## **Supporting Information**

## Copper on the inner surface of mesoporous TiO<sub>2</sub> hollow sphere: a highly selective photocatalyst for partial oxidation of methanol

## to methyl formate

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Figure 1s The diagram of reaction process



Figure 2s FTIR spectra of samples.



Figure 3s TG-DSC profile of the 3CuC@5Ti-Dr-S sample.



Figure 4s XRD profiles of samples with different hydrolysis duration. (a) samples dried in supercritical ethanol; (b) samples calcined at 600°C.



Figure 5s TEM images of samples. (a) 3Cu@5Ti-Dr-S(8); (b) 3Cu@5Ti-600(8); (c) 3Cu@5Ti-Dr-S(6); (d) 3Cu@5Ti-600(6); (e) 3Cu@5Ti-Dr-S(4); (f) 3Cu@5Ti-600(4); (g) 3Cu@5Ti-Dr-S(2); (h) 3Cu@5Ti-600(2)



Figure 6s Isotherms of samples. (a) 3Cu@3Ti-600; (b) 3Cu@5Ti-600; (c) 3Cu@6Ti-600; (d) 3Cu@8Ti-600-6; (e) 3Cu@10Ti-600; (f) 3Cu@5Ti-700.



Figure 7s UV-visible spectra of samples. (a) effect of copper content; (b) effect of hydrolysis time;

Table 1s Integration areas of the deconvolution curves attributed to different oxygen species

Sample name	In TiO <sub>2</sub>	In hydroxyl	In water
3CuC@5Ti-300	48895	42538	33983
3CuC@5Ti-400	44639	39873	33575
3CuC@5Ti-500	64128	39144	22103
3CuC@5Ti-600	68119	34202	11972
3CuC@5Ti-700	75990	23946	9199