text{NH}_3)_6^{3+}$ , anionic  $\text{Fe}(\text{CN})_6^{3-}$ , neutral ferrocene-dimethanol  $\text{Fc}(\text{MeOH})_2$ ) enables evidencing charge selectivity properties by means of cyclic voltammetry (CV) characterization (Figure 4C). For reversible probes as used here, peak currents recorded by CV are proportional to their concentration and rate of diffusion through the film, according to the Randles-Sevcik equation (Eq. 1 at 25°C):

$$i_p = 2.69 \times 10^5 n^{\frac{3}{2}} A D^{\frac{1}{2}} C v^{\frac{1}{2}} \quad (1)$$

where  $i_p$  is peak current,  $n$  number of exchanged electrons,  $A$  electrode area in  $\text{cm}^2$ ,  $D$  diffusion coefficient in  $\text{cm}^2 \cdot \text{s}^{-1}$ ,  $C$  concentration in  $\text{mol} \cdot \text{cm}^{-3}$ , and  $v$  potential scan rate in  $\text{V} \cdot \text{s}^{-1}$ .



**Figure 4.** (A) Illustration of the size and charge selectivity properties of the vertically aligned mesoporous silica film. (B) Size selectivity: (B<sub>1</sub>) TEM images (top view) of two nanochannel membranes with distinct pore diameters (2.0 & 2.9 nm); (B<sub>2</sub>) CV curves recorded with these two film electrodes using a nonaferrocenyl dendrimer (2.4 nm size) in solution. Reproduced with permission from ref. 39. Copyright 2016 American Chemical Society. (C) Charge selectivity: CV curves recorded at a film (pore  $\varnothing$  = 2.0 nm) electrode using (C<sub>1</sub>) Ru(NH<sub>3</sub>)<sub>6</sub><sup>3+</sup> cations, (C<sub>2</sub>) neutral

Fc(MeOH)<sub>2</sub>, and (C<sub>3</sub>) Fe(CN)<sub>6</sub><sup>3-</sup> anions in solution. Adapted with permission from ref. 41. Copyright 2019 Wiley-VCH Verlag. (D,E) Effect of pH and ionic strength on charge selectivity. (D) CV curves recorded at a film electrode using a Keggin-type heteropolyanion (POM) at pH 0.3 and 4. Adapted with permission from ref. 42. Copyright 2019 Elsevier. (E) CV curves recorded at a film electrode using Fe(CN)<sub>6</sub><sup>4-</sup> anions in solutions of low and high ionic strengths (respectively 1 & 300 mM NaNO<sub>3</sub>). Adapted with permission from ref. 41. Copyright 2019 Wiley-VCH Verlag.

Before surfactant removal (see red curves on Figure 4C), ions (Ru(NH<sub>3</sub>)<sub>6</sub><sup>3+</sup>, Fe(CN)<sub>6</sub><sup>3-</sup>) cannot cross the hydrophobic barrier and give no signal while the neutral Fc(MeOH)<sub>2</sub> species are likely to solubilize in the liquid crystalline phase and be detected (yet at higher potentials than on bare electrode for stability reasons).<sup>18</sup> After template extraction, all redox probes can cross the film and reach the electrode surface, but significant restriction is observed for Fe(CN)<sub>6</sub><sup>3-</sup> anions as a result of electrostatic repulsions from the negatively-charged silica surface, imparting thus charge permselectivity to the film.<sup>41</sup>

With this understanding, our group has been developing alternatives for controlling the anionic transport through the nanoporous membrane, which is achievable by tuning pH (Figure 4D) and the ionic strength of the medium (Figure 4E). The effect of pH has been demonstrated for bulky heteropolyanions (polyoxometalates, POM) which can easily cross the film at the condition of turning the silica walls surface from negative (silanolate groups) to positive (protonated silanols) by decreasing pH,<sup>42</sup> leading to much larger CV response (Figure 4D). To rationalize the effect of ionic strength, one needs to consider the thickness of the electrical double layer (i.e., the charged region developing in solution, opposite to fixed charges onto a solid surface), which is estimated from the Debye length ( $\lambda_D$ , which is proportional to the reciprocal of ionic strength (Eq. 2)):

$$\lambda_D = \sqrt{\frac{\epsilon_0 \epsilon_r K_B T}{2 N_A q^2 I}} \quad (2)$$

where  $\epsilon_0$  is the vacuum permittivity ( $8.85 \times 10^{-12} \text{.m}^{-1}$ ),  $\epsilon_r$  is the relative permittivity of water ( $7.84 \times 10^{-10} \text{ F.m}^{-1}$  at  $25^\circ\text{C}$ ),  $K_B$  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 ( $6.02 \times 10^{23} \text{ mol}^{-1}$ ).

To enable the free diffusion of anions,  $\lambda_D$  should be smaller than the mesopore radius (which can be achieved at high ionic strength).<sup>41</sup> In these conditions, an intense CV response can be obtained, while negligible currents are observed in very diluted electrolyte medium (Figure 4E). Otherwise, one can also imagine using non charge-excluded redox mediators diffusing freely through the film and acting as electron shuttles between the electrode surface and charge-excluded anions in solution.<sup>41</sup>

## 5. CHEMICAL MODIFICATION STRATEGIES

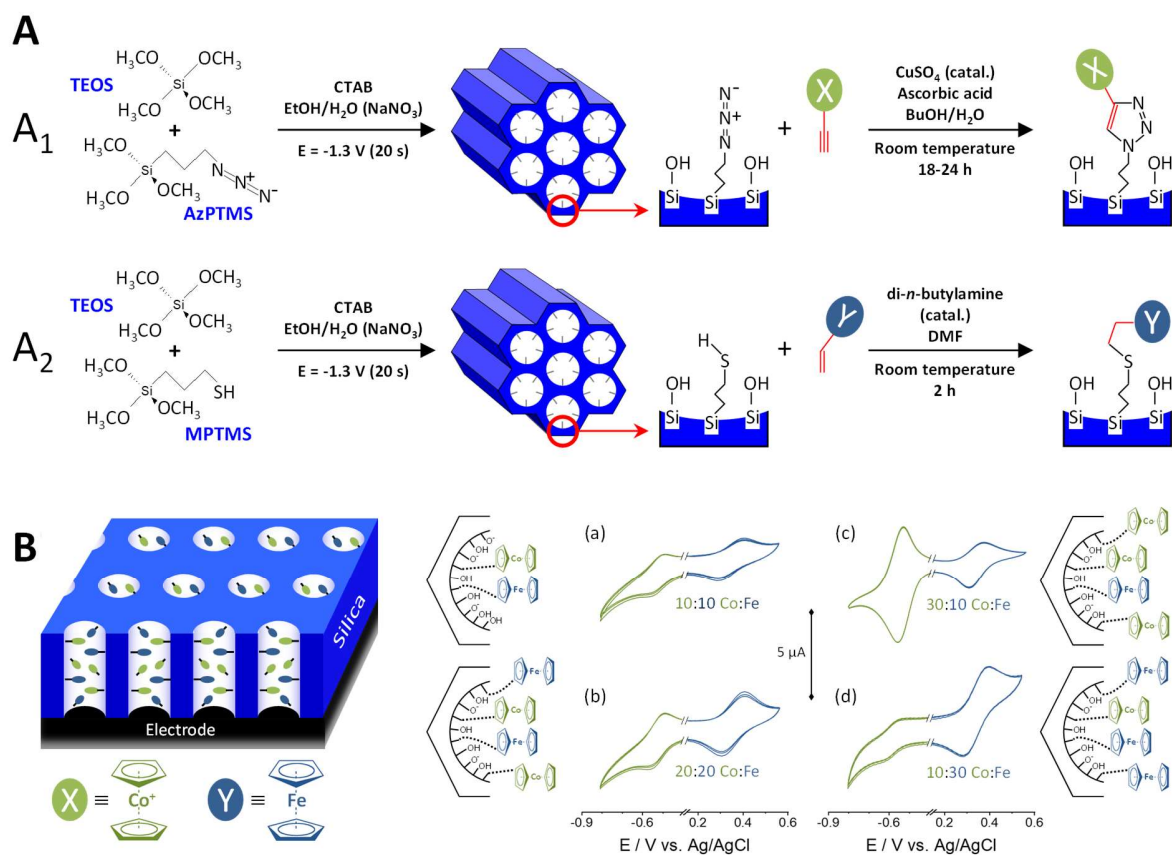
Extending the film properties would greatly benefit from the decoration of the mesochannels with organo-functional groups, if possible via covalent bonding to the silica walls. Silica chemistry offers huge functionalization possibilities through the use of organosilane reagents that can be involved in either post-synthesis grafting or *in situ* co-condensation reactions. However, in the particular case of nanochannel membranes coated on solid supports, grafting reactions usually lead to pore blocking,<sup>2</sup> and co-condensation is limited to very simple organic groups in restricted amounts (e.g., 10% organosilane for propylamine-functionalized films<sup>43</sup>) to keep the mesostructural order. It is therefore necessary to find an alternative functionalization route.

With this motivation in mind, we found that EASA enables to prepare oriented hybrid films bearing azide functions (by co-condensation of TEOS and (3-azidopropyl)trimethoxysilane



(AzPTMS)), which are then exploited for click coupling of a variety of alkyne-bearing molecules by Huisgen cycloaddition (Figure 5A<sub>1</sub>). Interestingly, one can use up to 40% AzPTMS in the electrodeposition medium without losing neither the high degree of mesostructuration nor the vertical alignment of nanochannels in the film.<sup>2</sup> This unusually high organic group content compatible with mesoscopic ordering is probably explained by the zwitterionic nature of azide groups, being stabilized between the cationic surfactant and negatively-charged silica walls. Similar strategy can be applied to generate up to 30% thiol-functionalized films (from (3-mercaptopropyl)trimethoxysilane (MPTMS)) and their further derivatization via thiol-ene click coupling (Figure 5A<sub>2</sub>). Bi-functionalized films can be obtained by combining these two click reactions successively from a material prepared with both azide and thiol groups.<sup>19</sup> Not only the total amount of organo-functional groups but also their relative contents in the material can be controlled by adjusting the TEOS/AzPTMS/MPTMS molar ratio, as illustrated for ferrocene- and cobaltocenium-functionalized films (Figure 5B). As shown, the corresponding CV peaks were proportional to the respective metallocene contents in the film and, due to the insulating silica matrix and the covalent bonding of the organo-functional groups to the mesopore walls, the charge transfer mechanism relies on the electron hopping between adjacent redox centers.<sup>19,31,44</sup> This also highlights the possibility of long-range (~100 nm) electronic percolation through a basically insulating thin film.<sup>39</sup> The versatility of such two-steps EASA-click approach opens new avenues for the covalent immobilization of highly reactive species that might be difficult to attach otherwise without losing their properties, as demonstrated for electroactive and fluorescent tetrazine derivatives.<sup>45</sup> Functionalizing only the pore bottom with suitable organic functions is also possible, either by chemical grafting or electrografting methods, respectively before or after generation of the mesoporous silica film,<sup>46,47</sup> leading to monolayer nanoarrays.

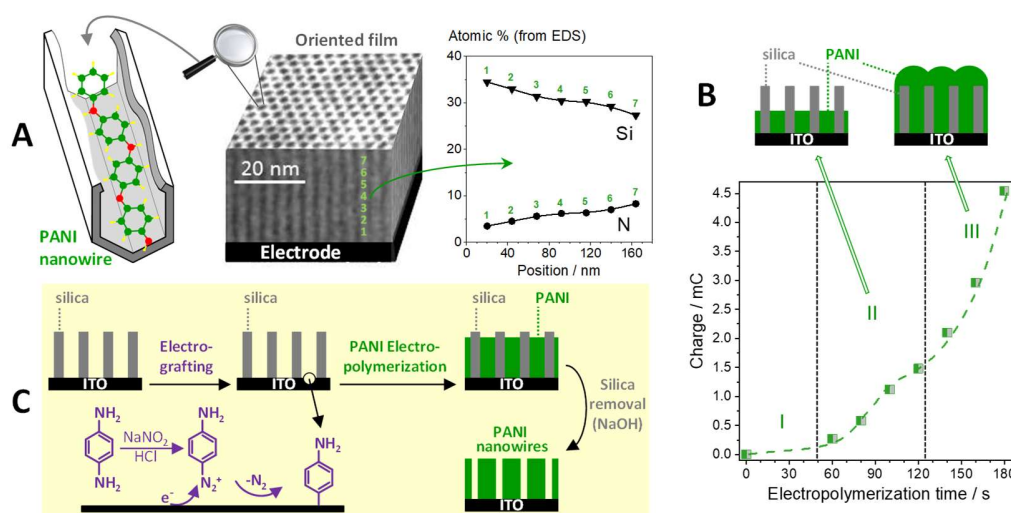
In a totally different strategy, we discovered recently that the modifier itself can serve as template, by exploiting the self-assembly of coordination polymers along with mesoporous silica growth by EASA, as demonstrated for the spin crossover  $\text{Fe}(\text{Htrz})_3$  (Htrz = 1,2,4,-1H-triazole) complex.<sup>48</sup> Due to durable immobilization of  $\text{Fe}(\text{Htrz})_3$  in the hybrid material, the resulting films exhibit highly stable electrochemical responses and electrocatalytic properties.<sup>49</sup>



**Figure 5.** (A) Illustration of the generation of (A<sub>1</sub>) azido- or (A<sub>2</sub>) mercapto-functionalized mesoporous silica films (by EASA cocondensation of TEOS and AzPTMS or MPTMS, respectively) and their subsequent derivatization by click reactions ((A<sub>1</sub>) azide – alkyne or (A<sub>2</sub>) thiol – ene). Adapted with permission from ref. 2. Copyright 2014 Wiley-VCH Verlag. (B) CV curves recorded with a film electrode bearing both ferrocene and cobaltocenium moieties attached to the mesoporous silica via the selective click coupling reactions as in (A). Reproduced with permission from ref. 19. Copyright 2016 Wiley-VCH Verlag.

Another functionalization strategy concerns the exploitation of the oriented nanochannels as a mould for generating arrays of vertical 1D nanostructures. Porous membranes can be basically used as hard template to grow arrays of nanowires or nanotubules of diameters typically in the 10-200 nm range.<sup>50</sup> However, if metal ions can be effectively reduced at EASA-film electrodes (with metal deposits detected by anodic stripping),<sup>43</sup> and if individual metal atomic contacts can be generated by local electrodeposition through such small-pore membranes,<sup>51</sup> the growth of mechanically stable metal nanowires remains restricted to pore diameters above 7 nm.<sup>52</sup> If wishing to synthesize electronically conducting nanowires of ultra-small dimensions, one can think about synthetic metals such as conducting polymers. Several attempts have been made to electropolymerize pyrrole, aniline or thiophene derivatives through such silica nanochannel membranes (see<sup>53</sup> and references cited therein), but diameters of the obtained polymeric nanostructures were larger (i.e., 5-30 nm) than the mesopore apertures (i.e., 2-3 nm), so that one can expect polymer growth out of the membrane or through film defects. Evidence for the presence of conducting polymer into the mesochannels was given for polyaniline (PANI) from transmission electron microscopy (TEM) and energy dispersive spectroscopy (EDS).<sup>54,55</sup> In particular, a careful EDS analysis at various depth of the film from a cross-section TEM micrograph (Figure 6A) enables to identify PANI in the whole mesopore volume, yet with increasing amounts of N species (and concomitant decrease of Si signal) from the electrode surface to the top of film, suggesting that single nanofilaments are first produced at the mesopore bottom and that further electropolymerization may then lead to additional branched PANI.<sup>55</sup> Monitoring current or charge variations as a function of the electropolymerization time enables to identify unambiguously three stages (induction period, filament growth, subsequent deposition outside the mesochannels, see Figure 6B), offering a simple and powerful mean for controlling

polymer growth in the nanopores. From these charges, one can also evaluate that 1-2 individual PANI chain(s) are produced per mesochannel.<sup>55</sup> The next step is to find a way to attach durably the polymer nanofilaments to the support in order to keep them fixed on the electrode surface after dissolution of the silica membrane. This is achieved either by preforming a polymer layer onto the electrode prior to mesoporous film formation and electropolymerization,<sup>53</sup> or via *in situ* electrografting of aniline moieties at the mesopore bottom and subsequent PANI growth (Figure 6C). This latter approach offer the advantage to get only the nanofilaments strongly attached to the electrode, without underneath bulk polymer.<sup>47</sup>



**Figure 6.** (A) TEM view of a silica membrane containing electropolymerized PANI nanowires and corresponding EDS data for N and Si elements at various height positions. Reproduced with permission from ref. 55. Copyright 2017 American Chemical Society. (B) Variation of charges as a function of PANI electropolymerization time, enabling to identify the three steps of the process (I nucleation, II growth through the nanochannels, III growth out of the film). Reproduced with permission from ref. 55. Copyright 2017 American Chemical Society. (C) Illustration of the formation of polyaniline (PANI) nanowires array via the electrografting of aminophenyl at the pore bottom and subsequent electropolymerization through the nanochannels, which can be followed by removal of the silica hard template to get the PANI wires covalently bound to the ITO surface. Reproduced with permission from ref. 47. Copyright 2021 Elsevier.

## 6. APPLICATIONS

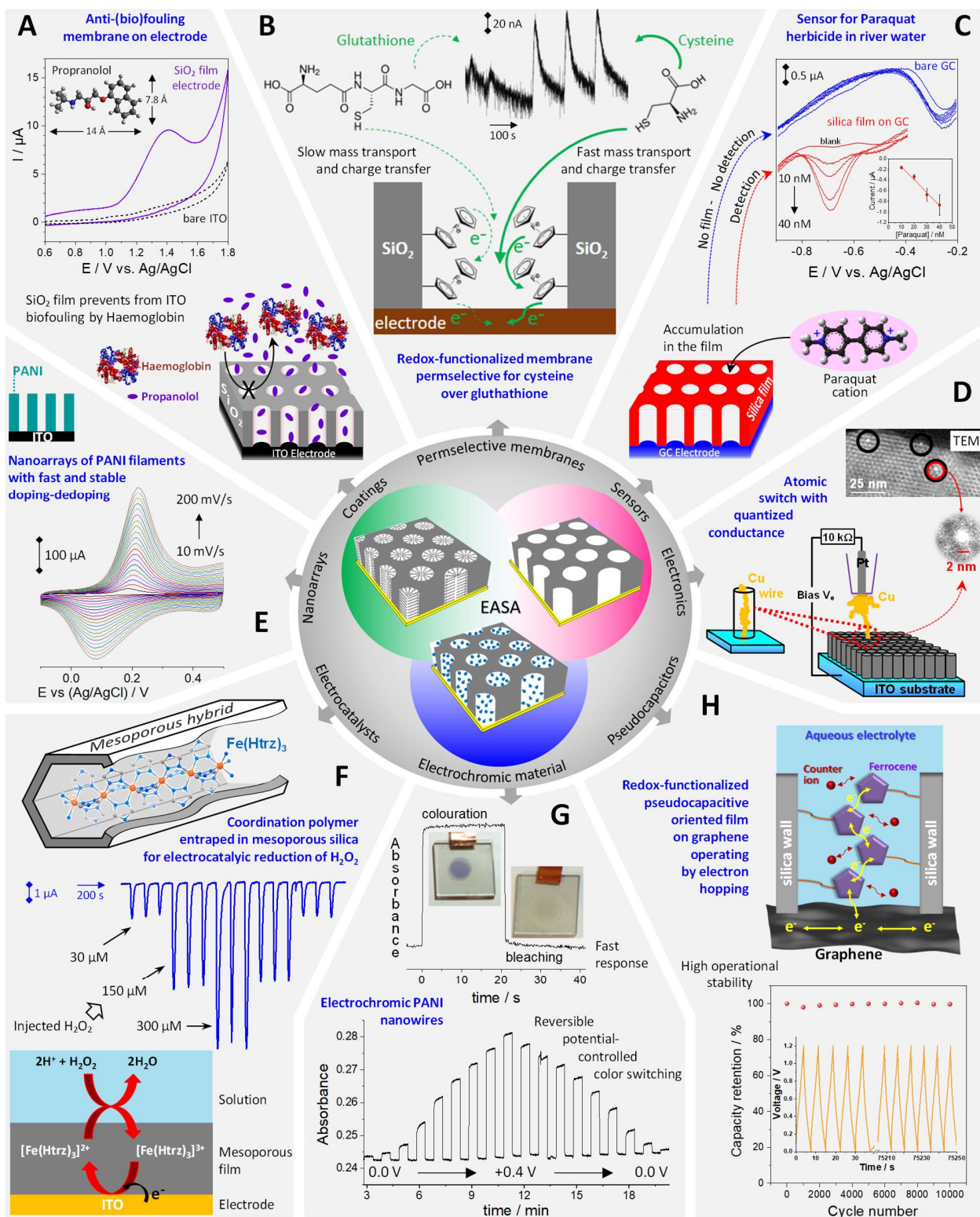
These mesoporous films with ultrahigh density of mesochannels ( $7.5 \times 10^{12}$  pores. $\text{cm}^{-1}$ )<sup>18</sup> of unique orientation are attractive for practical applications. At the beginning, they were mainly devoted to electrochemical sensors and separation,<sup>56</sup> but the access to multiple functionalization (section 5) has recently opened the door to wider scope (see some illustrations from our group in Figure 7). A more extensive compilation of EASA-based films uses is given in Table S2. A brief taste of the numerous application possibilities is given hereafter, the interested reader being directed to the corresponding papers for deeper consideration.

*Electrochemical sensors and biosensors.* Mesoporous materials are attractive for designing electroanalytical devices,<sup>57</sup> but vertically aligned mesochannels bring unique advantages. They can act as molecular filter protecting against biofouling,<sup>38</sup> enabling the detection of pharmaceuticals (e.g., propranolol) usually impossible in the absence of membrane due to biomolecules (e.g., haemoglobin) adsorption onto the electrode surface (Figure 7A). Other examples include the direct analysis of various species in complex media (beverages, biological fluids including whole blood, environment, see Table S2).<sup>56</sup> The oriented membranes are likely to accumulate efficiently selected analytes, via either electrostatic interactions or hydrophobic extraction,<sup>3,56-58</sup> leading to selective and sensitive electrochemical sensors. Illustrative examples are the determination of paraquat in river water in the nanomolar range (Figure 7C), exhibiting a detection limit lower than permissive levels for such herbicide,<sup>3</sup> or the selective detection of dihydroxybenzene isomers in environmental samples.<sup>58</sup> Permselective properties of functionalized films are also exploited, for example in the field of geno- and aptasensors relying on hindered diffusion of redox probes through a film derivatized with oligonucleotide/aptamer gated by recognition of the biomarker.<sup>59</sup> Ferrocene-functionalized films are used for the indirect

amperometric sensing of non-redox anions,<sup>60</sup> or for the selective detection of cysteine over glutathione by combining size selectivity and modulated charge transfer (Figure 7B).<sup>61</sup>

*Electrocatalysis.* Except for nanostructured metals which possess intrinsic electrocatalytic properties,<sup>25</sup> the use of oriented mesoporous films in electrocatalysis remains underexploited to date in spite of promising avenues arising from functionalization (section 5). One interesting example is the electrocatalytic reduction of hydrogen peroxide by a redox-active Fe(Htrz)<sub>3</sub> coordination polymer confined in the oriented mesochannels (Figure 7F) during film production for which highly reversible response can be obtained owing to the very high stability of the material upon redox cycling.<sup>48,49</sup> A way to improve the electrocatalytic properties can be via confinement of metal nanoparticles in the nanochannels.<sup>62</sup>

*Separation.* The permselective silica membranes can be removed from their support and used for molecular separation and controlled molecular transport applications,<sup>63</sup> which can be adjusted by pore size tuning or pH-gating transport, or for electrochemically controlled mass transfer at liquid-liquid nanointerfaces.<sup>56</sup> So far, selective molecular transport applications were based on mesoporous silica membranes prepared by Stöber solution growth, but the EASA ones offer the advantage of better ordering (especially when functionalized<sup>64</sup>) which might be exploited in the future for separation purposes.



**Figure 7.** Illustration of some applications of the vertically aligned mesoporous silica films. (A) Protective coating: CV curves recorded in 100  $\mu\text{M}$  propranolol in the presence of 5  $\mu\text{M}$

haemoglobin at bare ITO and film electrodes. Adapted with permission from ref. 38. Copyright 2015 Elsevier. (B) Permselective membrane: flow injection analysis of 50  $\mu\text{M}$  of glutathione (left) and cysteine (right) at a ferrocene-functionalized film electrode. Adapted with permission from ref. 61. Copyright 2020 Wiley-VCH Verlag. (C) Electrochemical sensor: square wave voltammograms recorded in Meuse River water samples at bare (blue) and film (red) electrodes after spiking with 0, 10, 20, 30, and 40 nM paraquat. Reproduced with permission from ref. 3. Copyright 2018 American Chemical Society. (D) Atomic switches: electrochemical deposition of individual copper nanowires through nanochannels and TEM imaging. Reproduced with permission from ref. 51. Copyright 2017 Nature Publishing Group. (E) Nanoarrays: CV curves recorded at various potential scan rates for an array of oriented polyaniline (PANI) nanofilaments on ITO electrode. (F) Electrocatalysts: flow injection analysis of  $\text{H}_2\text{O}_2$  (30, 150 and 300  $\mu\text{M}$ ) at a film electrode templated with an iron triazole ( $\text{Fe}(\text{Htrz})_3$ ) coordination polymer biased at -0.4 V. Adapted with permission from refs. 48 & 49. Copyright 2019 American Chemical Society & 2020 Wiley-VCH Verlag. (G) Electrochromic materials: absorbance variations of PANI nanofilaments measured by switching potentials from -0.2 V to various anodic values (from 0.0 to +0.4 V, by steps of 50 mV); one colouration-bleaching cycle is enlarged on top, including photo of samples. (H) Pseudocapacitive materials: capacity retention of a ferrocene-functionalized film on graphene electrode on 10.000 successive charge-discharge cycles. Reproduced with permission from ref. 4. Copyright 2020 American Chemical Society.

*Energy.* Thanks to effective charge transfer by electron hopping and fast diffusion of charge-compensating ions,<sup>44</sup> mesoporous silica films bearing large amounts of redox-active moieties are novel pseudocapacitive materials, which can be deposited onto graphene electrodes for high rate energy storage (Figure 7H),<sup>31</sup> or exploited as a novel functionalization and mesostructuring strategy for tuning the efficiency of electron hopping likely to be used as power sources for the next generation of transparent electronic systems.<sup>4</sup> Fast and stable cycling behavior can be also achieved with nanoarrays of conducting polymers (Figure 7E), being also promising for energy applications.



*Electrochromism.* PANI nanofilaments<sup>47</sup> or iron-terpyridine complexes<sup>65</sup> covalently anchored in the mesochannels are electrochromic materials exhibiting fast potential-controlled color switching, offering great promise for incorporation in electronic display at the nanoscale. Extremely fast electrochromic response can be achieved when removing the silica membrane (e.g.,  $\sim 0.1$  for PANI coloring-beaching), with highly reversible and stable electrochemical switching (Figure 7G), which is explained by the very small size of the individual nanowires.

*Electronics.* Atomic switches can be generated using an ultramicroelectrode tip from which metal nanowires can grow through single mesochannels (Figure 7D), leading to atomic contacts that are stabilized by the silica matrix.<sup>51</sup> Current rectification is achievable by exploiting the ionic strength effects at interfaces between two films of distinct surface charges.<sup>56</sup> The nanoconfinement of electron-donor-acceptor complexes<sup>65</sup> could be also appealing for molecular electronics. It is anticipated that the functionalization strategies reported here will open new avenues for ship-in-a-bottle building of oriented supramolecular electronic systems.

## 7. CONCLUSIONS AND OUTLOOK

EASA is a facile and fast synthetic route to vertically oriented mesoporous thin films thanks to the versatility of electro-induced sol-gel processing combined to surfactant self-assembly on electrode surfaces. Conceptually different from other film deposition methods, EASA enables the mesostructure growth from the underlying substrate, as a kinetic product, explaining the preferential orientation that is ideal for efficient transport phenomena through the membrane. Moreover, it is compatible with covalent functionalization via click coupling, offering a real platform for designing organic-inorganic hybrids of variable composition. Film characteristics

and properties can be tuned not only by controlling the synthesis conditions but also by adjusting external parameters (solution composition), leading to attractive applications in various fields.

Yet, the EASA technique has some limitations such as the absolute need of cationic surfactants to achieve mesopore orientation, restricting thereby the pore diameters up to 3 nm. This might be improved by adding swelling agents (*e.g.*, tri-substituted benzene derivatives) or via the use of larger surfactants (long-chain gemini or ionic liquid cations). Another issue, common to all silica-based materials, is a rather poor chemical stability in aqueous media (especially at high pH and ionic strength). Two ways likely to enhance stability are the hydrophobization of the silica surface<sup>66</sup> or the preparation of mixed metal films combining silica and another oxide less subject to dissolution.<sup>67,68</sup> As other metal oxides (*e.g.*, TiO<sub>2</sub>, ZrO<sub>2</sub>) can be generated electrochemically,<sup>69</sup> one could hope adapting EASA to the generation of more inert mesoporous oxides by using suitable surfactants for their cooperative self-assembly.

Besides, we believe that many opportunities still exist to expanding the scope of exploiting the uniqueness of vertical nanochannels far beyond the few examples described here, especially via widening the range of organo-functional groups in the material. In addition to (bio)sensors for which the challenge is gaining in selectivity (requiring efforts in specific recognition and electrocatalysts developments), future advances are expected in molecular electronics and energy. Nanochannels are notably ideal hosts for building supramolecular structures that could not occur otherwise (*e.g.*, spatial arrangement of confined metal-ligand complexes), with unidirectional electronic wiring localized in insulating coatings potentially interesting for nanoelectronics or for photo(electro)chemistry and electrochromism. Deposition of oriented hybrid films onto novel nanomaterials (such as MXenes) is another promising avenue for dealing with the energy/power density challenge in electrochemical energy storage.

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## SUPPORTING INFORMATION

A figure on pH effect on hydrolysis/condensation rates and two tables with detail on film properties and applications.

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