Supporting information

Small-angle x-ray scattering (SAXS) of different combinations of metal oxide films

The SAXS data of the films in Fig. S1 were acquired in transmission mode, i.e. the angle of incidence between the incoming x-ray beam and the film surface was 90°. Thus, the 2D patterns reflect the in-plane mesoscopic order of the films. It is seen that after treatment at 300° C, i.e. at a temperature lower than the crystallization temperature of both oxides, the films generate a Bragg ring, corresponding to a well-ordered mesoporosity, except for the WO₃/WO₃/WO₃. Thus, the SAXS data show that an intermediate, mesostructured TiO₂ layer is beneficial to keep mesostructural order in the WO₃ films. In general, the signals similar to those of our previous publications on WO₃ and TiO₂ using the KLE template.



Figure S1: 2D-SAXS transmission of WO₃/WO₃ (S1.a), WO₃/WO₃ (S1.b), WO₃/TiO₂ (S1.c), and WO₃/TiO₂/WO₃ (S1.d) after annealing at 300°C.

Figure S2 shows that already at an annealing at 300° C differences are seen in the mesostructure of multilayer films (WO₃/WO₃ vs. WO₃ films with TiO₂ intermediate layers). At this temperature, the matrices are still amorphous, which shows that indeed the differences in the quality of the mesoscopic order are mainly due to the self-assembly process, and not the annealing: the films having a TiO₂ sub- or intermediate layer show better mesoscopic order than those without such layers.



Figure S2: 2D-SAXS data (all of them are measured at an angle of incidence of 10° between the x-ray beam and the surface of the films) of WO₃/WO₃ (S2.a), WO₃/WO₃ (S2.b), TiO₂/WO₃ (S2.c), WO₃/TiO₂ (S2.d) and WO₃/TiO₂/WO₃ (S2.e) after annealing at 300°C.

Figure S3 shows that $WO_3/WO_3/WO_3$ films prepared without TiO_2 intermediate layers loose their mesoscopic order (Fig. a: transmission mode), while those with a TiO_2 intermediate layer show good order even at elevated annealing temperature.



Figure S3: 2D-SAXS reflexion of WO₃/WO₃/WO₃ (S3.a), and WO₃/TiO₂/WO₃ (S3.b) after annealing at 450°C and 550°C respectively.

Figure S4: SEM of a TiO₂/WO₃ film.



Figure S4 shows that the films are absolutely crack-free. The inset shows the mesopores on the surface.