Supplementary Information

TiO_2/Vanadates ($Sr_{10}V_6O_{25}$, $Ni_3V_2O_8$, $Zn_2V_2O_7$) Heterostructure Photocatalyst with Enhanced Photocatalytic Activity on Photoreduction of CO_2 into CH_4

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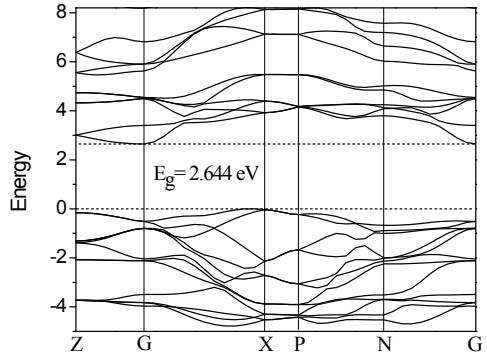


Figure S1. Band structure for pure TiO_2.

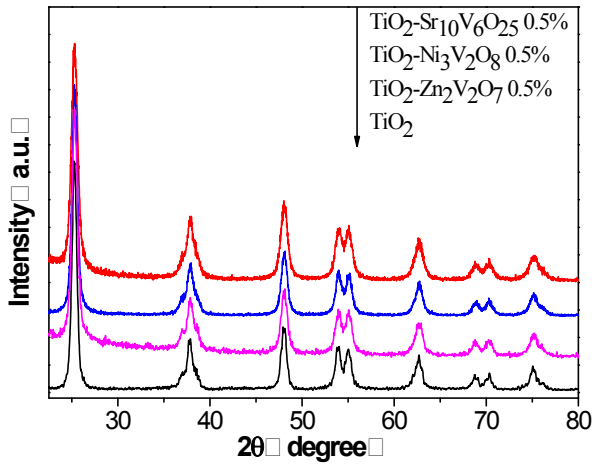


Figure S2. XRD patterns of pure TiO_2, TiO_2-$Sr_{10}V_6O_{25}$ 0.5%, TiO_2-$Ni_3V_2O_8$ 0.5% and TiO_2-$Zn_2V_2O_7$ 0.5% samples.

Table S1. Cell Parameters, Crystallite Size, and Specific Surface Area of Pure TiO_2, TiO_2-$Sr_{10}V_6O_{25}$ 0.5%, TiO_2-$Ni_3V_2O_8$ 0.5% and TiO_2-$Zn_2V_2O_7$ 0.5% samples.

Samples	Lattice parameter (Å)		cell volume (Å^3)	crystal size (nm)	S_{BET} (m^2g^{-1})
	a=b	c			
TiO_2	3.780	9.481	135.9	14.51	63.1
TiO_2-$Zn_2V_2O_7$ 0.5%	3.780	9.504	135.8	13.71	70.8
TiO_2-$Ni_3V_2O_8$ 0.5%	3.780	9.485	135.8	13.19	76.3
TiO_2-$Sr_{10}V_6O_{25}$ 0.5%	3.778	9.484	135.3	12.15	79.1

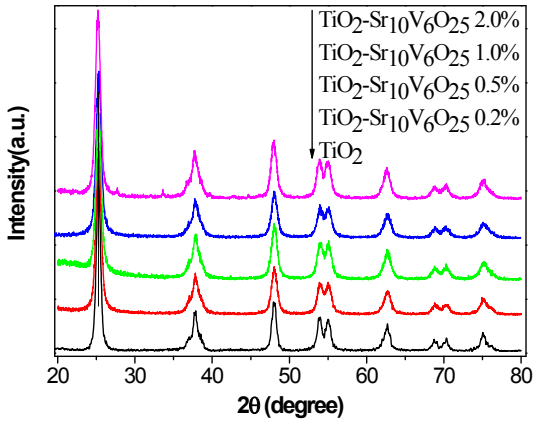


Figure S3. XRD patterns of pure TiO_2 and TiO_2-$Sr_{10}V_6O_{25}$ x% samples.

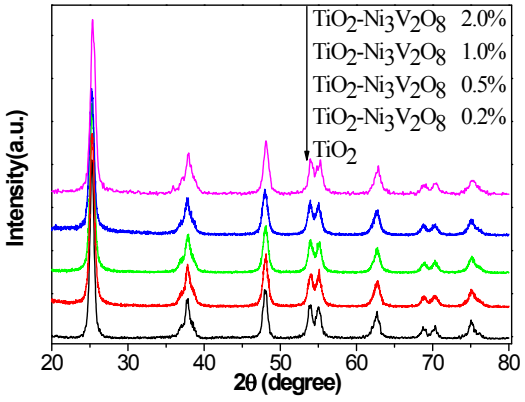


Figure S4. XRD patterns of pure TiO_2 and TiO_2-$Ni_3V_2O_8$ x% samples.

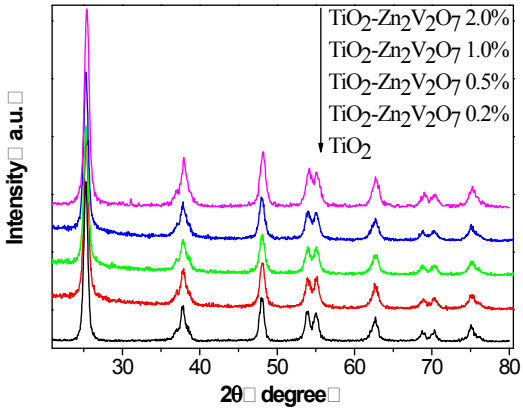
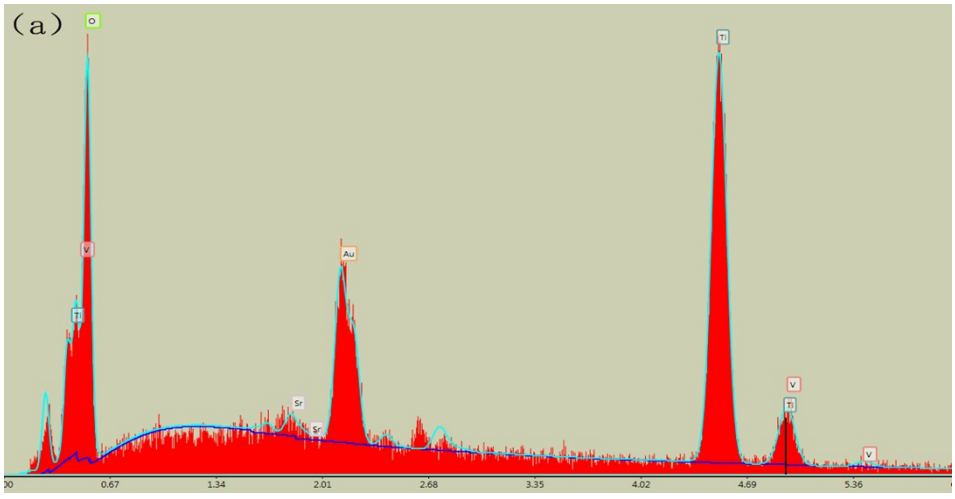
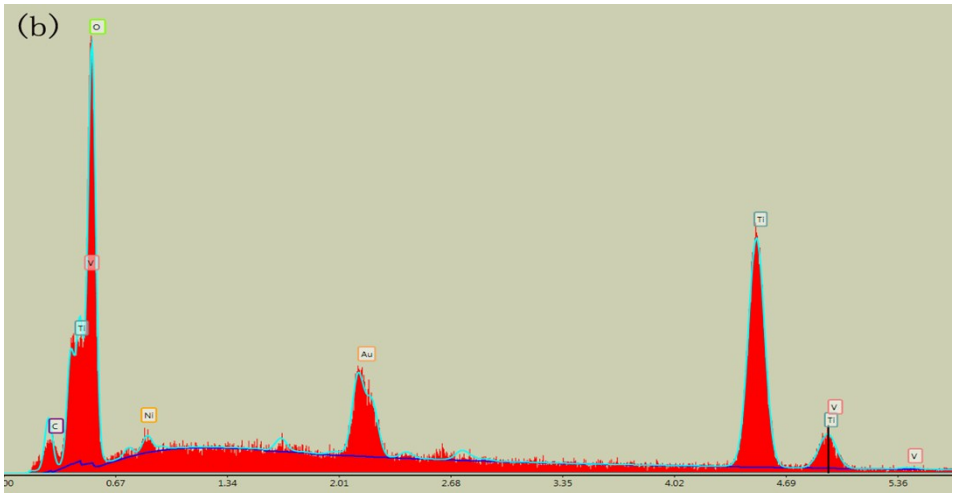


Figure S5. XRD patterns of pure TiO_2 and TiO_2-$Zn_2V_2O_7$ x% samples.





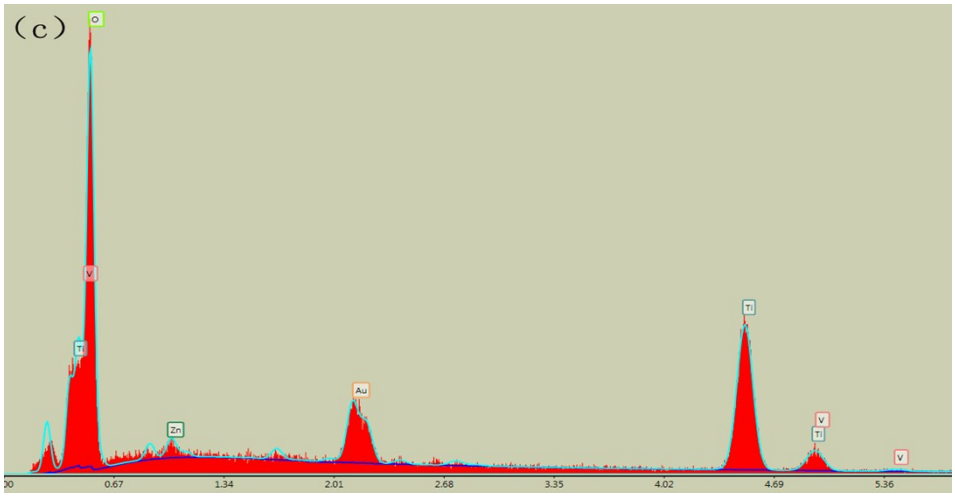


Figure S6. EDX spectrum of (a) TiO_2-$Sr_{10}V_6O_{25}$ 2.0%, (b) TiO_2-$Ni_3V_2O_8$ 2.0% and (c) TiO_2-$Zn_2V_2O_7$ 2.0% samples.

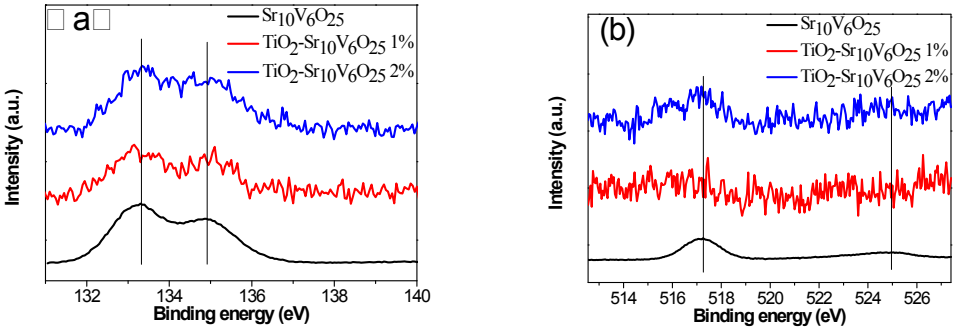


Figure S7. Sr 3d (a) XPS spectra of $Sr_{10}V_6O_{25}$ and TiO_2-$Sr_{10}V_6O_{25}$ x%; V 2p (b) XPS spectra of $Sr_{10}V_6O_{25}$ and TiO_2-$Sr_{10}V_6O_{25}$ x%.

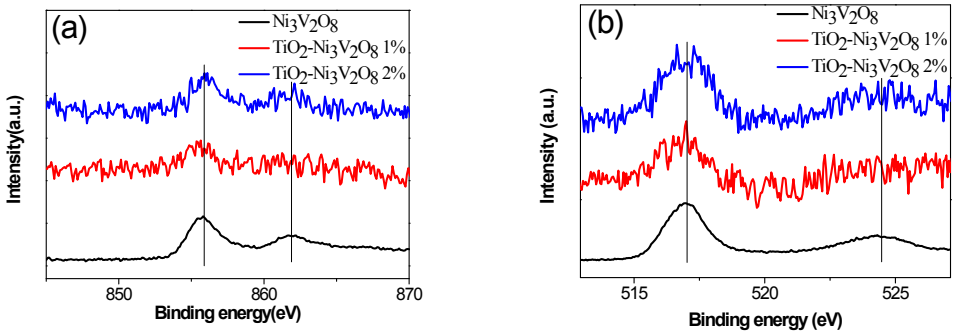


Figure S8. Ni 2p (a) XPS spectra of $Ni_3V_2O_8$ and TiO_2-$Ni_3V_2O_8$ x%; V 2p (b) XPS spectra of $Ni_3V_2O_8$ and TiO_2-$Ni_3V_2O_8$ x%.

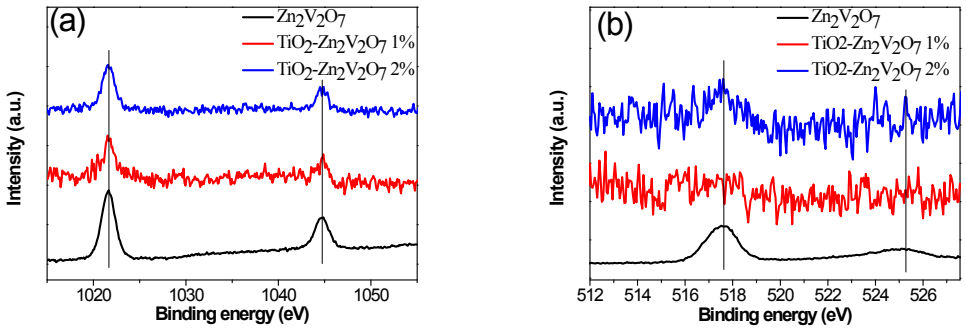


Figure S9. Zn 2p (a) XPS spectra of $Zn_2V_2O_7$ and TiO_2-$Zn_2V_2O_7$ x%; V 2p (b) XPS spectra of $Zn_2V_2O_7$ and TiO_2-$Zn_2V_2O_7$ x%.

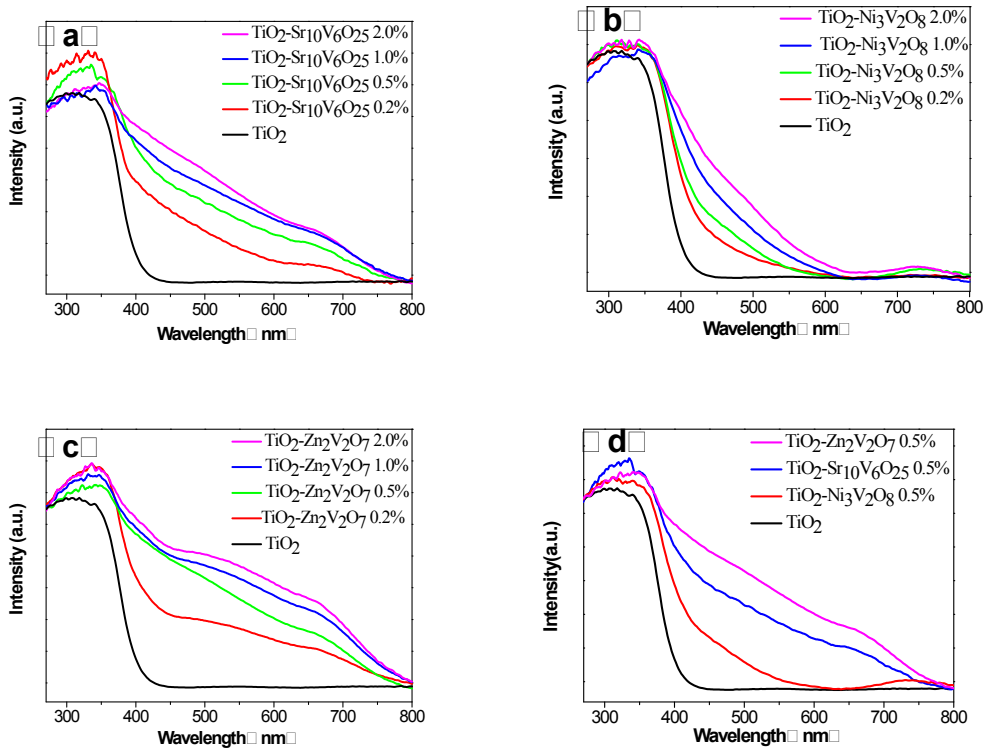


Figure S10. Diffuse reflectance UV-Vis spectra of (a) TiO_2 and TiO_2-$Sr_{10}V_6O_{25}$ x%; (b) TiO_2 and TiO_2-$Ni_3V_2O_8$ x%; (c) TiO_2 and TiO_2-$Zn_2V_2O_7$ x%. (d) TiO_2, TiO_2-$Sr_{10}V_6O_{25}$ 0.5%, TiO_2-$Ni_3V_2O_8$ 0.5% and TiO_2-$Zn_2V_2O_7$ 0.5% samples.

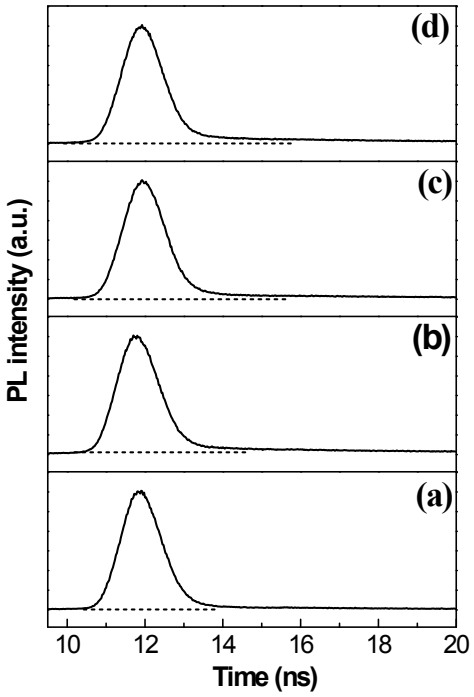


Figure S11. Time-resolved PL decay curves for (a) pure TiO_2, (b) TiO_2-$Zn_2V_2O_7$ 0.5%, (c) TiO_2-$Ni_3V_2O_8$ 0.5% and (d) TiO_2-$Sr_{10}V_6O_{25}$ 0.5% samples.

Table S2. Photocatalytic activity of pure TiO_2, TiO_2-$Sr_{10}V_6O_{25}$ 0.5%, TiO_2-$Ni_3V_2O_8$ 0.5% and TiO_2-$Zn_2V_2O_7$ 0.5% under UV light irradiation for 8 h.

sample	CH_4 generation amount (10^{-6}mol)	Specific photocatalytic activity [a] (10^{-6}mol·g^{-1}·h^{-1})	CO generation amount (10^{-6}mol)	specific photocatalytic activity [b] (10^{-6}mol·g^{-1}·h^{-1})
Blank	0.399	0.499	1.699	2.12
TiO_2	0.409	0.512	2.143	2.68
TiO_2-$Sr_{10}V_6O_{25}$ 0.5%	3.369	4.21	2.788	3.49
TiO_2-$Ni_3V_2O_8$ 0.5%	2.184	2.73	2.786	3.48
TiO_2-$Zn_2V_2O_7$ 0.5%	1.972	2.46	2.652	3.32

[a]specific photocatalytic activity of CH_4, CH_4 generation amount per unit mass catalyst per hour;

[b]specific photocatalytic activity of CO, CO generation amount per unit mass catalyst per hour.

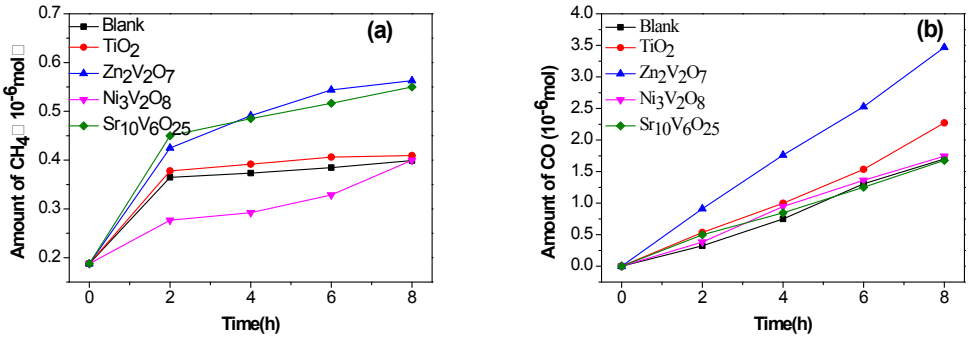


Figure S12. Photocatalytic activity for reduction of CO_2 into CH_4 (a) and CO (b) of TiO_2, $Zn_2V_2O_7$, $Ni_3V_2O_8$ and $Sr_{10}V_6O_{25}$ under UV light irradiation for 8 h.

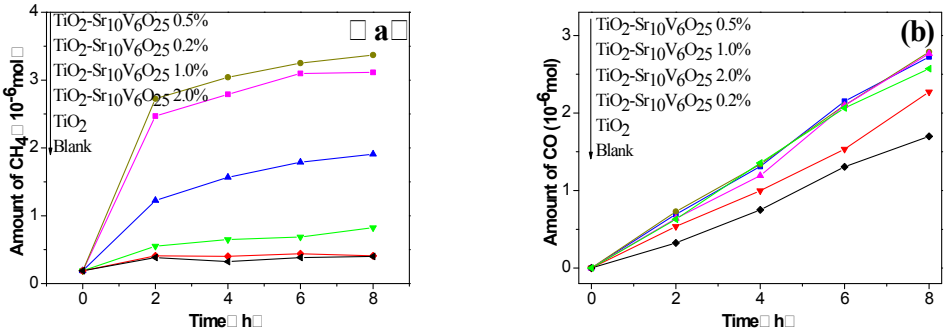


Figure S13. Photocatalytic activity for reduction of CO_2 into CH_4 (a) and CO (b) of TiO_2 and TiO_2-$Sr_{10}V_6O_{25}$ x% under UV light irradiation for 8 h.

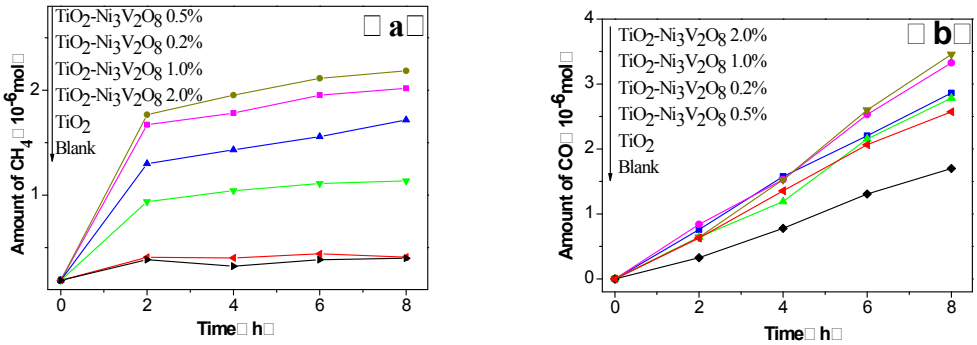


Figure S14. Photocatalytic activity for reduction of CO_2 into CH_4 (a) and CO (b) of TiO_2 and TiO_2-$Ni_3V_2O_8$ x% under UV light irradiation for 8 h.

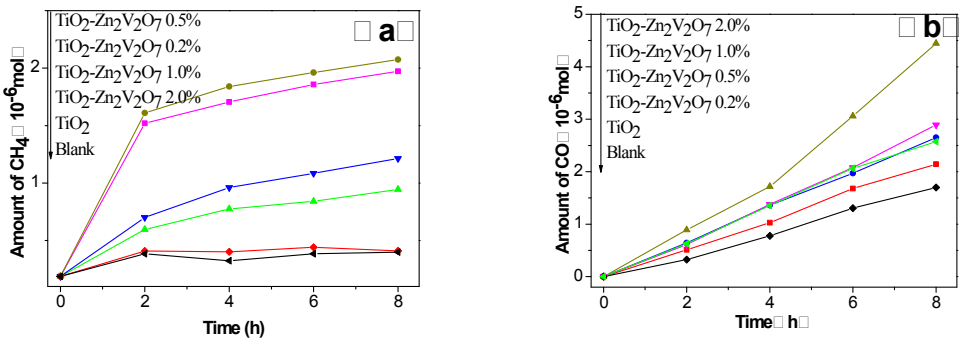


Figure S15. Photocatalytic activity for reduction of CO_2 into CH_4 (a) and CO (b) of TiO_2 and TiO_2-$Zn_2V_2O_7$ x% under UV light irradiation for 8 h.

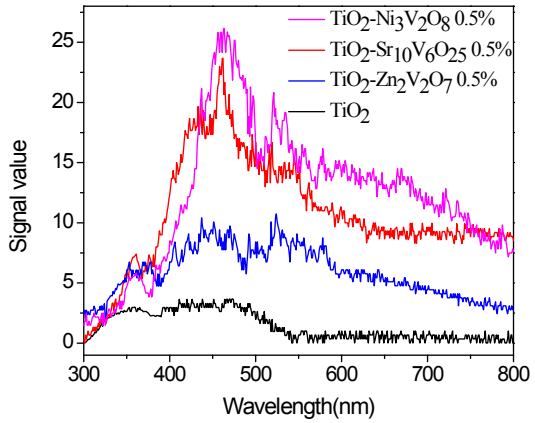


Figure S16. Photocurrent action spectra of pure TiO_2, TiO_2-$Sr_{10}V_6O_{25}$ 0.5%, TiO_2-$Ni_3V_2O_8$ 0.5% and TiO_2-$Zn_2V_2O_7$ 0.5%