

Ordered mesoporous titania from highly amphiphilic block copolymers: tuned solution conditions enable highly ordered morphologies and ultra-large mesopores

Morgan Stefik, Juho Song, Hiroaki Sai, Stefan Guldin, Patrick Boldrighini, M. Christopher Orilall, Ullrich Steiner, Sol M. Gruner, Ulrich Wiesner

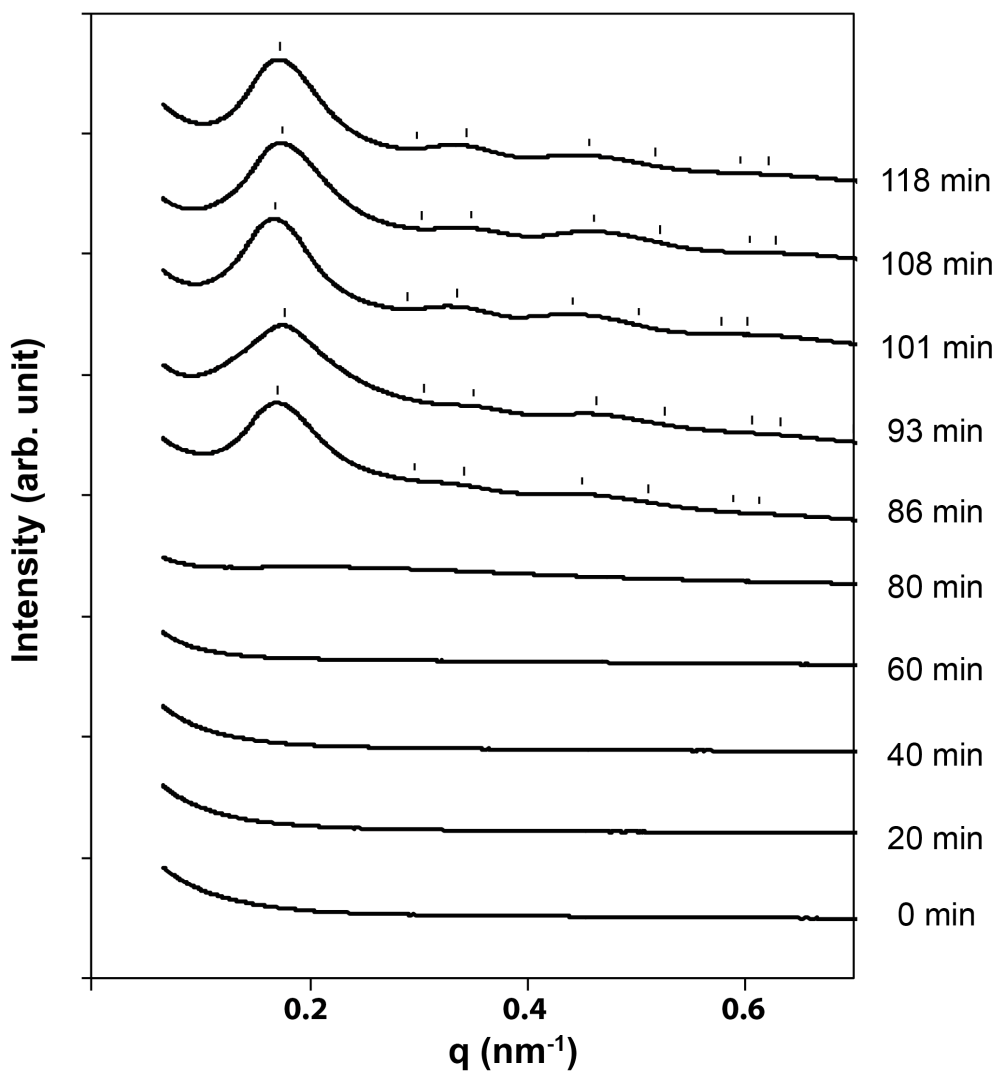


Figure S1. *In-situ* small-Angle X-ray Scattering data during the evaporation process depicting the evolution of the hexagonally arranged mesostructure of IO28K-h1.

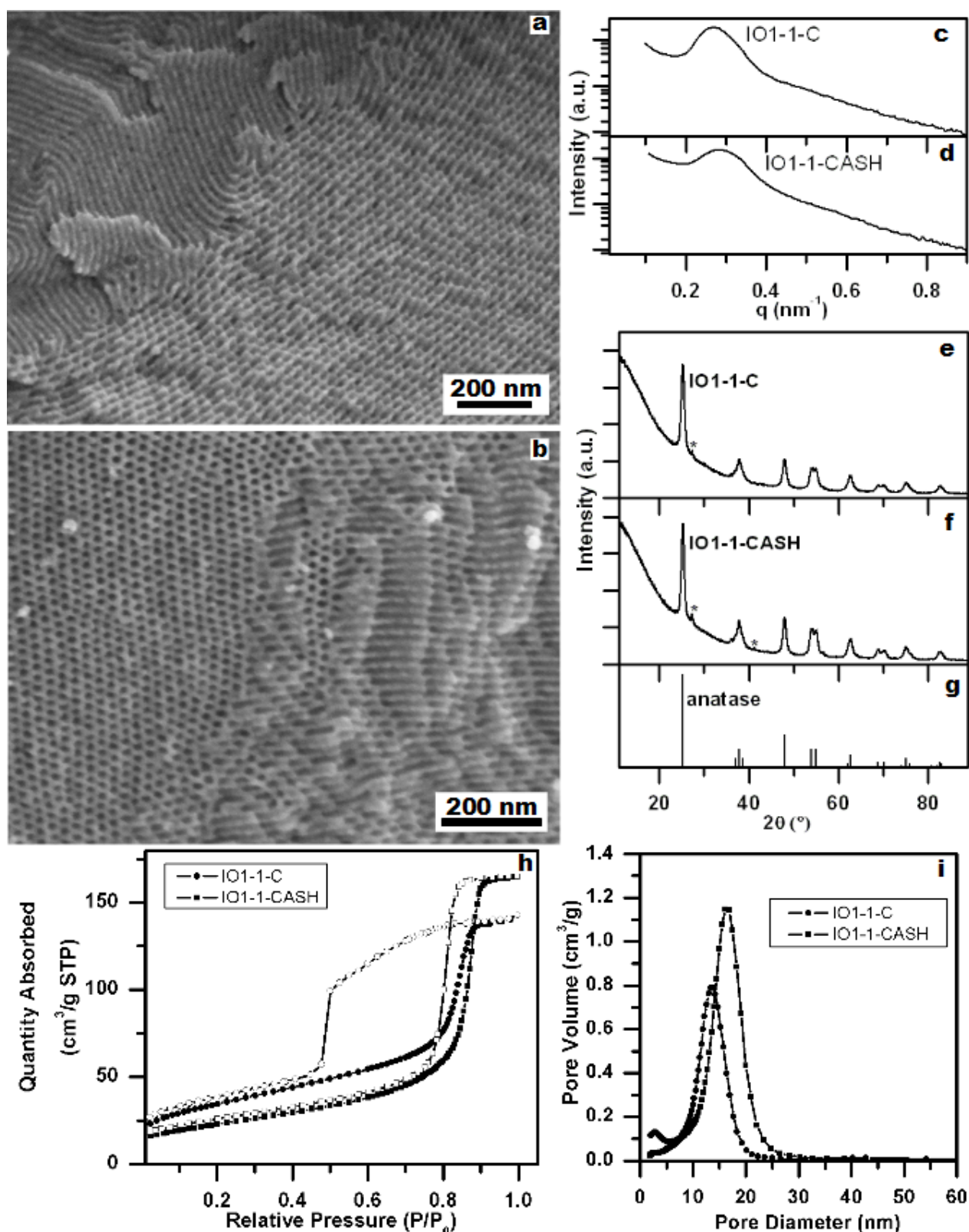


Figure S2. An ordered mesostructure of IO28K-h1-C after the first calcination in inert atmosphere is confirmed by SEM (a) and SAXS (c). The subsequent calcination in air also preserves the ordered mesostructure of IO28K-h1-CASH as confirmed by SEM (b) and SAXS (d). XRD analysis indicates that the first heat treatment results in crystallization of the amorphous titania sol to anatase (e), which is preserved after the second heat treatment (f). XRD peaks are consistent with anatase titania (g, PDF#21-1272) with the exception of trace rutile peaks (*). Nitrogen physisorption measurements indicate that both samples are mesoporous (h) with narrow BJH pore size distributions (i).

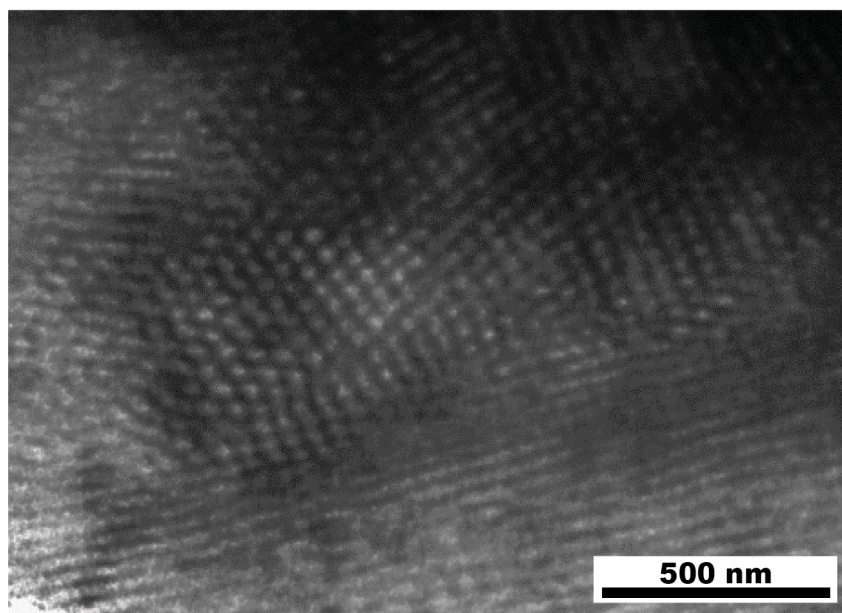


Figure S3. TEM image of IO92K-CASH indicating that mesoporosity is preserved after CASH heat treatments.

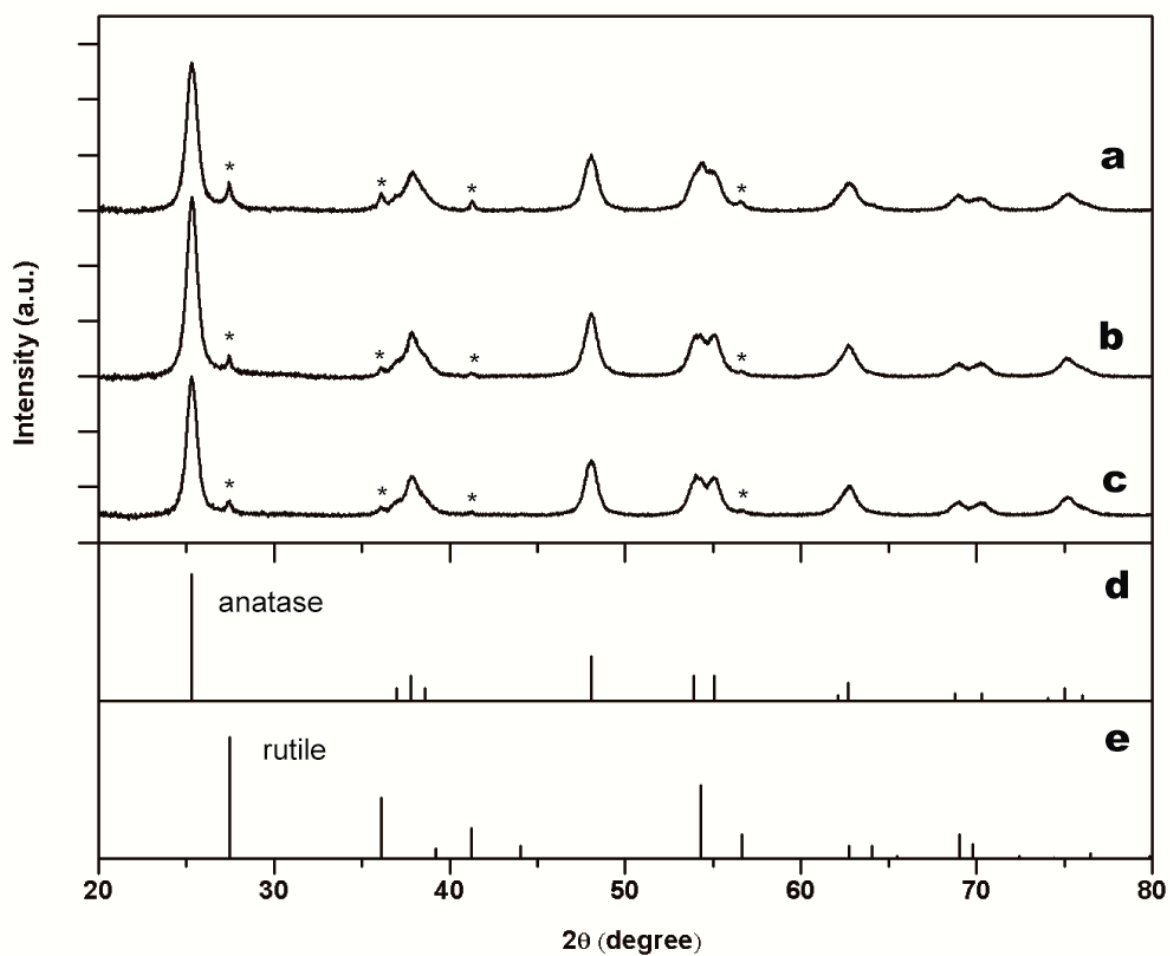


Figure S4. The XRD patterns for mesoporous crystalline titania after CASH heat treatments; IO92K-CASH (a), IO41K-CASH (b), IO13K-CASH (c), standard anatase TiO₂ (d, PDF#21-1272) and rutile TiO₂ (e, PDF#21-1276). Samples were first calcined at 700 °C for 4 hrs under nitrogen atmosphere. The second calcination was then carried out at 450 °C for 4 hrs in air.

Table S1. CASH heat processing conditions for PI-*b*-PEO/titania hybrid materials. The temperature and time of the first heat treatment step are adjusted to give pure anatase crystalline phase for titania from IO13K-h, IO41K-h and IO92K-h.

Titania-IO(PI-<i>b</i>-PEO)	IO7K-CASH	IO13K-CASH	IO41K-CASH	IO92K-CASH
Heat treatment -1 (under nitrogen)				
Temperature, °C	700	600	600	700
Dwelling time, hr	4	2	2	2
Ramp rate, °C/min	5	1	1	1
Heat treatment -2 (under air)				
Temperature, °C	450	450	450	450
Dwelling time, hr	4	2	2	2
Ramp rate, °C/min	5	1	1	1

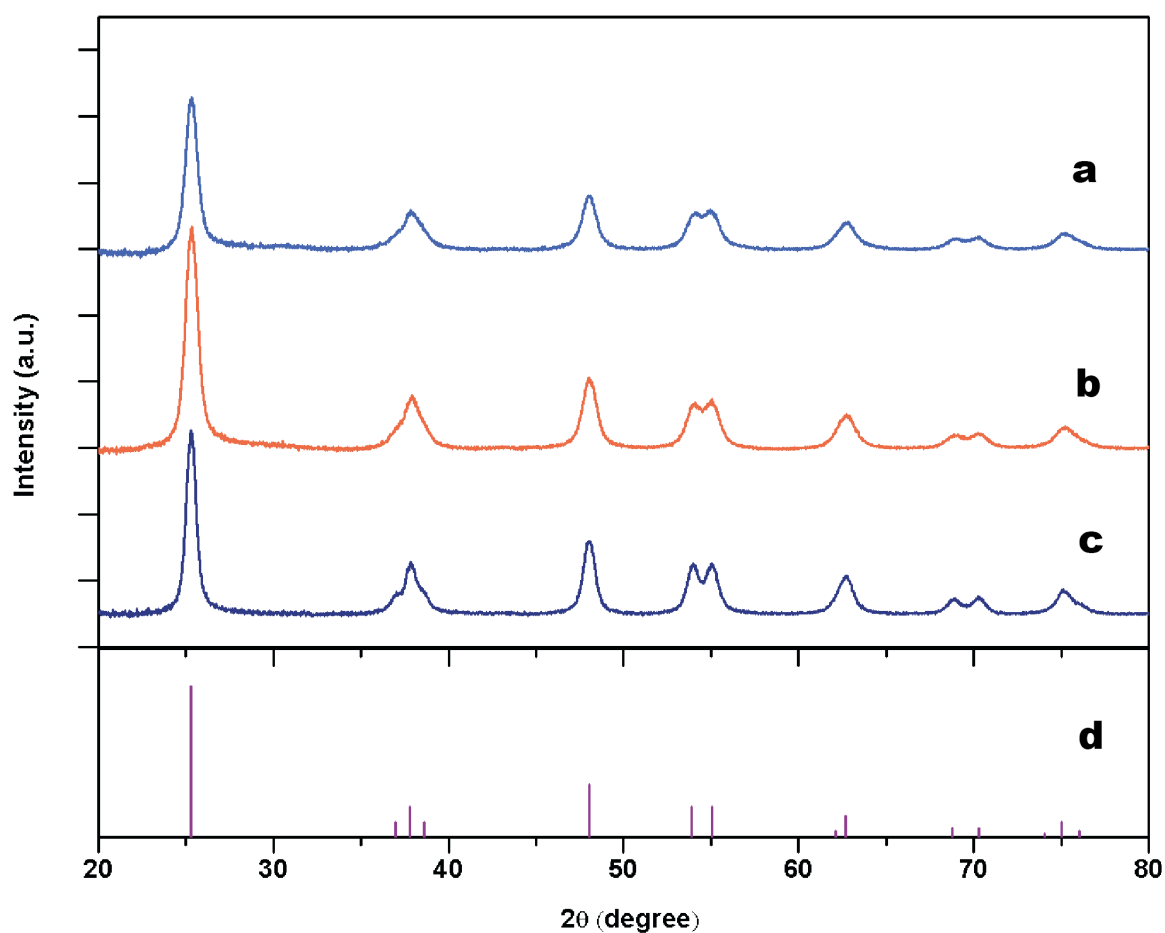


Figure S5. XRD patterns for mesoporous crystalline titania after CASH heat treatments as described in Table S1.; IO41K-CASH (a), IO13K-CASH (b) and IO7K-CASH (c). Bar markers indicate peaks for standard anatase TiO₂ structure (d, PDF#21-1272).

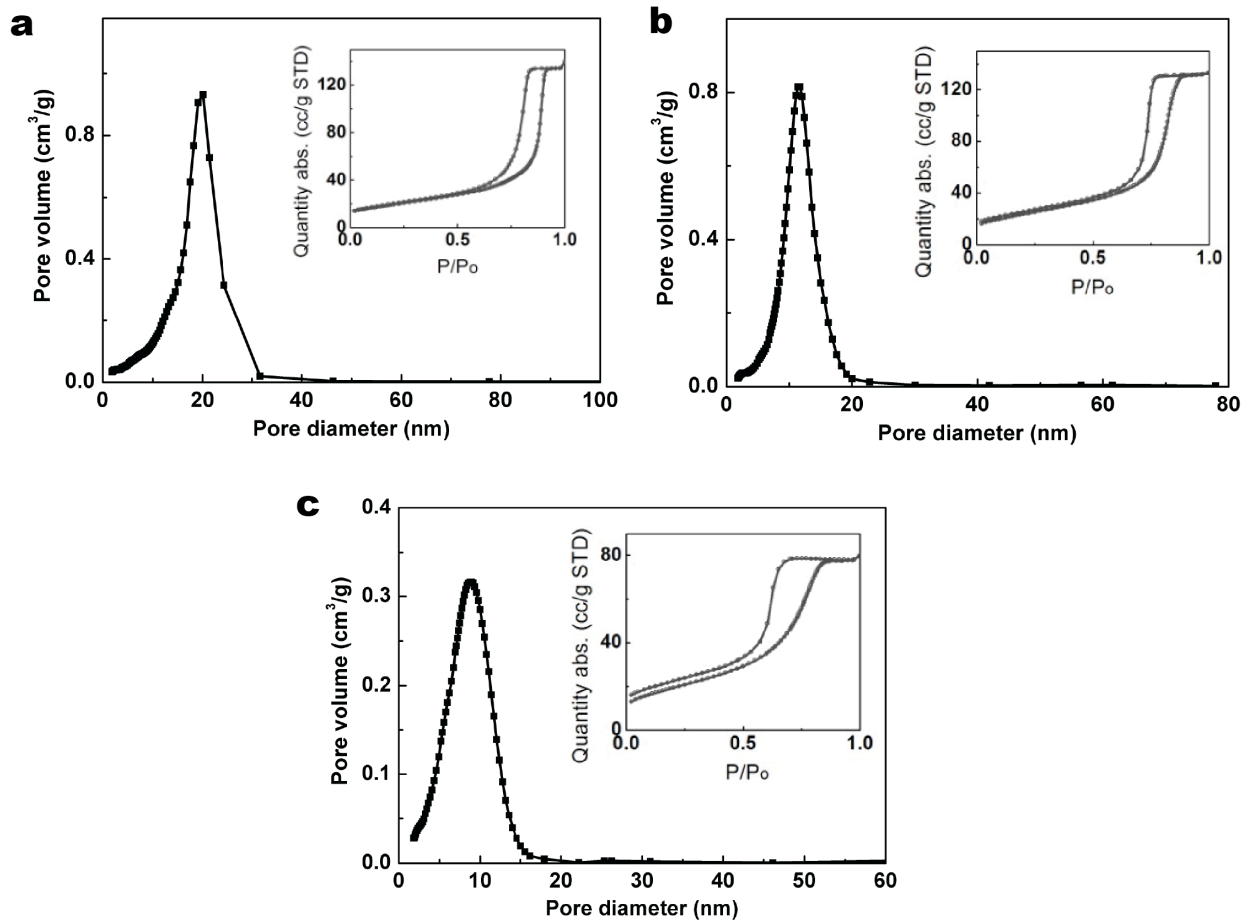


Figure S6. Pore size distributions of mesoporous titania from IO41K-CASH (a), IO13K-CASH (b) and IO7K-CASH (c). Pore sizes were calculated using the BJH adsorption pore analysis method. Insets show the corresponding nitrogen adsorption and desorption isotherms.