Electronic Supplementary Material (ESI) for Chemical Communications.

Mesoporous $TiO_2/Zn_2Ti_3O_8$ Hybrid Films by Polymeric Micelle Assembly

Experimental Section

Materials

The poly(styrene-2-vinylpyridine-ethylene oxide) ($PS_{(14500)}$-$PVP_{(20000)}$-$PEO_{(33000)}$) triblock copolymer with polydispersity index 1.15 (the numbers in the parentheses indicate the molecular weights of each block) was purchased from Polymer Source. Tetrahydrofuran (THF, Wako), hydrochloric acid (HCl, Nacalai), titanium tetraisopropoxide (TTIP, Wako) and zinc nitrate ($Zn(NO_3)_2$, Wako) were used without further purification.

Characterization

The hydrodynamic diameter of the polymeric micelles was measured using the dynamic light scattering measurement (DLS, Otsuka ELSZ particle and zeta-potential analyzer). The crystalline phases were investigated by thin film X-ray diffractometer (XRD, Shimadzu XRD-7000). The thermal stability of the micelles composites was tested by thermogravimetric analysis (SEIKO-6300 TG/DTA instruments). The morphology of the mesoporous films was observed under field-emission scanning electron microscope (SEM, Hitachi SU-8000) and transmission electron microscope (TEM, JEOL JEM-1210).

Photocatalytic testing

The photocatalytic H_2 evolution test was investigated in a glass reactor (220 mL) with a closed gas circulation and evacuation system. 300 W UV-enhanced Xe lamp light source was used. $TiO_2/Zn_2Ti_3O_8$ mesoporous thin films on the quartz substrate (2.0×2.0 cm) were placed in the bottom of the glass reactor contained aqueous methanol solution (10 mL methanol in 50 mL H_2O). The evolution of H_2 gas was analyzed with an online gas chromatography (GC-8A, Shimadzu) with a thermal conductivity detector.

Fig. S1

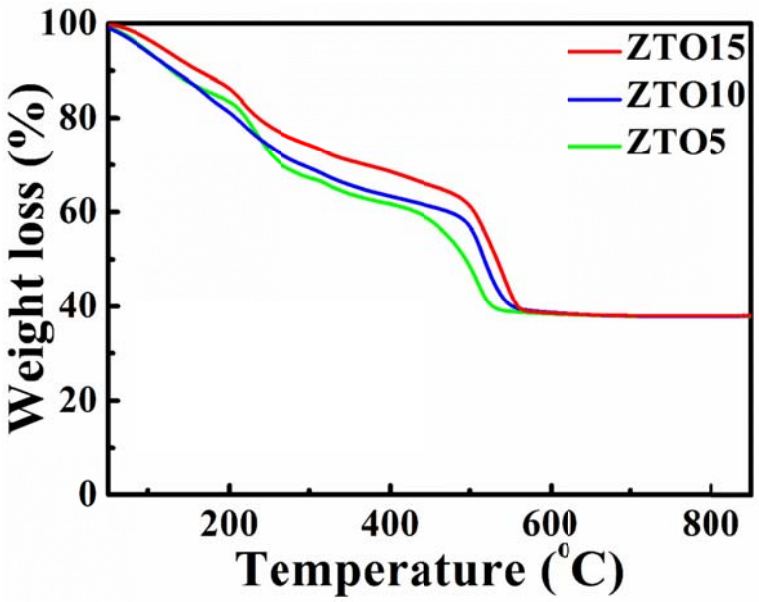

Fig. S1 The thermogravimetric analysis (TGA) of $TiO_2/Zn_2Ti_3O_8$/PS-PVP-PEO composite micelles.

Fig. S2

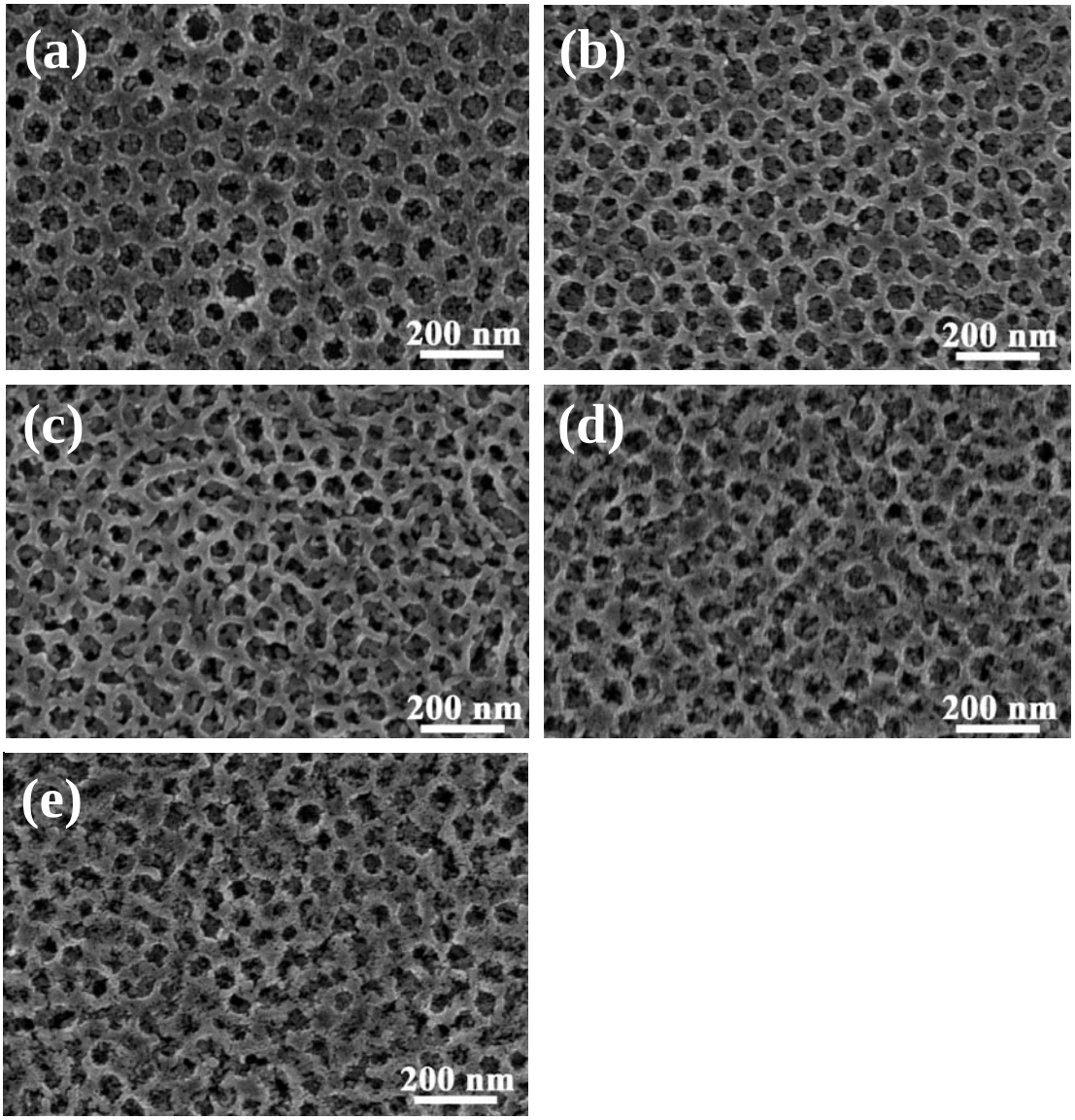

Fig. S2 The SEM images of mesoporous films of various phase compositions calcined at 550 ^{o}C (a) ZTO0, (b) ZTO5, (c) ZTO10, (d) ZTO15, and (e) ZTO20.

Fig. S3

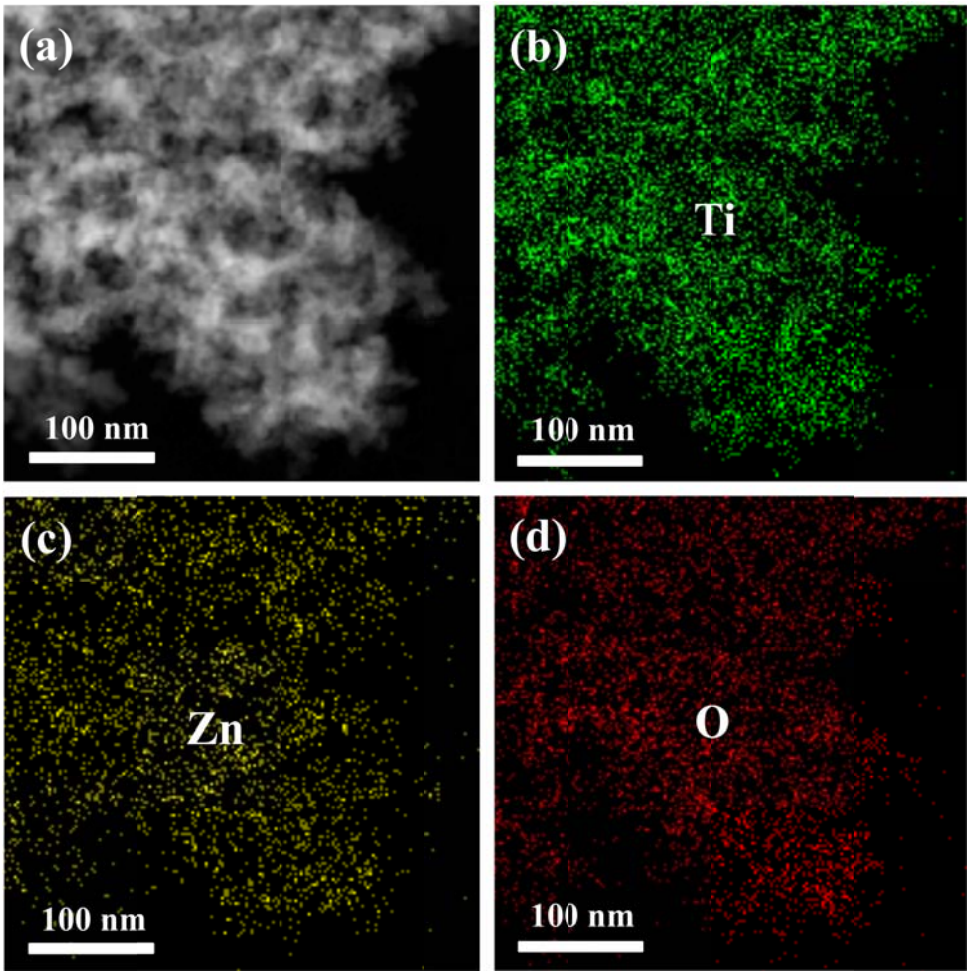

Fig. S3 (a) HAADF-STEM image and nanoscale elemental mapping of b) Ti and c) Zn, and d) O of mesoporous film of ZTO15.

Fig. S4

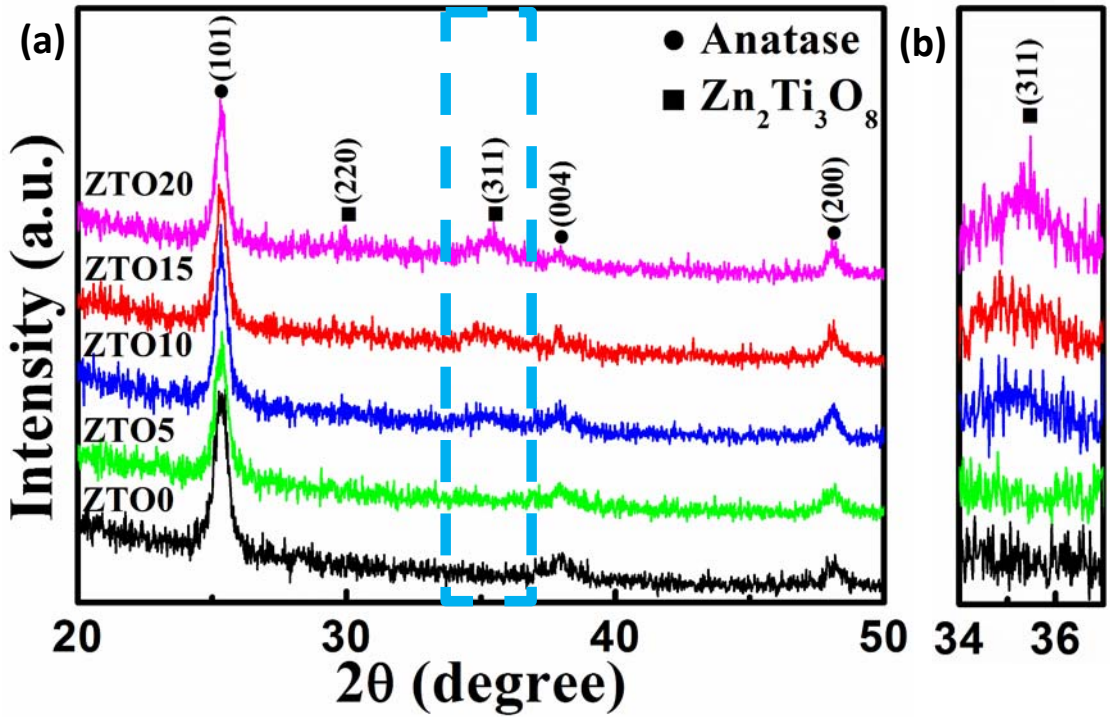

Fig. S4 The XRD patterns of $TiO_2/Zn_2Ti_3O_8$ mesoporous thin films. The enlarge (311) peak is shown in (b)

Table S1. Phase compositions and H_2 evolution rate of different mesoporous films.

Samples	TiO_2 (%)	$Zn_2Ti_3O_8$ (%)	$k(H_2)$ ($\mu mol.h^{-1}$)
ZTO0	100	0	6.78
ZTO5	93.9	6.1	7.91
ZTO10	89.2	10.8	8.45
ZTO15	86.0	14.0	10.16
ZTO20	79.3	20.7	7.54

Fig. S5

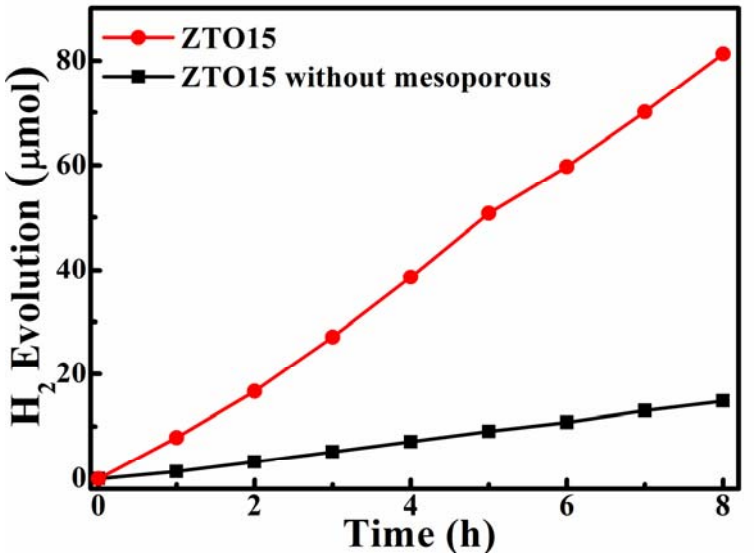

Fig. S5 Comparison of photocatalytic activity for H_2 evolution of ZTO15 and $TiO_2/Zn_2Ti_3O_8$ composites, $TiO_2/Zn_2Ti_3O_8$ composites without mesoporous was synthesized in the absence of block copolymer.