Supplementary Information

Adjustment and Matching of Energy band of TiO_2-based Photocatalysts by Metal Ions (Pd, Cu, Mn) for Photoreduction of CO_2 into CH_4.

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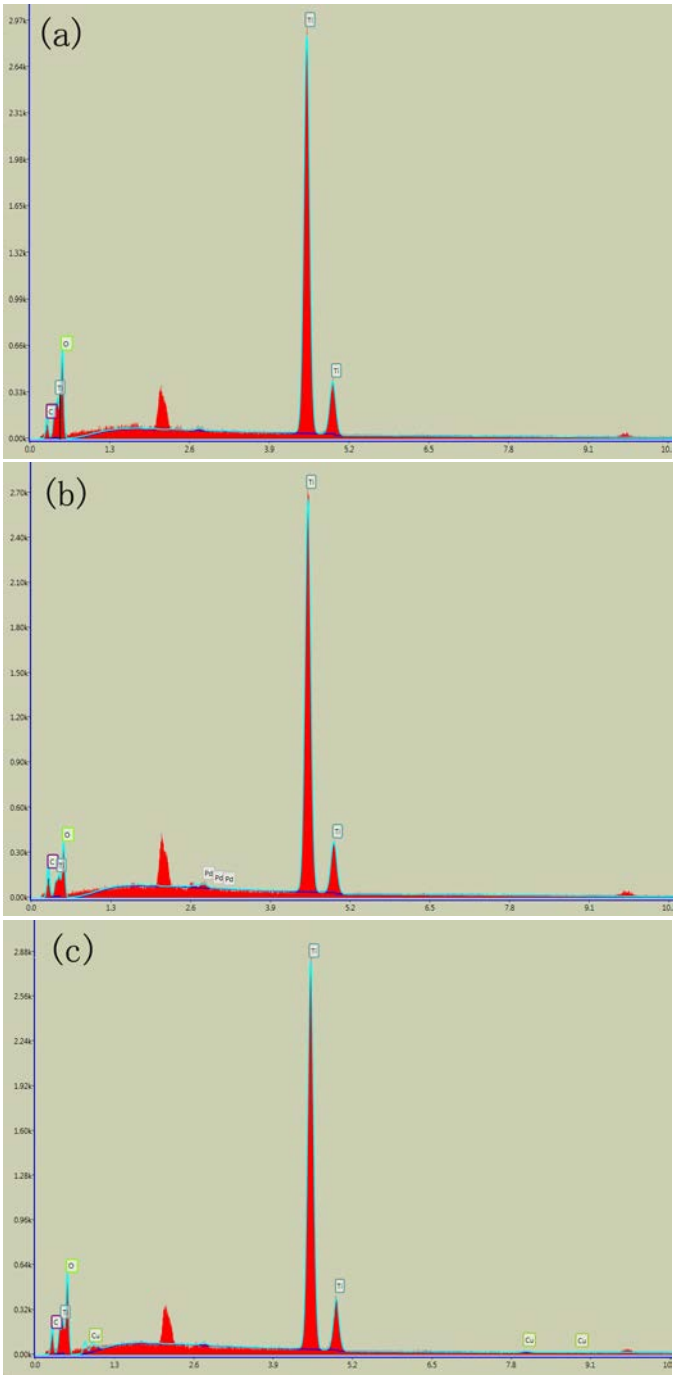

(a)
(b)
(c)

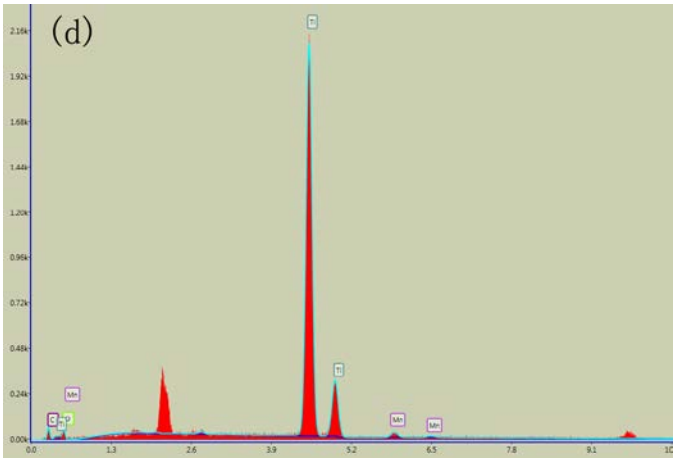


Figure S1. EDAX spectra of (a) pure TiO_2, (b) TiO_2-Pd 1%, (c) TiO_2-Cu 1% and (d) TiO_2-Mn 1% samples.

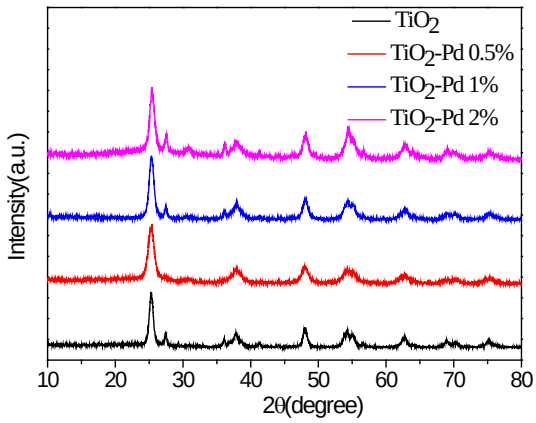


Figure S2. XRD patterns of pure TiO_2, TiO_2-Pd x% samples.

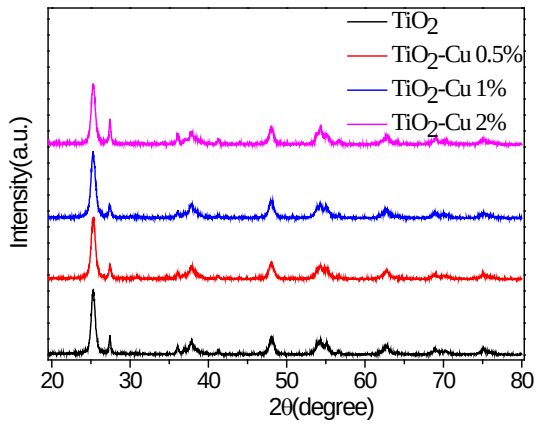


Figure S3. XRD patterns of pure TiO_2, TiO_2-Cu x% samples.

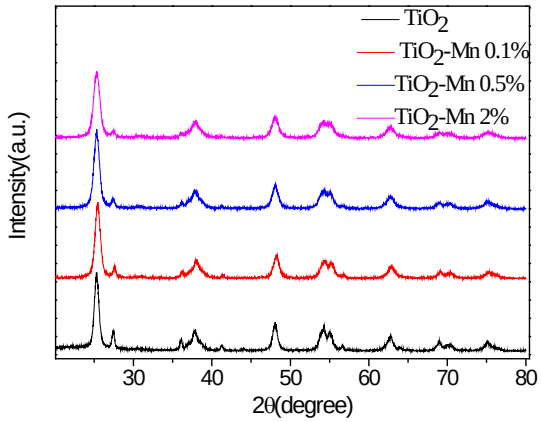


Figure S4. XRD patterns of pure TiO_2, TiO_2-Mn x% samples.

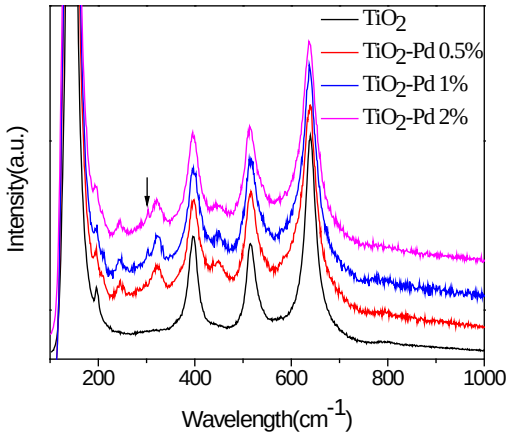


Figure S5. Raman spectra of pure TiO_2, TiO_2-Pd x% samples.

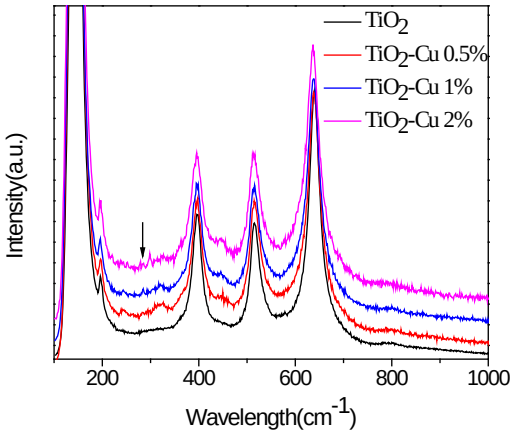


Figure S6. Raman spectra of pure TiO_2, TiO_2-Cu x% samples.

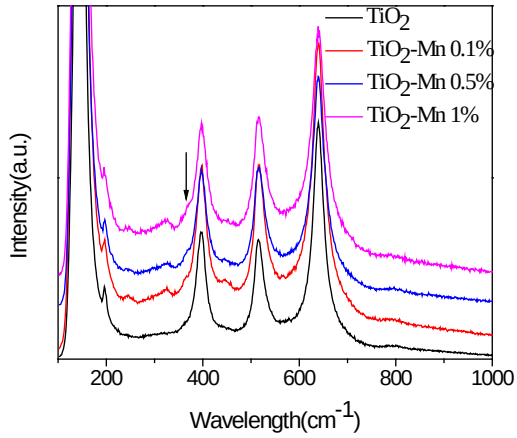


Figure S7. Raman spectra of pure TiO_2, TiO_2-Mn x% samples.

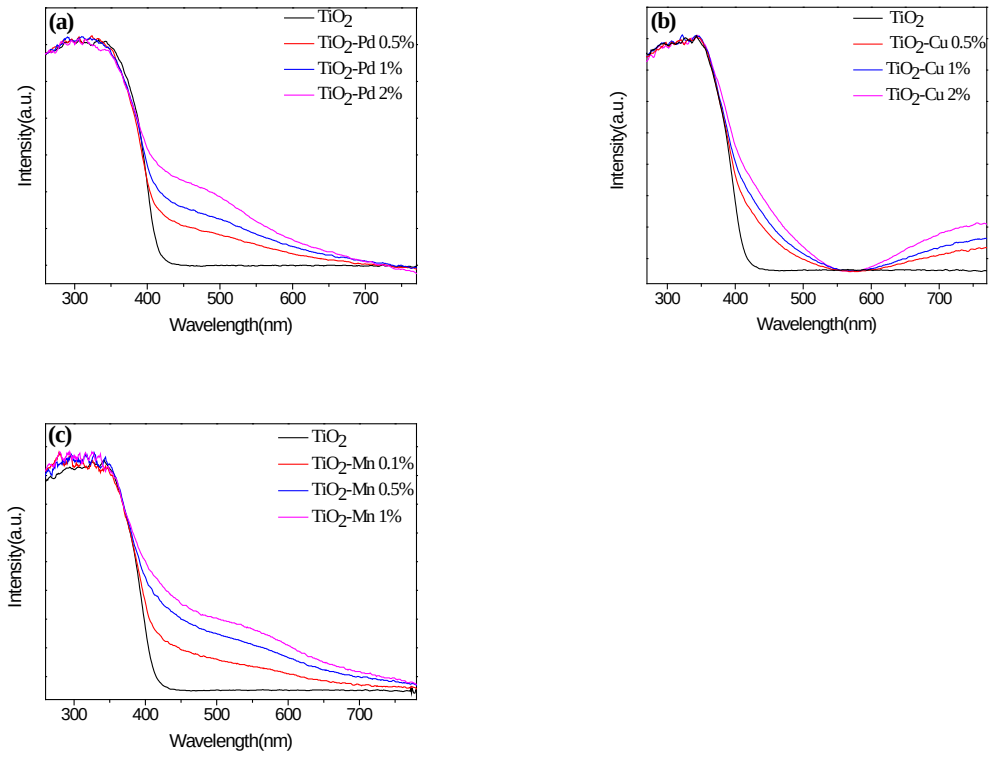


Figure S8. Diffuse reflectance UV-Vis spectra of (a) TiO_2 and TiO_2-Pd x%; (b) TiO_2 and TiO_2-Cu x%; (c) TiO_2 and TiO_2-Mn x% samples.

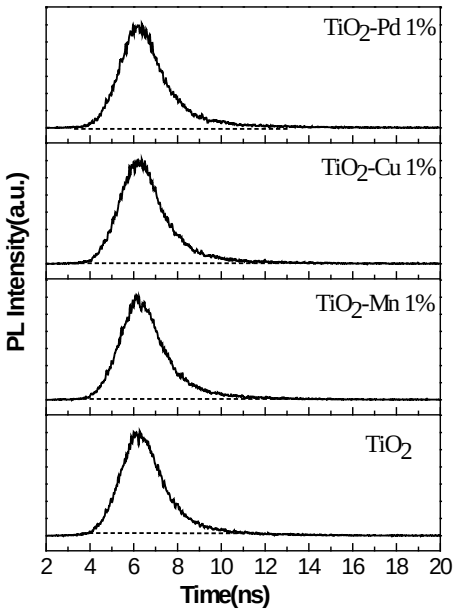


Figure S9. Time-resolved PL decay curves for pure TiO_2, TiO_2-Mn 1%, TiO_2-Cu 1% and TiO_2-Pd 1% samples.

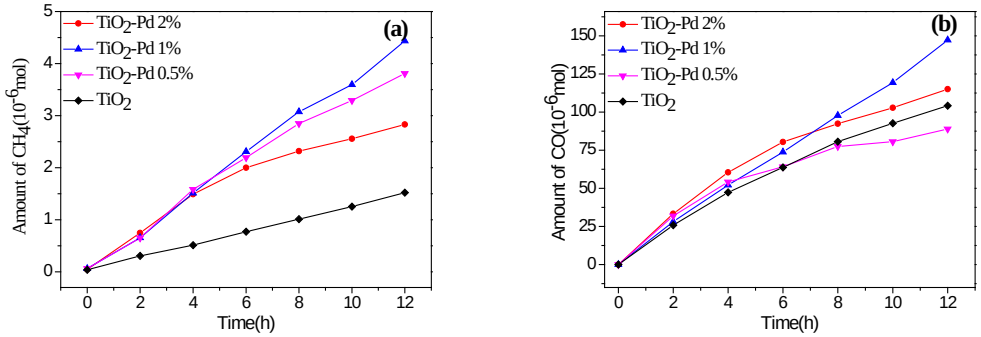


Figure S10. Photocatalytic activity for reduction of CO_2 into CH_4 (a) and CO (b) of pure TiO_2 and TiO_2-Pd x% samples.

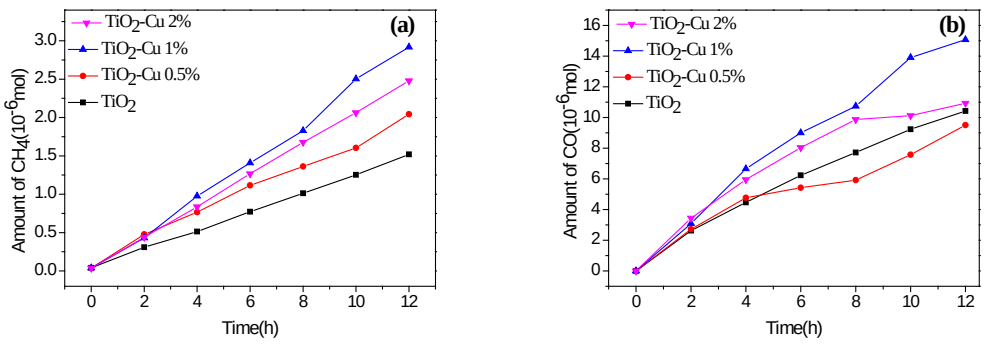


Figure S11. Photocatalytic activity for reduction of CO_2 into CH_4 (a) and CO (b) of pure TiO_2 and TiO_2-Cu x% samples.

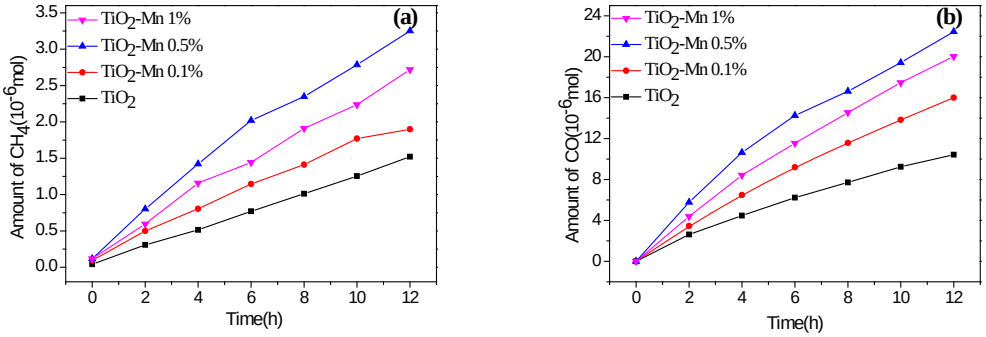


Figure S12. Photocatalytic activity for reduction of CO_2 into CH_4 (a) and CO (b) of pure TiO_2 and TiO_2-Mn x% samples.

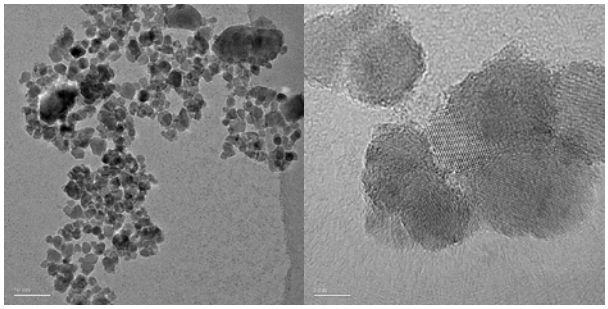


Figure S13. TEM and HR-TEM images of TiO_2-Pd1%.

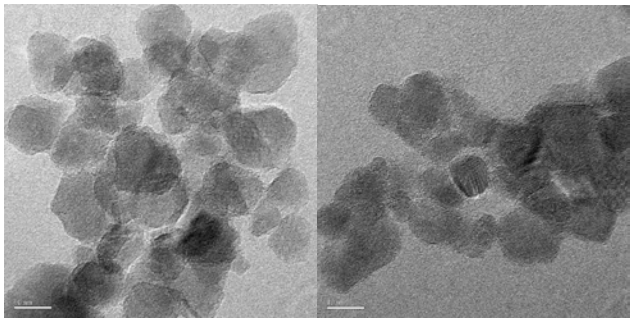


Figure S14. HR-TEM images of TiO_2-Cu1% and TiO_2-Mn1%.

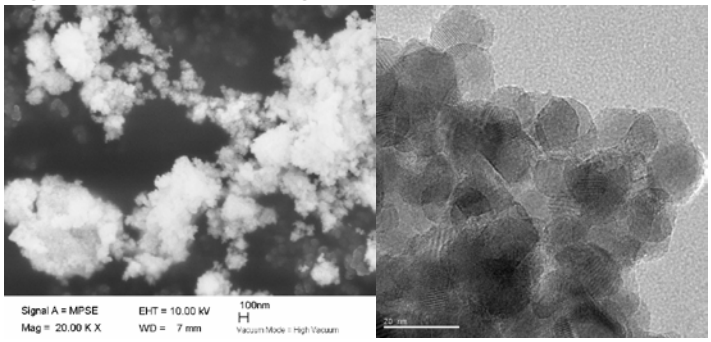


Figure S15. SEM and HR-TEM images of TiO_2.

The TEM and HR-TEM images of TiO2-Pd1%, TiO2-Cu1% and TiO2-Mn1% are shown in Figure S13, S14 and S15, respectively. It is clear from the Figure S13 that the as-prepared samples consist of anatase nanoparticles with an average diameter of 10 nm, which is consistent with the XRD analysis. Moreover, some larger nanoparticles whose diameter is almost more than 50 nm are ascribed to rutile. For the HR-TEM images of TiO2-Pd1%,

TiO2-Cu1% and TiO2-Mn1% , A fringe spacing (d) of 3.52 Å, corresponding to the (101) plane of anatase TiO2 is observed for all samples, which suggests that the introduced Pd, Cu and Mn ions are not doped into the TiO2 lattice in the substitutional or interstitial mode. There is no other phase, such as PdO, CuO and MnO_x observed in the TEM images. These TEM and HR-TEM images further demonstrate the introduced Pd, Cu and Mn ions are existing as unique surface O-Me-O species.

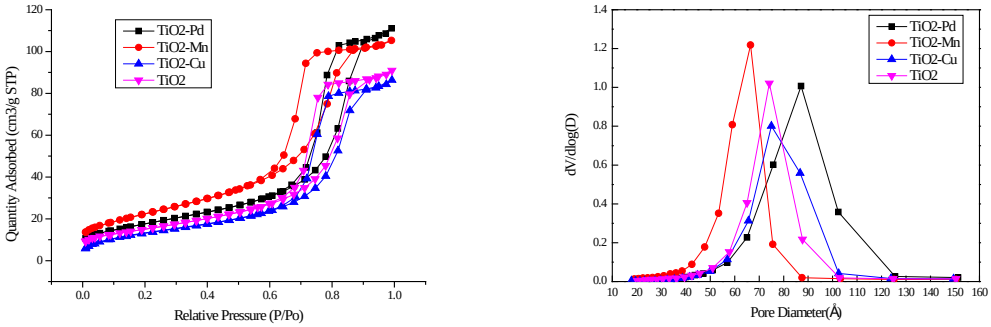
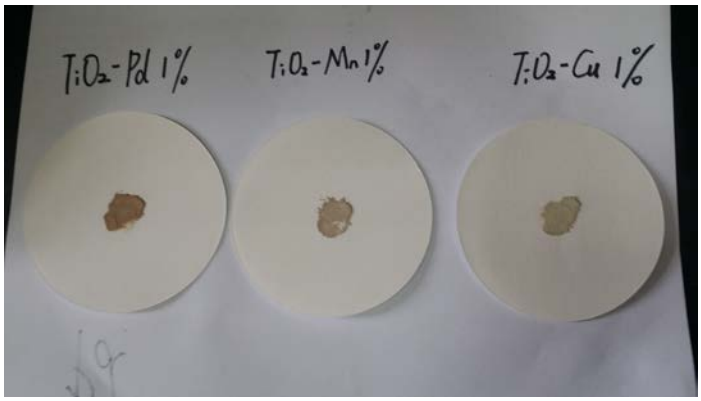


Figure S16. N2 adsorption isotherms and pore size distribution for TiO2-Pd, TiO2-Mn, TiO2-Cu and TiO2.

This figure shows that the adsorption isotherm for all samples are similar and display hysteresis loops at relative pressures (P/P0) close to unity, which can be categorized as type IV according to IUPAC classification. It is found that a pure size distribution in 6-9 nm range is observed for TiO_2-Pd, TiO_2-Mn, TiO_2-Cu and TiO_2 samples. The TiO_2 nanoparticles agglomerate together, to form mesoporous microspheres with several hundreds of nanometers in length. This mesoporosity may be caused by the agglomeration of nanoparticles with an average size of 10-18 nm. As shown in SEM and TEM images, when the irregular global TiO_2 nanoparticles agglomerate together, the agglomeration results in the formation of porosity, whose diameter is almost half the nanoparticles.



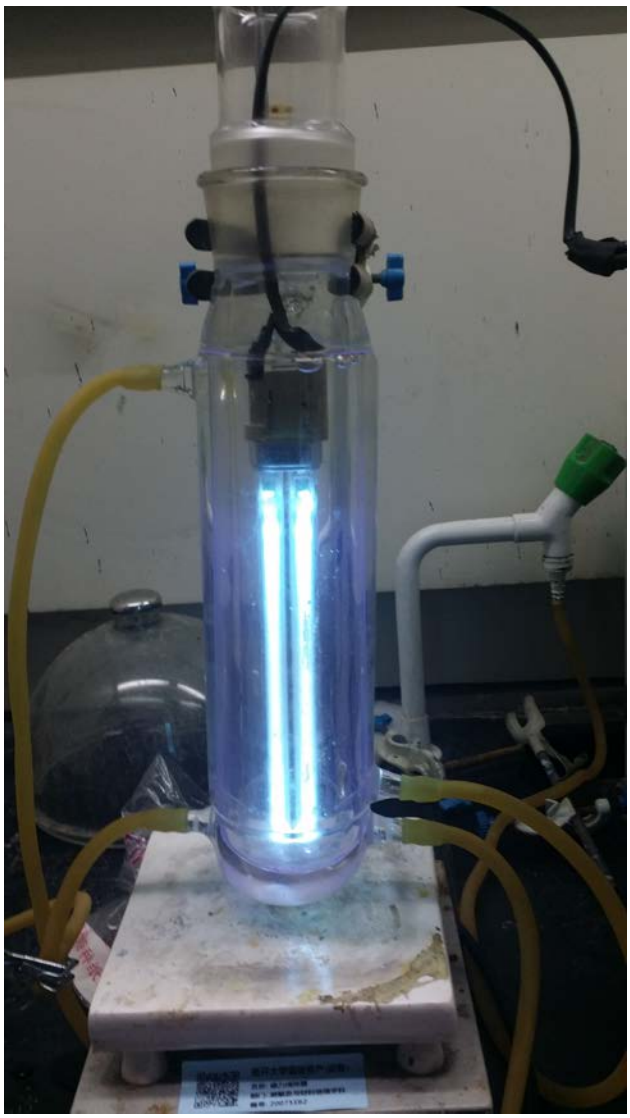


Figure S17. The as-prepared TiO_2-Pd1%, TiO_2-Mn1% and TiO_2-Cu1% powders and reactor in operation without any catalyst.