

Supporting information:

Pore size and surface charge control in mesoporous TiO₂ using post-grafted SAMs.

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1. IR Measurements

Representative IR spectra of the modified films are shown in the figure below and the frequency assignments of the absorption bands are tabulated in table 1.

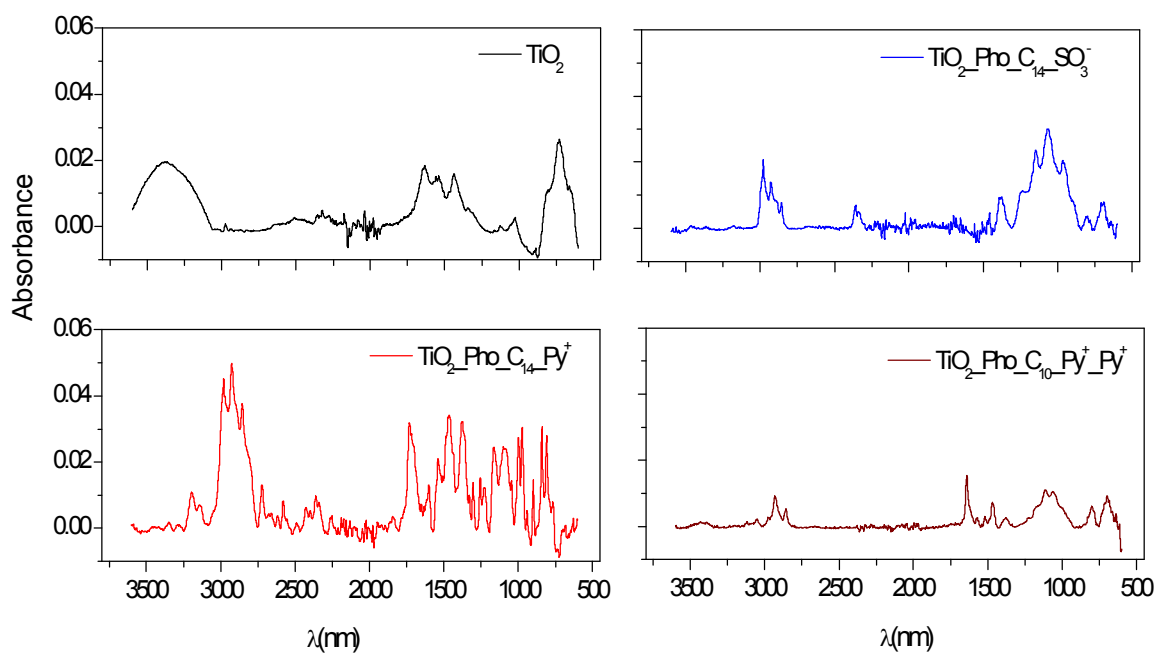


Figure 1: Selected IR spectra of unmodified and modified mesoporous TiO₂ films.

Table 1: Frequency assignments for the IR Absorption bands

| film | Frequency | Assignment | ref |
|---|------------------|--|------|
| TiO ₂ | 3000- 3600 | O-H stretching (H ₂ O) | 1 |
| | 1640, 1540, 1440 | O-H bending, | |
| | 730 | lattice vibration | |
| TiO ₂ _PhO_C ₁₄ _R ⁺ | 3080-3200 | C-H stretching (aromatic system) | 2 |
| | 2926 | C-H asymmetric stretching (aliphatic CH ₂) | 3 |
| | 2854 | C-H symmetric stretching (aliphatic CH ₂) | 2 |
| | 1600-1700 | C=C, C=N stretching (ring) | 4 |
| | 1000-1150 | O-P stretching | |
| TiO ₂ _PhO_C ₁₄ _R ⁻ | 2928 | CH ₂ asymmetric stretching | 2, 4 |
| | 2856 | CH ₂ symmetric stretching | |
| | 1375 | S=O asymmetric stretching | |
| | 1000-1150 | O-P-O stretching | |

Table 1: Surface coverage of the different phosphonic acid (from IR Spectroscopy) on mesoporous s-TiO₂ thin films.

| Charge | Phosphonic acids | Γ_{IR} (mol/cm ²) x 10 ⁻⁷ |
|----------|---|---|
| Positive | Pho-C ₆ -Py ⁺ | 0.7 |
| | Pho-C ₁₀ -Py ⁺ | 1.1 |
| | Pho-C ₁₄ -Py ⁺ | 1.1 |
| Negative | Pho-C ₆ -SO ₃ ⁻ | 0.3 |
| | Pho-C ₁₀ -SO ₃ ⁻ | 0.7 |
| | Pho-C ₁₄ -SO ₃ ⁻ | 0.8 |

Note: surface concentrations are not corrected for roughness factor (≈ 400).

Electrochemical Measurements

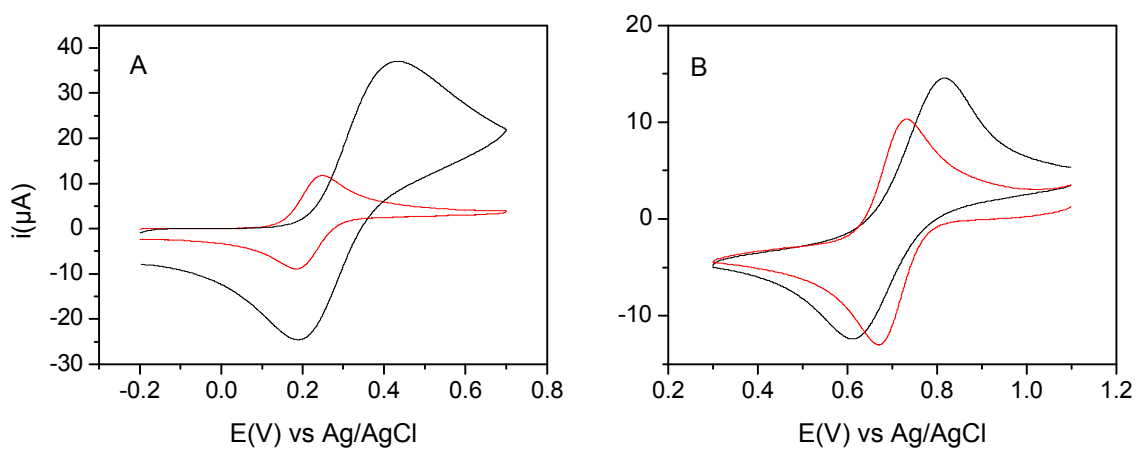


Figure 2: Cyclic voltatmmetry, (A) 0.1mM $[\text{Fe}(\text{CN})_6]^{4-}$ and (B) 0.1mM $[\text{IrCl}_6]^{2-}$ on bare TiO_2 (black) and FTO(red).

Influence of the carbon chain length on the pore size: a case of the negatively charged phosphonic acid with negatively charged redox ions.

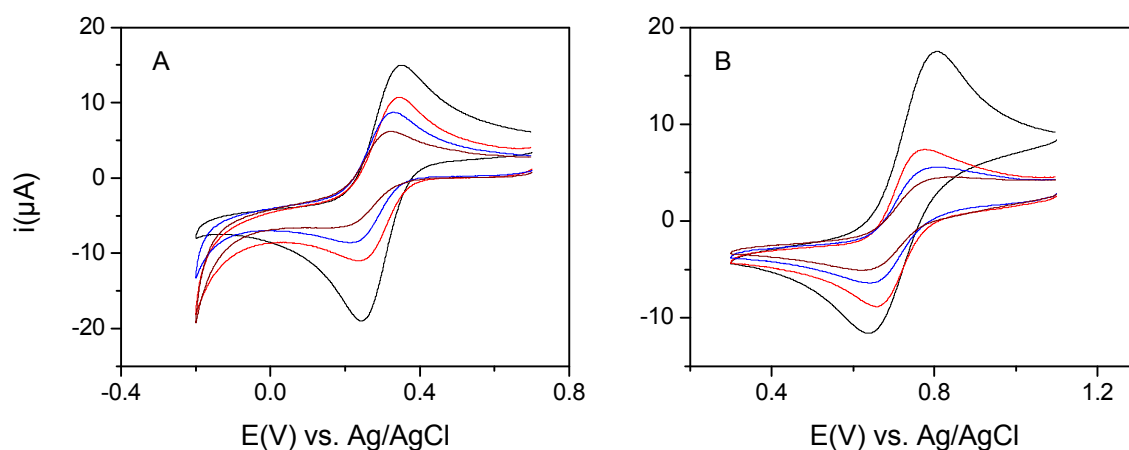


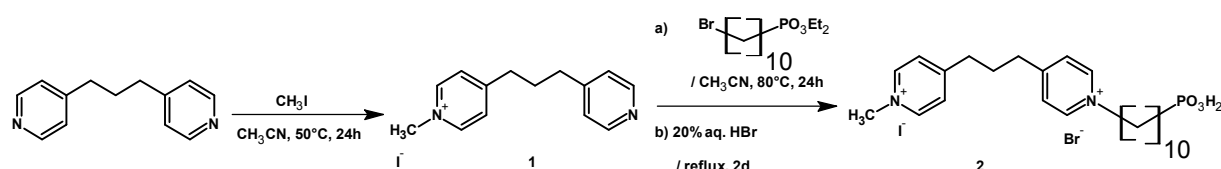
Figure 3: Cyclic voltatmmetry, (A) 0.1mM $[\text{Fe}(\text{CN})_6]^{3-}$ and (B) 0.1mM $[\text{IrCl}_6]^{2-}$ on s- TiO_2 _Pho_C_n_SO₃⁻ electrode with different carbon chain: bare s- TiO_2 (black), n=6(red), n=10 (blue) and n=14 (wine).

Table 2: Increase of peak to peak separation (ΔE_p) on $\text{TiO}_2\text{-Pho-C}_n\text{-SO}_3^-$ electrode for negatively charged redox ions.

| Electrode | $[\text{IrCl}_6]^{2-/3-}$ | | $[\text{Fe}(\text{CN})_6]^{3-/4-}$ | |
|--|---------------------------|-------------------------|------------------------------------|-------------------------|
| | $I_{a,p}(\mu\text{A})$ | $\Delta E_p(\text{mV})$ | $I_{a,p}(\mu\text{A})$ | $\Delta E_p(\text{mV})$ |
| $\text{TiO}_2\text{-Pho-C}_6\text{-SO}_3^-$ | 7 | 101 | 11 | 85 |
| $\text{TiO}_2\text{-Pho-C}_{10}\text{-SO}_3^-$ | 5 | 127 | 8 | 91 |
| $\text{TiO}_2\text{-Pho-C}_{14}\text{-SO}_3^-$ | 3 | 153 | 7 | 102 |

Synthesis

The dialkylation of 1,3-trimethylene dipyridine is well known in literature,^{5, 6} but its monoalkylation with methyl iodide or other alkylating agents has not been reported so far. After several unsuccessful trials we found a way using one equivalent of 1,3-trimethylene dipyridine and a sub-stoichiometric amount (1/5 equivalent) of methyl iodide in acetonitrile as a solvent. The synthesis follows scheme:



Scheme

1-methyl-4-[3-(pyridin-4-yl)propyl]pyridinium iodide: To a solution of 2g (10.08mmol) 1,3-trimethylenedipyridine in 20ml MeCN at 50°C a solution of 0.13ml (2.017mmol) methyl iodide in 20ml acetonitrile was added dropwise over 4h and stirred for another 20h. MeCN was then distilled off under reduced pressure, to yield a slurry, which was dissolved in water and washed with dichloromethane. Removal of

the water under reduced pressure gave solid which was then dried under high vacuum to afford 0.600g (1.76mmol, 87%) 1-methyl-4-[3-(pyridin-4-yl)propyl]pyridinium iodide as a dark brown solid.

¹H NMR (250 MHz, D₂O, δ): 8.46 (d, *J* = 6.52 Hz, 2H), 8.33 (d, *J* = 6.16 Hz, 2H), 7.72 (d, *J* = 6.42 Hz, 2H), 7.37 (d, *J* = 6.09 Hz, 2H), 4.18 (s, 3H), 2.84 (t, 2H), 2.71 (t, 2H), 2.09-1.93 (m, 2H).

1-methyl-4-{3-[1-(10-phosphonodecyl) pyridinium-4-yl]propyl} pyridinium bromide iodide: 0.4g (1.17mmol) of 1-methyl-4-[3-(pyridin-4-yl)propyl]pyridinium iodide and 0.84g (2.35mmol) diethyl(10-bromodecyl)phosphonate were reacted in 20ml MeCN at 80°C for 24h. After 24h, MeCN was distilled off under reduced pressure, the residue dissolved in water, and washed with ethylacetate. Removal of water under reduced pressure yielded a dark reddish brown solid which was hydrolysed using 20ml 20% aqueous HBr at 100°C for 2 days, followed by removal of the solvent under reduced pressure to yield a black oily residue. It was dissolved in 20ml MeOH, loaded with 0.5g charcoal, heated and filtered through Celite. The filtrate thus obtained was evaporated under reduced pressure yielding a pale brown semisolid of 0.55g (.85 mmol, 73%).

¹H NMR (250 MHz, D₂O, δ): 8.56 (dd, *J* = 6.34 Hz, 4H), 7.81 (t, *J* = 5.65 Hz, 4H), 4.44 (t, 2H), 4.22 (s, 3H), 2.92 (t, 4H), 2.08 (t, 2H), 1.96-1.81 (m, 2H), 1.75-1.56 (m, 2H), 1.53-1.33 (m, 2H), 1.17 (d, 12H).

References

- 1 P. A. Connor, K. D. Dobson and A. J. McQuillan, *Langmuir*, 1999, **15**, 2402-2408.
- 2 R. M. Silverstein, F. X. Webster and D. Kiemie, *Spectrometric Identification of Organic Compounds, 7th Edition*, John Wiley and Sons, Danvers, MA, USA. 2002; Chapter 2
- 3 D. Taffa, M. Kathiresan and L. Walder, *Langmuir*, 2009, **25**, 5371-5379.
- 4 P. A. Connor and A. J. McQuillan, *Langmuir*, 1999, **15**, 2916-2921.
- 5 A. R. Katritzky, W. Q. Fan and Q. L. Li, *J. Heterocycl. Chem.*, 1988, **25**, 1311-1314.
- 6 X. Jiao, Y. Niu, H. Zhang, L. Zhu and F. Zhao, *J. Chem. Crystallogr.*, 2006, **36**, 685-689.