Mesostructured Tungsten Oxide Film Prepared from Tungstic Acid via a Surfactant Templated Sol-Gel Method

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Background

- Electrochromic coatings have huge potential applications as smart windows:

  e.g. sun-protective windows, self-dimming rear-view car mirrors.

- WO_3 is of particular interest due to
  - ✓ reversible colour change between blue ($W^{IV/V}$) and transparent (W^{VI})
  - ✓ Improved electrochromic stability for long-lifetime applications

  Drawback: Low-responsive time on the order of **minutes**

- Mesostructures lead to fast coloration/bleaching switching on the order of **seconds**.

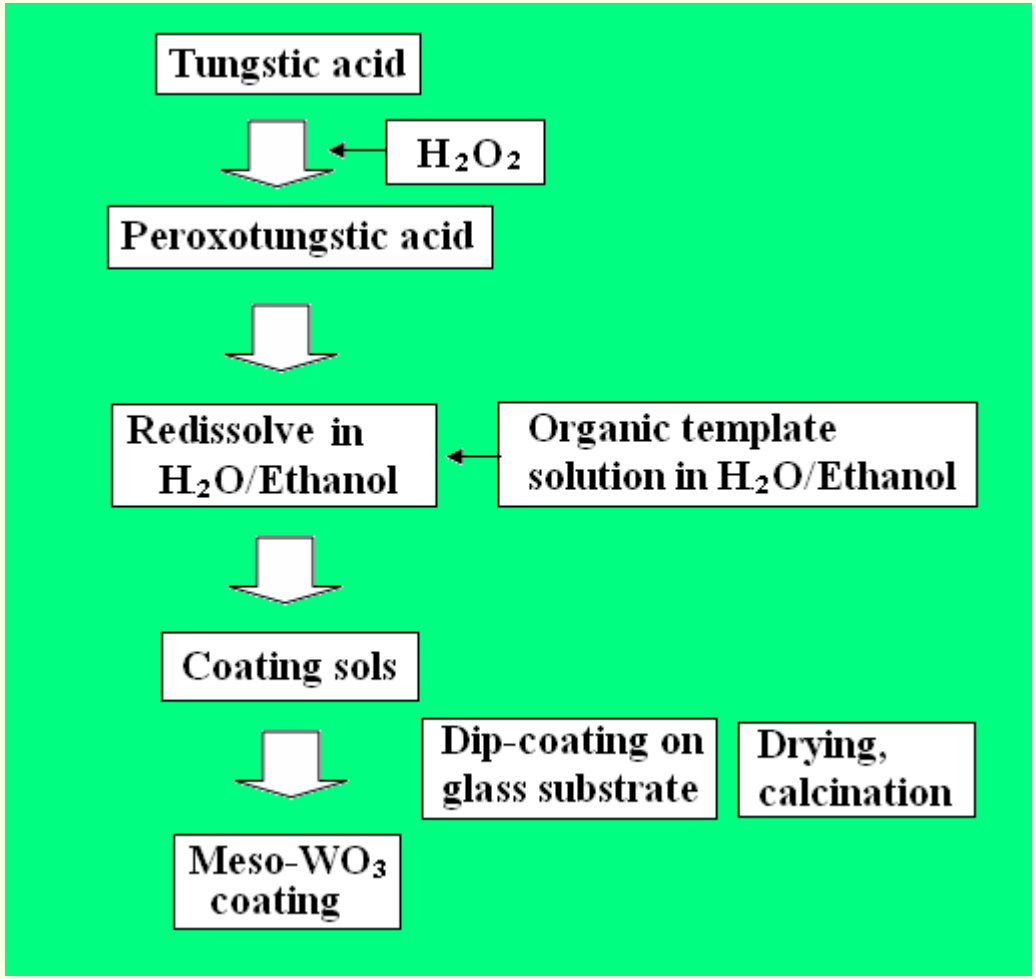
Objectives of this work

- Cheap and easy-handling W precursor: Tungstic acid

  WCl_6, although expensive and moisture sensitive, is the most often chosen as W precursor for meso-WO_3, as Tungstic acid is shown just not to work to prepare meso-WO_3 .

- Mesostructural WO_3
- Facile fabrication
- Comparable electrochromic performance with WCl_6 derived meso-WO_3

Synthesis route



Cyclic voltammetry:

Three electrodes system:

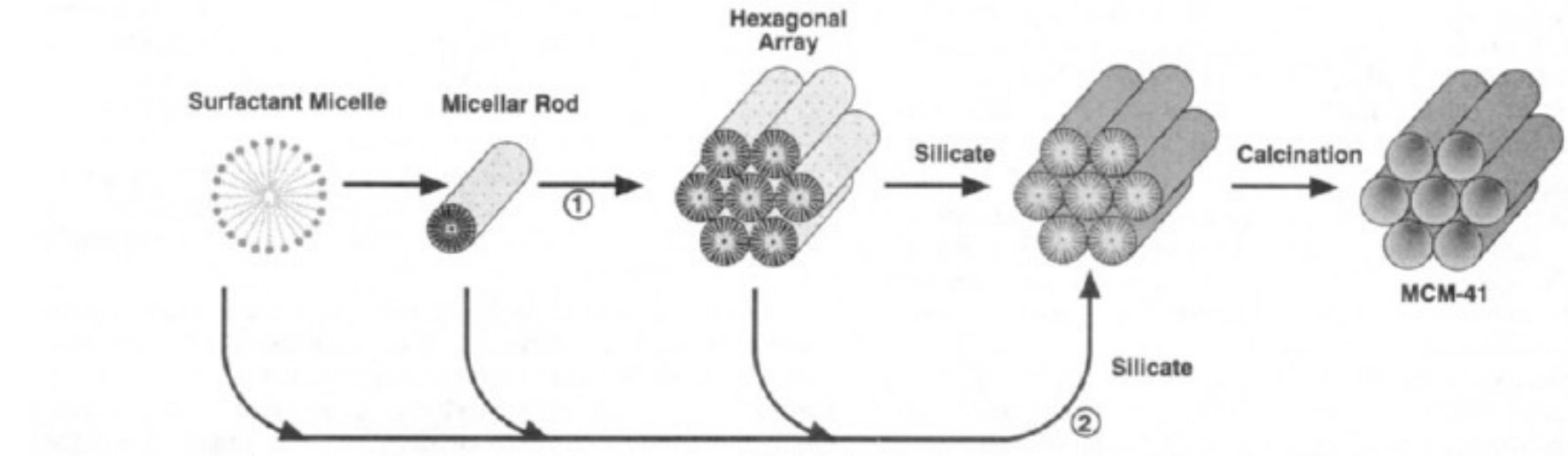
Ag/AgCl in saturated KCl as reference,

Pt as counter electrode.

WO3 coated ITO as working electrode.

To characterize mesostructures, XRD and TEM were employed.

Surfactant template mechanism

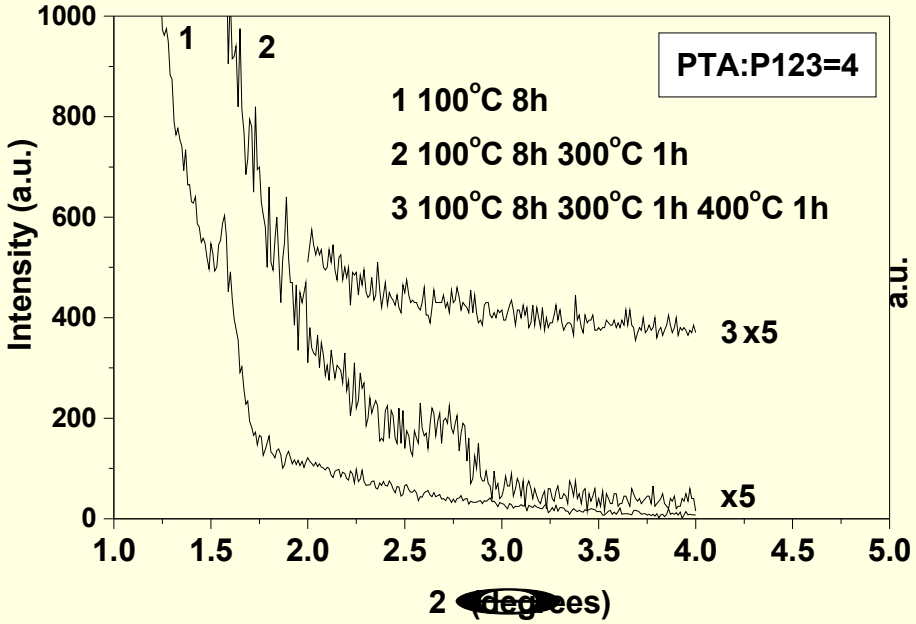


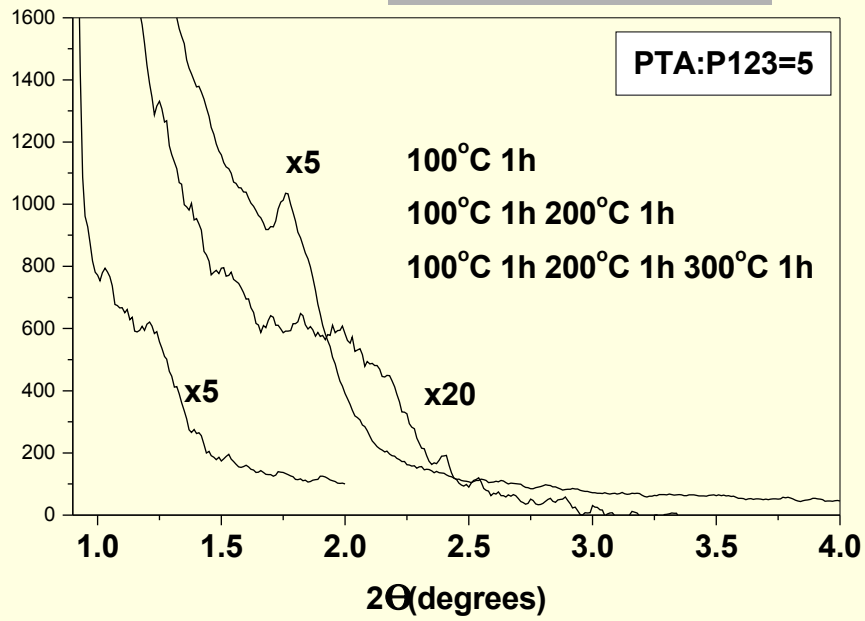
J.S. Beck,et al, JACS,1992, 114, 10834

Experimental parameters studies (EPS)

P123 ($EO_{20}PP_{70}EO_{20}$)

Templated PTA hybrids film

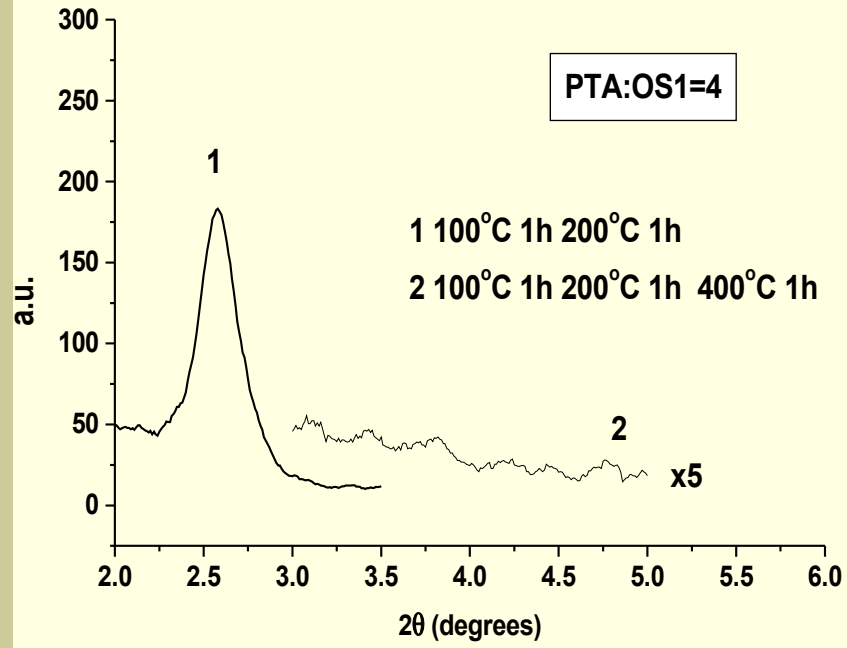


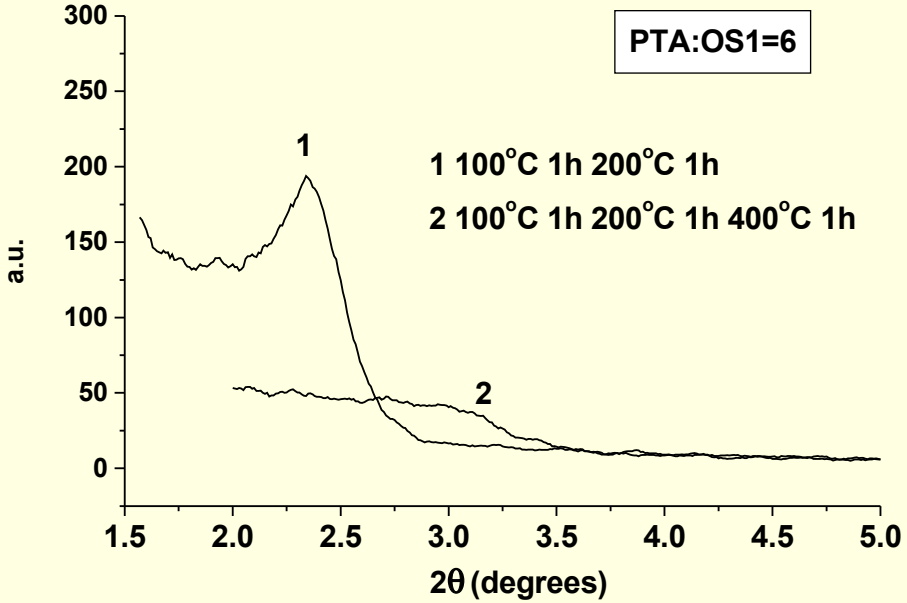


Disordered mesostructures lacking of long-range ordering

Poor thermal stability (~300°C)

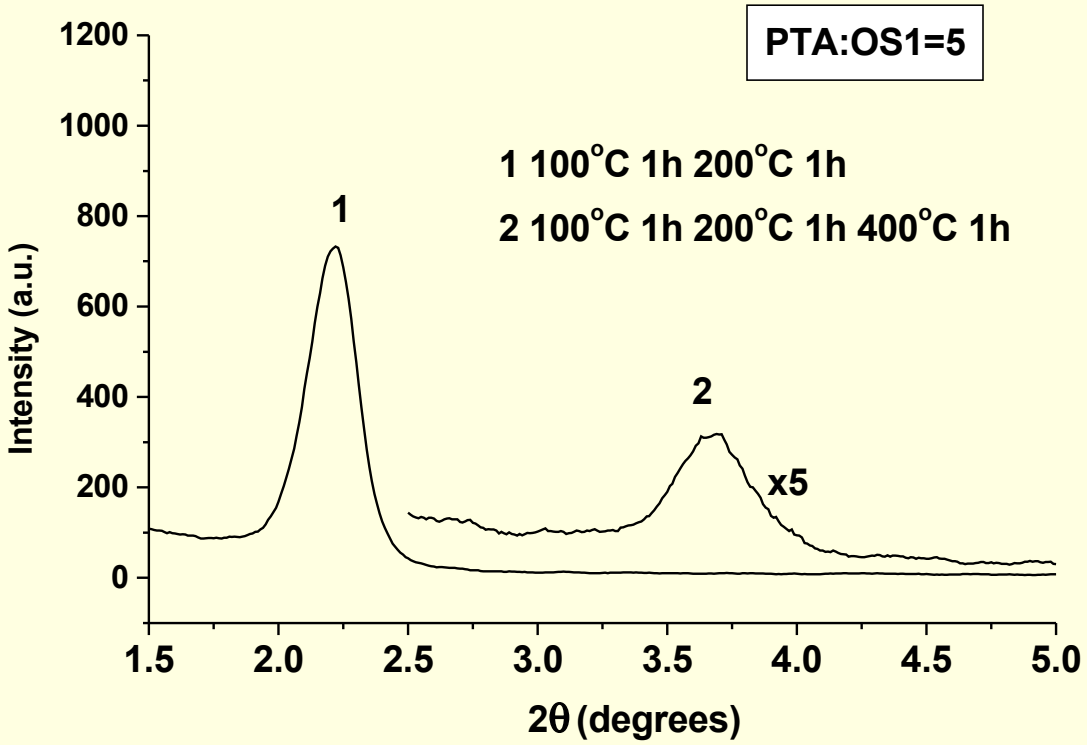
EPS--OS-1 Templated PTA hybrids film (A)





levels of organic surfactant template (OS-1) are important to achieve good thermal stability. The more the OS-1, the more flexible the frameworks of the hybrids, the worse the thermal stability.

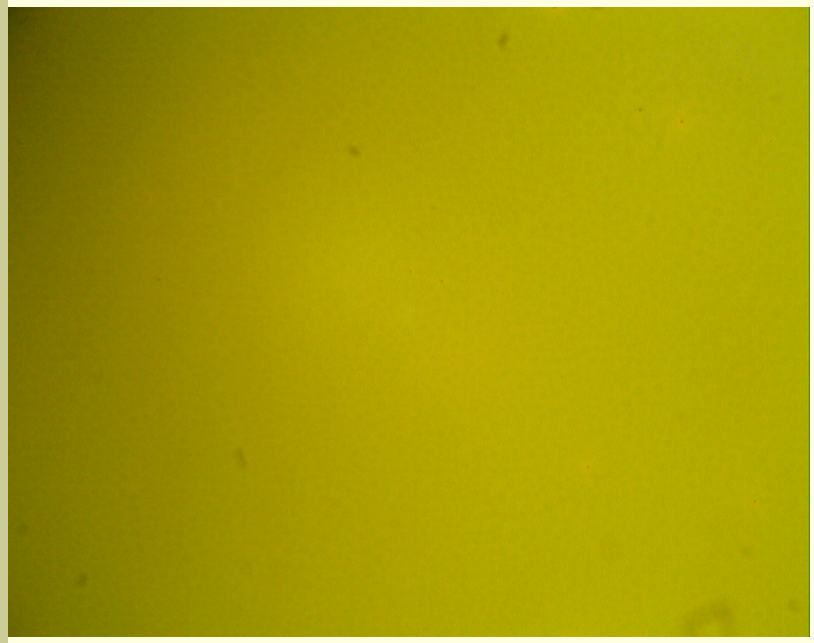
EPS--OS1 Templated PTA hybrids film (B)



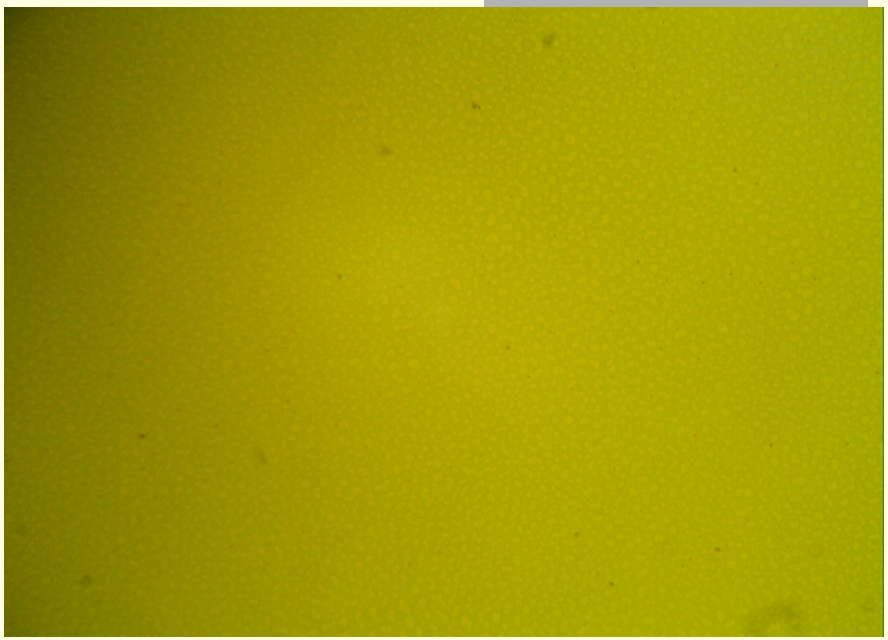
Weight ratio of PTA to OS-1 equivalent of 5 yields the most thermally stable mesostructures.

Resolved low-angle peaks, improved ordering of mesostructures

EPS--OS-1) Templated PTA hybrids film (C)



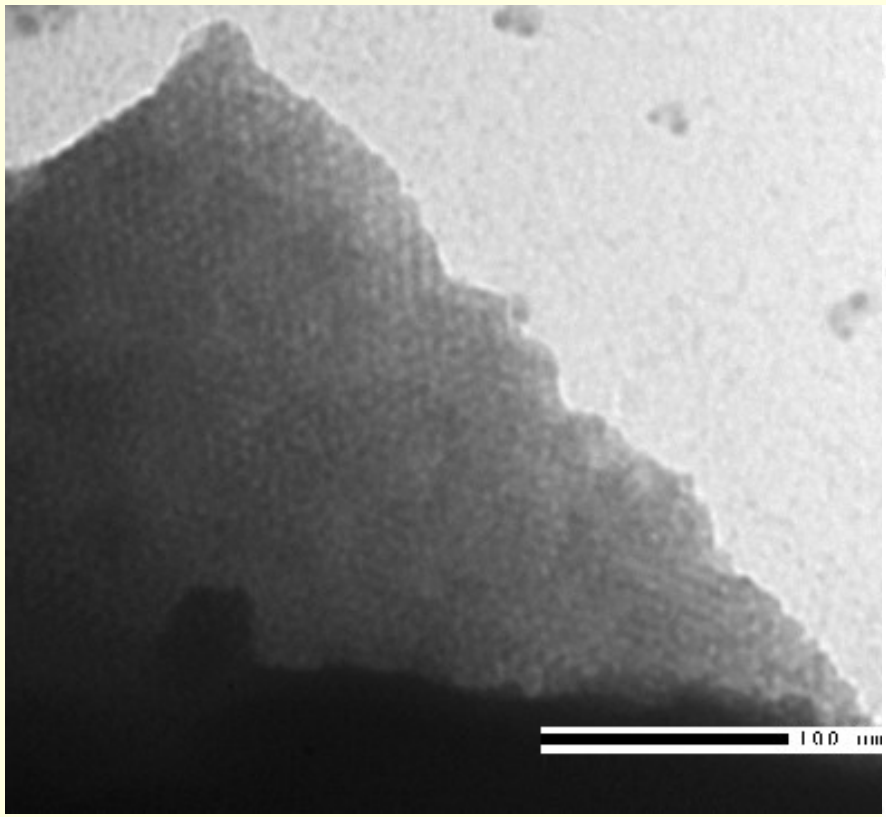
250°C 3h



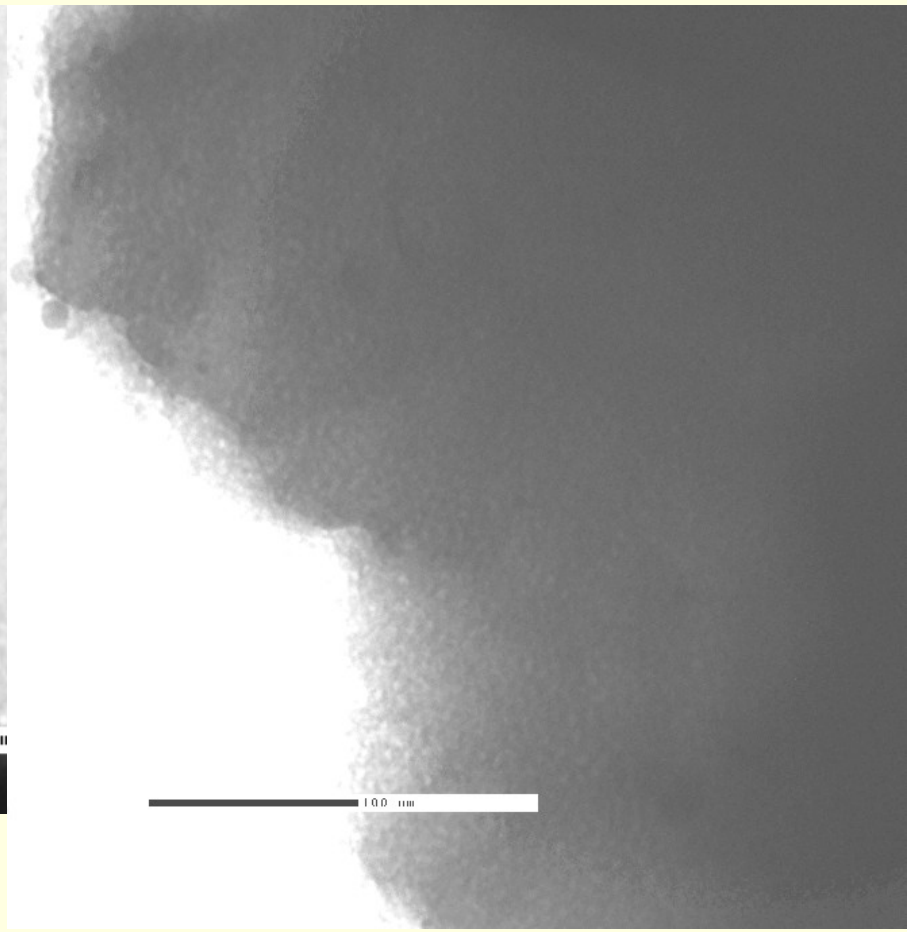
400°C 2h

Optical Microscope Micrographs

EPS--OS-1) Templated PTA hybrids film (D)



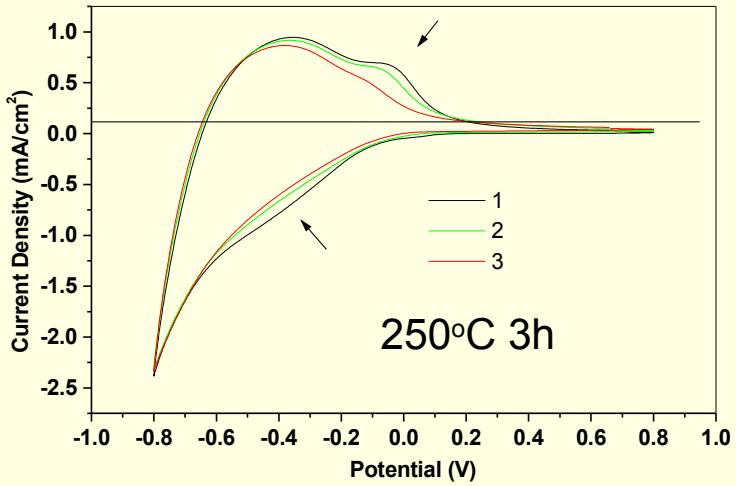
100°C 1h

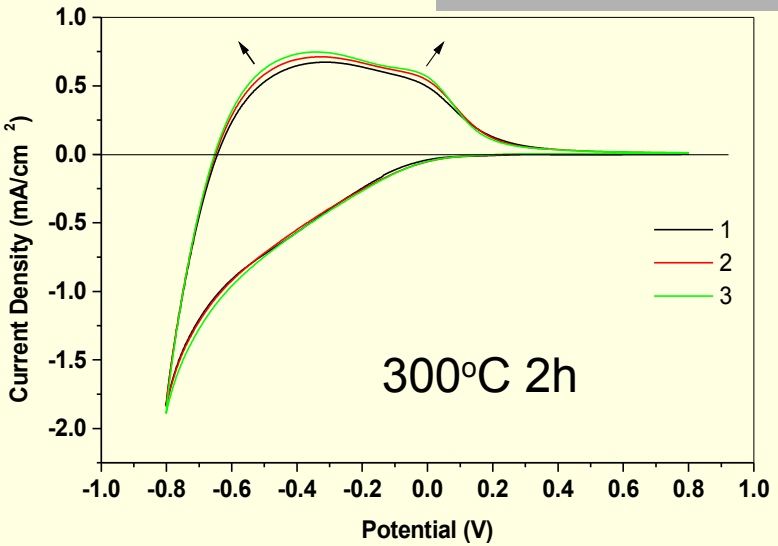


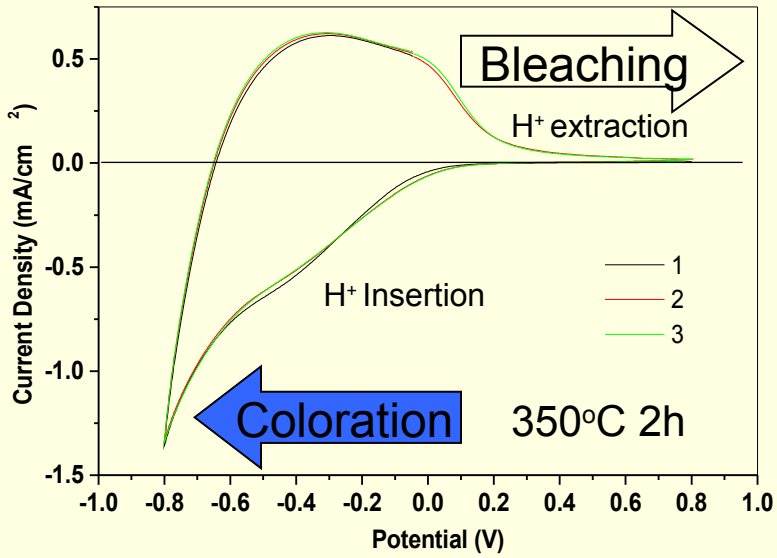
400°C 2h

TEM micrographs

Electrochromic properties (A)







WO_3 (colorless)+xM^++xe^- ↔M_xWO_3 (blue)

Cyclic voltammetry of meso-WO3 dried at different temperatures

Electrochromic properties (B)

Sample		Amount of charge inserted Q^-/ mC cm^2	Amount of charge extracted Q^+/mC cm^2	Q^+/Q^-(reversibility)
250°C 3h	C1	83.5	55.55	0.67
	C2	77.25	55.2	0.72
	C3	74.05	50.65	0.68
300°C 2h	C1	62.75	42.55	0.68(0.72[a])
	C2	62.85	46.6	0.74
	C3	64.85	48.4	0.75
350°C 2h	C1	--	--	--
	C2	52	41.65	0.80(0.7[400°C[a]])
	C3	52.2	42.4	0.81

a: W. Cheng, et al, J. Mater. Chem. 2001, 11, 92

Summary on electrochromic measurements

- In acidic medium, WO_3 is not very stable. For 250°C dried film, coloration ⇔bleaching was continued for 3 cycles, while 6 cycles for 300°C dried before loss of anodic peak due to film dissolution in diluted H_2SO_4. In nonaqueous Lithium-base electrolyte, WO_3 is known to be much more stable.
- More work on the electrochromic properties, such as coloration efficiency and chronoamperometry, are under way.

Conclusion

- ✓By choosing suitable organic surfactant template, tungstic acid can also be used as inorganic precursor to synthesize thermally stable nanostructures. OS-1 was proved to the suitable as structure-directing agent for the preparation meso-WO3 films.
- ✓Mesostructures can be stabilized against calcination at 400^{o}C for 2hrs by optimizing the drying processes.
- ✓Based on current results, comparable electrochromic properties were observed compared with WCl_6 derived meso-WO_3 films.

Thank you so much