Supporting information for

Synergistic Effect of Zn and Pd species in TiO2 towards Efficient Photo-Reduction of CO_2 into CH_4

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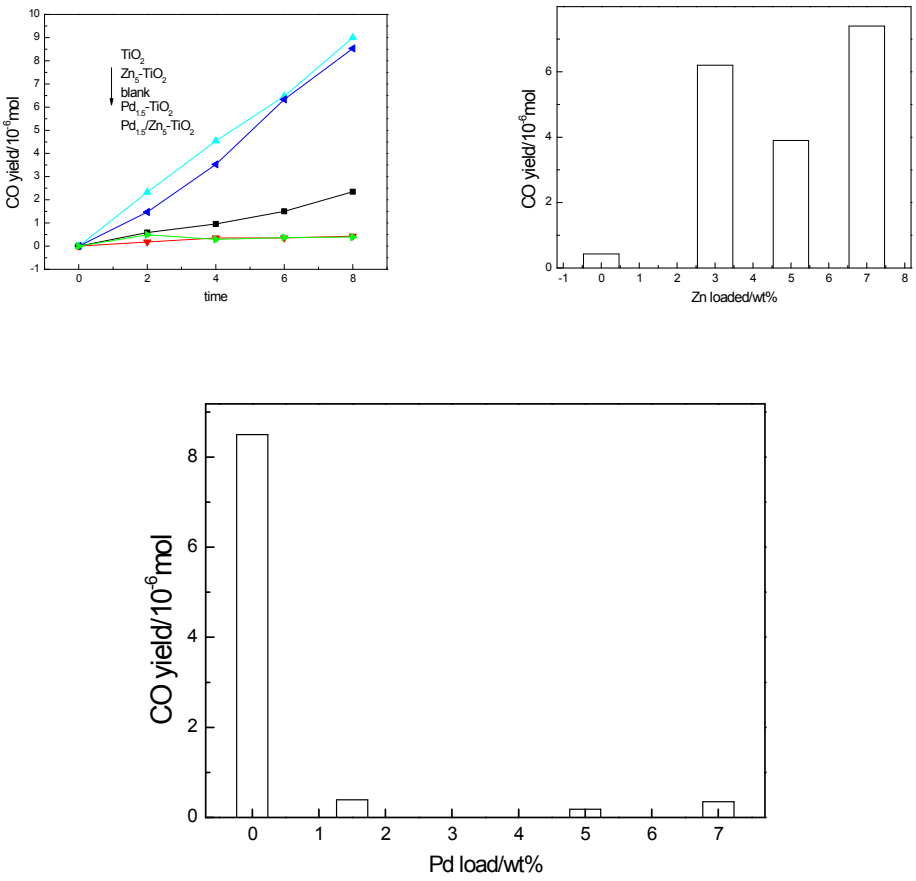


Figure S1. amount of CO generation for TiO_2, TiO_2-Pd, TiO_2-Zn and TiO_2-Pd1.5%-Zn5%(a), TiO_2-Pd1.5%-Znx%(b) and TiO_2-Pdy-Zn5%(c) under Xe lamp irradiation after 8 h.

Table S1. Photocatalytic activity of pure TiO_2, TiO_2-Zn, TiO_2-Pd and TiO_2-PdX-ZnY samples under Xe lamp irradiation after 8 h.

Sample	CO generation amount (10-6mol)	specific photocatalytic activity [b] (10-6mol·g-1·h-1)
blank [a]	0.31±0.01	-
TiO2(P25)	0.36±0.02	0.30±0.02
TiO2	0.35±0.03	0.29±0.02
TiO2-Zn	0.85±0.02	0.71±0.02
TiO2-Pd	3.77±0.47	3.14±0.39
TiO2-Pd1.5%-Zn3%	6.48±0.27	5.40±0.23
TiO2-Pd1.5%-Zn5%	7.99±0.28	6.66±0.23
TiO2-Pd1.5%-Zn7%	3.60±0.35	3.00±0.29
TiO2-Pd5%-Zn5%	7.14±0.45	5.95±0.38
TiO2-Pd7%-Zn5%	5.44±0.73	4.53±0.61

[a]Blank is the photolysis of CO_2; [b]specific photocatalytic activity of CO, CO generation amount per unit mass catalyst per hour

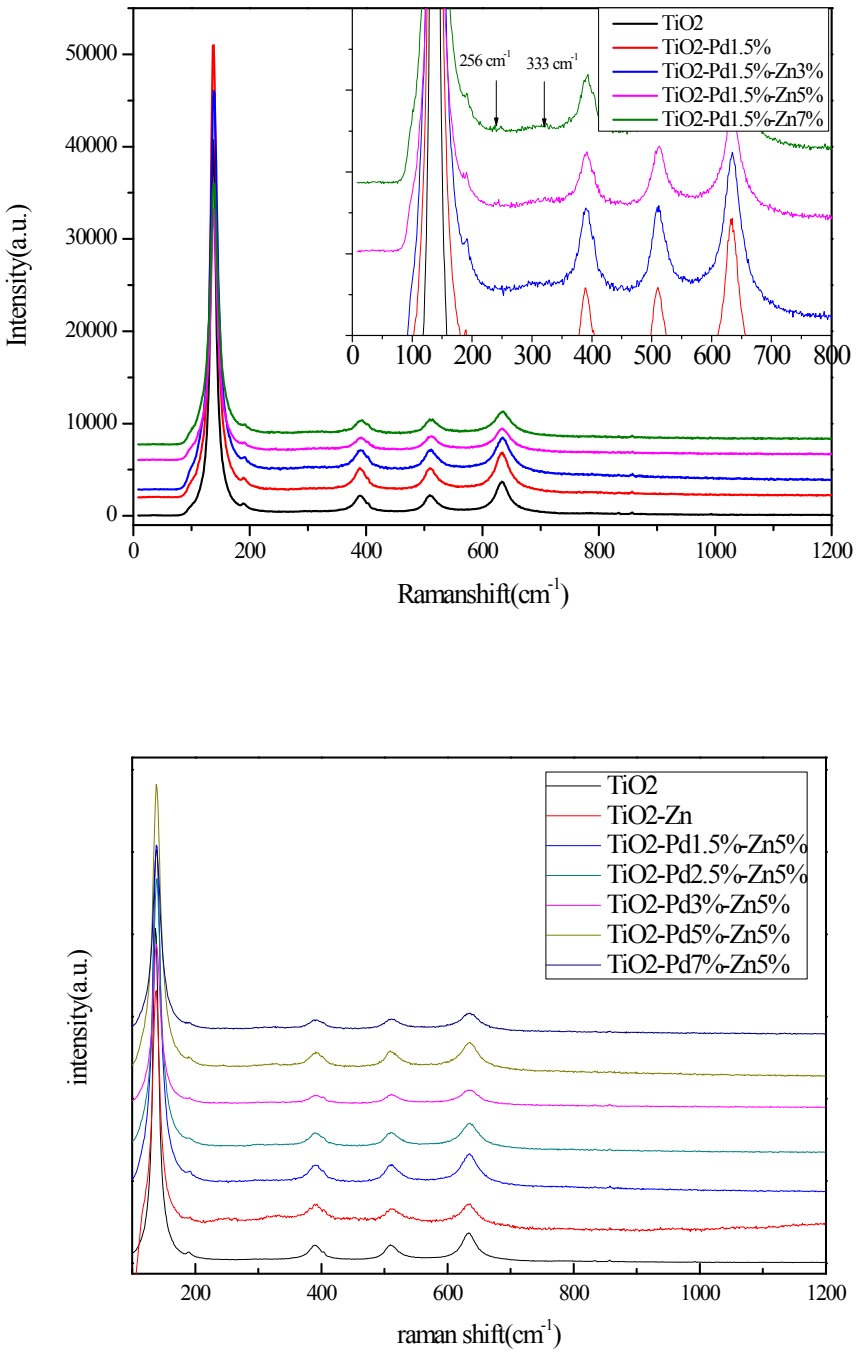


Figure S2. Raman spectra of TiO_2, TiO_2-Zn, TiO_2-Pd and TiO_2-PdX-ZnY.

X-Ray diffraction (XRD) patterns were acquired on a Rigaku D/max 2500 X-ray diffraction spectrometer (Cu Ka, λ=1.54056 Å) at a scan rate of 0.02° 2θ s^{-1}. The average crystal size was calculated using the Scherrer equation (D=kλ/Bcosθ).

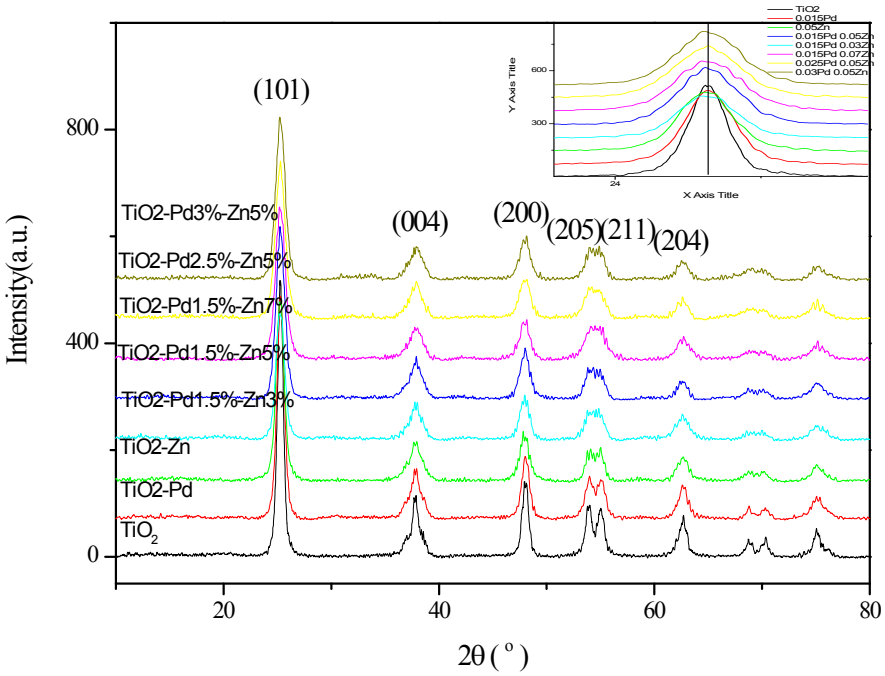


Figure S3 XRD patterns of pure TiO_2 (curve a), TiO_2-Pd, TiO_2-Zn and TiO_2-PdX-ZnY(X=1.5%~3%; Y=3%~7%) samples. Inset shows the enlargement of (101) plane.

Table S2 Lattice parameters, cell volume, crystal size and specific surface areas of the TiO_2, TiO_2-Pd, TiO_2-Zn and TiO_2-PdX-ZnY samples

Samples	Lattice parameter (Å)		cell volume ($Å^3$)	crystal size (nm)	S_{BET} ($m^2 g^{-1}$)	Phase Composition
	a	c				
TiO_2	3.7857	9.5118	136.32	12.4	57	anatase
TiO_2-Pd1.5%	3.7842	9.5042	136.10	9.6	75	anatase
TiO_2-Zn5%	3.7876	9.4963	136.23	8.9	63	anatase
TiO_2-Pd1.5%-Zn5%	3.7851	9.4875	135.93	7.7	79	anatase

Table S3 Atom percentage Ti, Zn, Pd , Cl and C of the TiO_2, TiO_2-Pd, TiO_2-Zn and TiO_2-Pd-Zn samples

Samples	Ti	Zn	Pd	Cl	C
TiO_2	28.36			2.01	19.19
TiO_2-Pd1.5%	18.82		0.63	2.36	19.88
TiO_2-Zn5%	18.05	3.74		6.49	15.18
TiO_2-Pd1.5%-Zn5%	13.25	3.37	0.91	5.25	15.34

DFT Calculation

The calculations were carried out by a first-principle calculation software package CASTEP. Generalized gradient approximation (GGA) based density-functional theory (DFT) was used to calculate the electronic band structure and density of states (DOS) for pure TiO_2, TiO_2-Zn and TiO_2-Pd, respectively. An anatase TiO_2 model of 76 atoms with exposed (101) facet is created. The vacuum lamb is set as 10 Ai. For TiO_2-Pd, one Pd ion is linked with two surface bridge O ions on the (101) facet. For TiO_2-Zn, one Zn ion is linked with one surface bridge O ion on the (101) surface of anatase and one Cl ion. The valence electronic configurations for O, Ti, Cl, Zn and Pd atoms were $2s^22p^4$, $3s^23p^63d^24s^2$, $3s^23p^5$, $3d^{10}4s^2$ and $4d^{10}$, respectively. The plane wave energy cutoffs were taken to be 420 eV. In all the cases, geometry optimizations were carried out first, and convergence was assumed when the forces on atoms were less than 50 meV/Å. Compared with experimental results, the theoretical calculation usually results in an underestimated band gap, caused by the shortcoming of the exchange-correction functional in describing the excited states[23, 24].

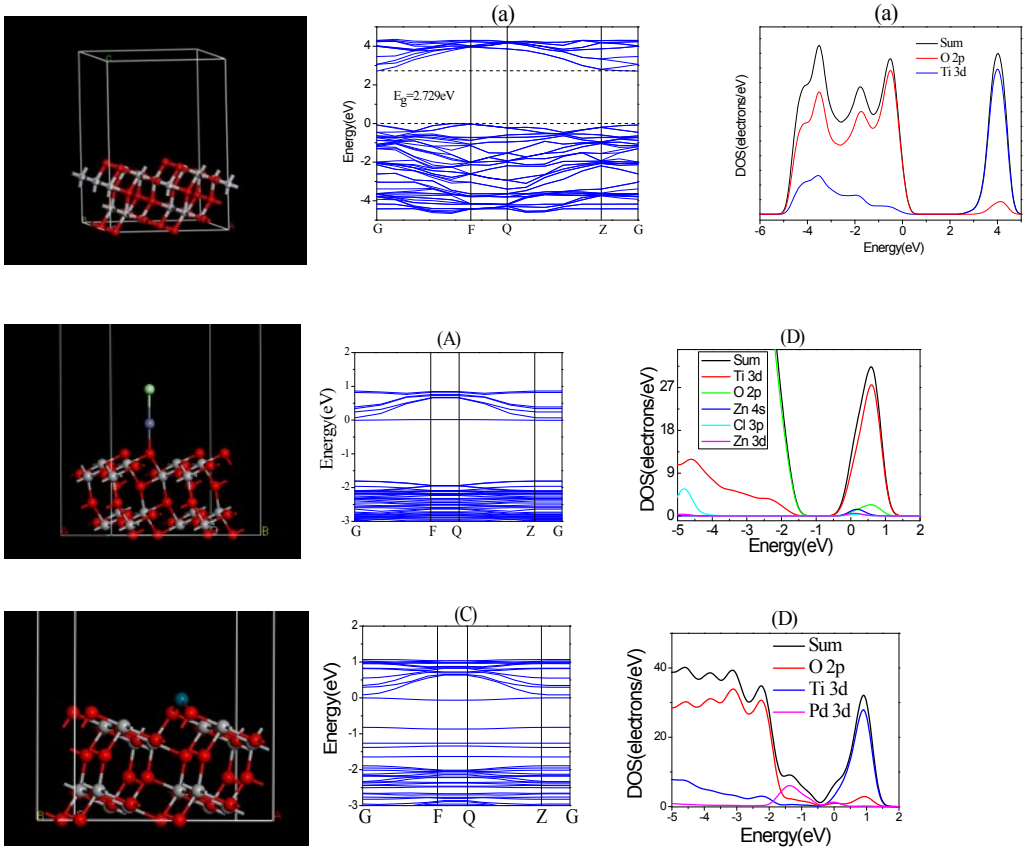


Figure S4. Theoretical calculated band structure and Projected density of states (PDOS) for the TiO_2, TiO_2-Zn and TiO_2-Pd.

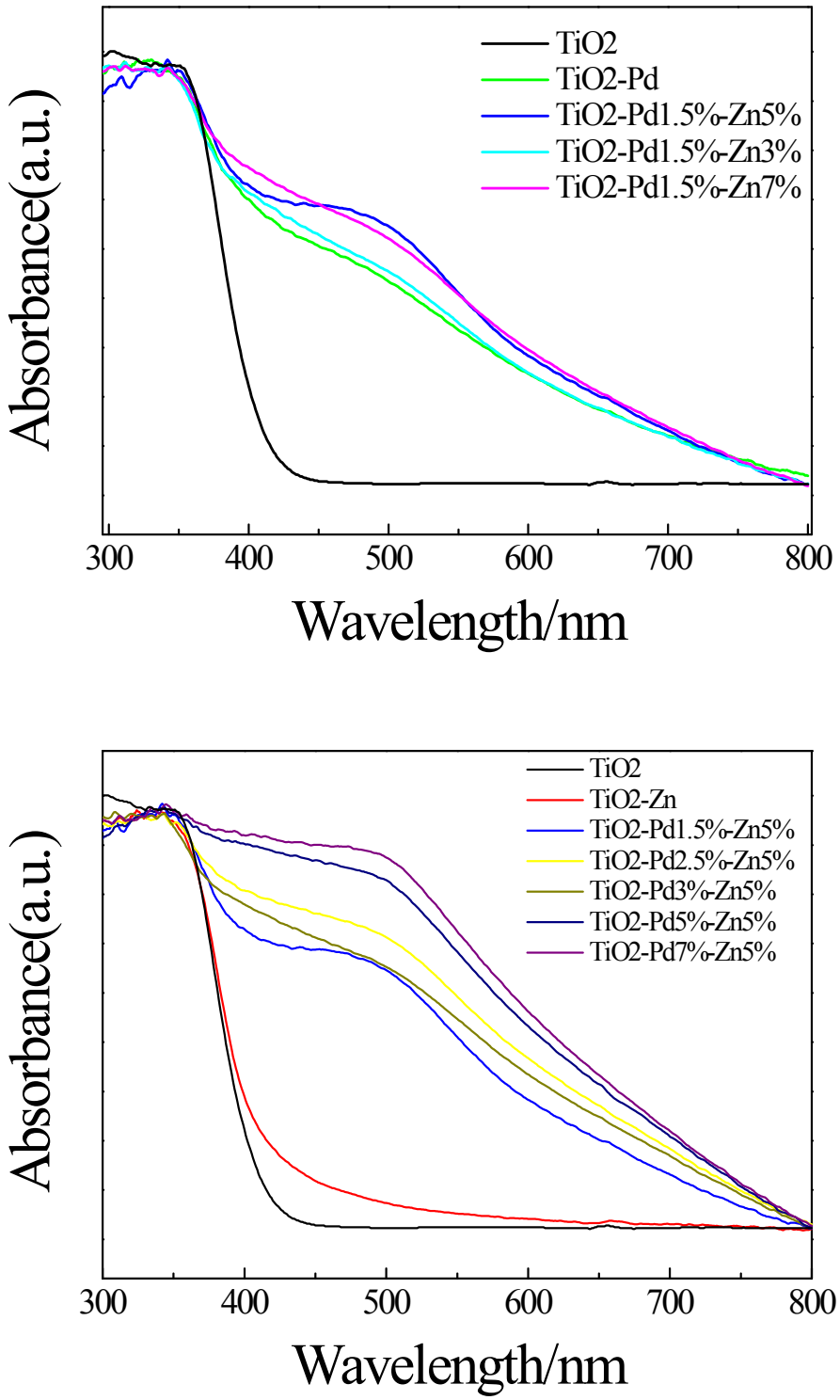


Figure S5. Absorption spectra of TiO_2, TiO_2-Zn, TiO_2-Pd and TiO_2-PdX-ZnY.

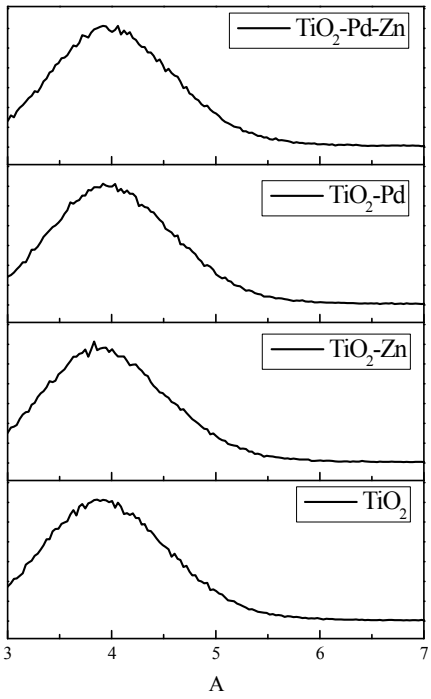


Figure S6. The time-resolved PL decay curve of the pure TiO_2, TiO_2-Zn, TiO_2-Pd and TiO_2-Pd-Zn samples

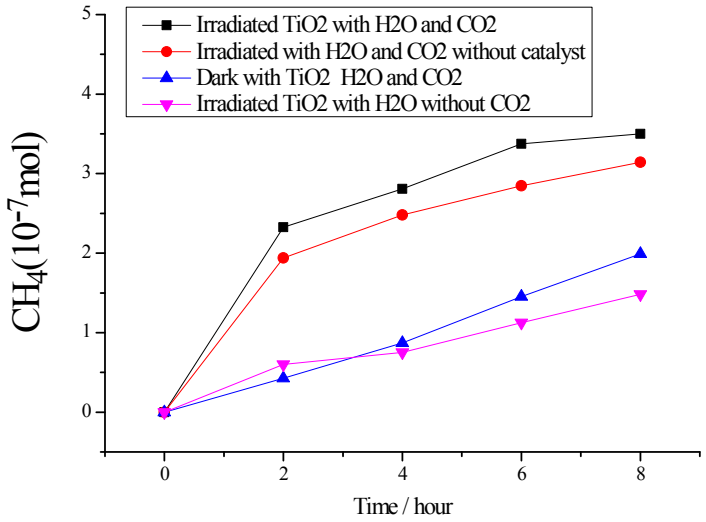
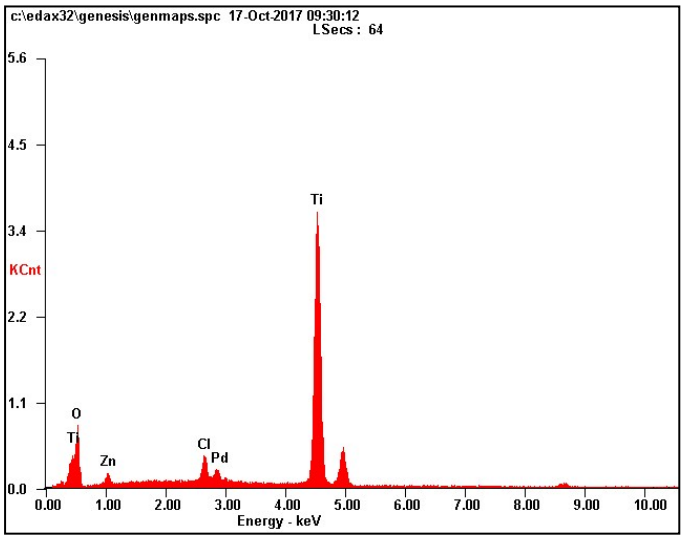


Figure S7. Blank experiment test (UV-illuminated of CO2 + H2O without the photocatalyst, without of UV-illuminated only CO2 + H2O with the photocatalyst in the dark, UV-illuminated photocatalyst in H2O without the CO2)



Element	Wt%	At%
OK	30.79	57.81
ZnL	04.67	02.14
ClK	02.73	02.31
PdL	03.01	00.85
TiK	58.80	36.88
Matrix	Correction	ZAF

Figure S8. EDS of TiO_2-Pd-Zn

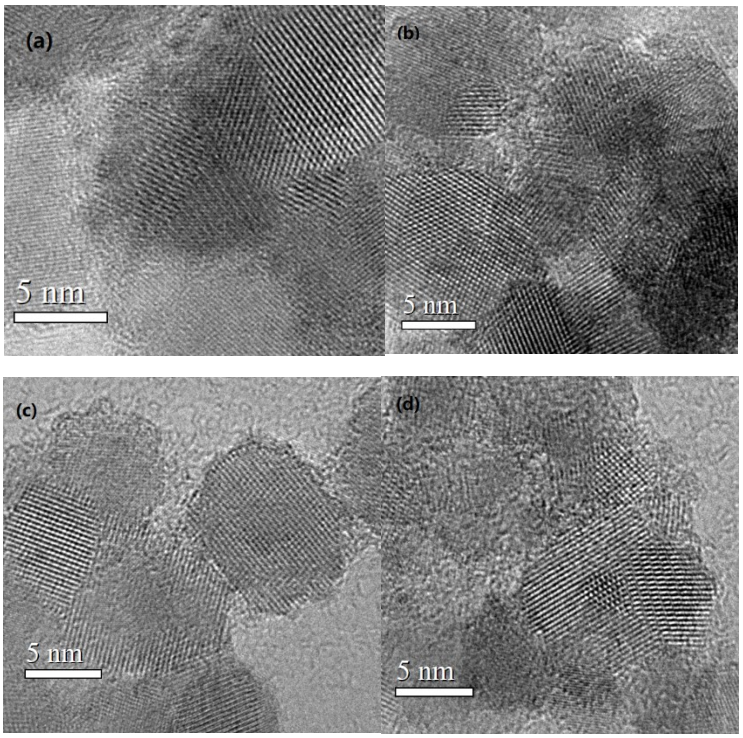


Figure S9. The HR-TEM of the pure TiO_2, TiO_2-Zn, TiO_2-Pd and TiO_2-Pd-Zn samples

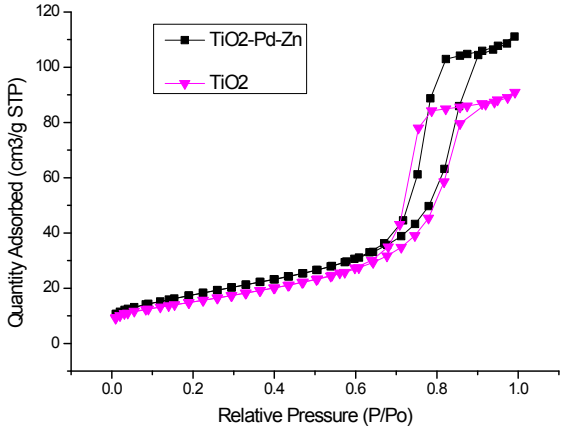


Figure S10. Nitrogen adsorption-desorption isotherm of TiO_2 and TiO_2-Pd-Zn.