

Supplementary Information for

**Straightforward Nonhydrolytic Sol-Gel Route**

**to Mesoporous Mixed-Conducting Tungsten Oxide**

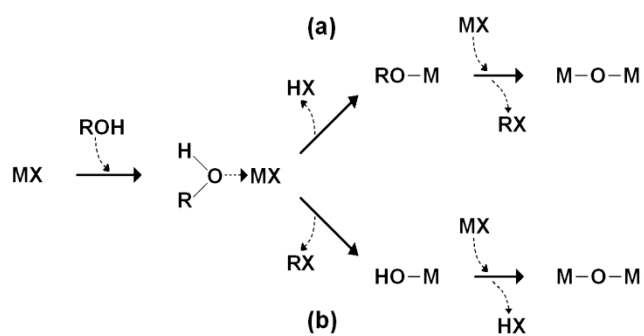
*Gabriele Orsini and Vincenzo Tricoli*

Dipartimento di Ingegneria Chimica, Chimica Industriale e Scienza dei Materiali,

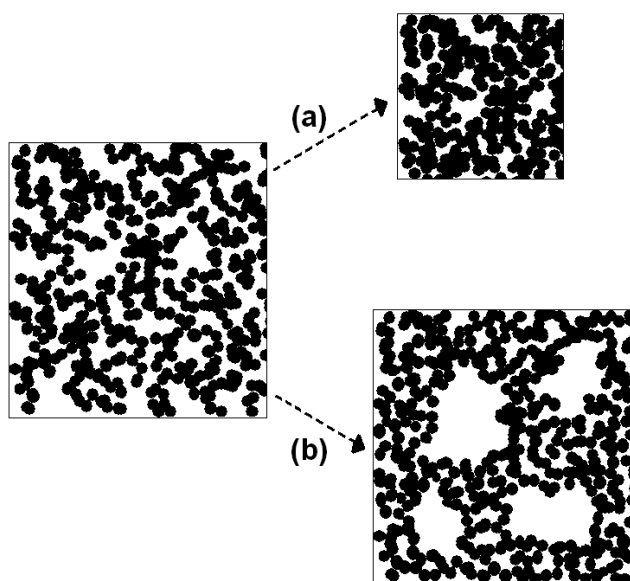
Università di Pisa, largo L. Lazzarino 1, 56126, Pisa, Italy

***Nonhydrolytic Sol-Gel Mechanisms***

The initial step is the coordination of the alcohol oxygen to the metal centre to give an intermediate complex, whose evolution depends on the alcohol nature. For primary and secondary alcohols (case *a* in Fig. S1), carbocations are energetically unstable and bad leaving groups as compared to the hydrogen ion, but the opposite occurs for benzylic and tertiary alcohols (case *b*). Thus, in case *a* the leaving of hydrogen ion yields a metal alkoxide, whereas in case *b* the leaving of carbocation yields a metal hydroxyl. Oxide formation is finally achieved by condensation of alkoxide and hydroxyl groups with halide groups. Although the overall reaction is the same, mechanisms involved are different and imply different kinetics (hydroxyl groups are significantly more reactive than alkoxide groups) with different microstructure in final products.



**Fig. S1** Gelation mechanisms in metal-halide/alcohol systems. (a) Mechanism for primary and secondary alcohols. (b) Mechanism for benzylic and tertiary alcohols. R, M and X denote respectively an organic group, a metal atom and a halogen atom.



**Fig. S2** Syneresis in a particulate gel monolith. (a) Macro-syneresis with global volume contraction.  
(b) Micro-syneresis with enlargement in pore size and no reduction in total volume.

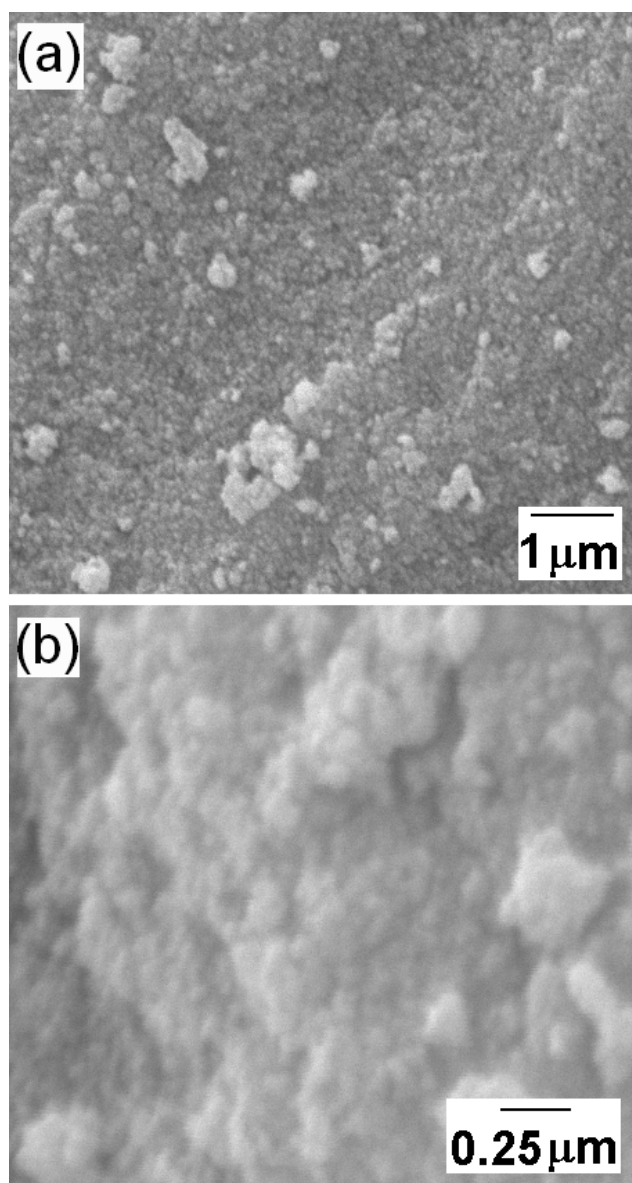


Fig. S3 SEM images of a sample with  $X=50\%$  at two different magnifications.