NJC

Electronic Supplementary Information

The order of loading affects photocatalytic nitrogen fixation activity of the ternary composites of PdO/Au-TiO$_2$

Xuejing Wang, Sifan Liu, Ruixiao Ma, Wenwen Yang, Yanmei Chen, Juan Xu and Yanhui Zhang*

College of Chemistry, Chemical Engineering and Environment, Fujian Province Key Laboratory of Morden Analytical Science and Separation Technology, Minnan Normal University, Zhangzhou, 363000, P.R. China

*To whom correspondence should be addressed. E-mail Address: zhangyh@mnnu.edu.cn

1. The calculation formula and details of ICP-OES are as follows:

$$C_x(mg/kg)=\frac{C_0(mg/L)\times f\times V_0(mL)\times 10^{-3}}{m(g)\times 10^{-3}}=\frac{C_1(mg/L)\times V_0(mL)\times 10^{-3}}{m(g)\times 10^{-3}} \quad (1)$$

$$C_1(mg/L)=C_0(mg/L)\times f \quad (2)$$

$$W(\%)=\frac{C_x(mg/kg)}{10^6}\times 100\% \quad (3)$$

Among them, m_0, V_0 , C_0, f, C_1, C_x and W are quality of sample, constant volume, test solution element concentration, dilution multiple, element concentration of digestion solution/original sample solution, sample element concentration and sample element content.

2. The AQEs experiment was performed as follows:

25 mg of PdO/Au-TiO$_2$ was dispersed in 130 mL mixture of ultrapure water and ethylene glycol (V:V=9:1) and irradiated under a xenon lamp with bandpass filters (λ = 365, 400, 500, 550, 600 nm, irradiation area 0.0044 m^2), the calculation formula and details of AQEs are as follows:

$$N_{photo}=\frac{t(s)\times P(W\bullet m^{-2})\times S(m^2)\times \lambda(m)}{h(J\bullet s)\times c(m\bullet s^{-1})} \quad (4)$$

$$AQEs(\%)=\frac{3NH_4^+(mol)\times N_A(mol^{-1})}{N_{photo}}\times 100\% \quad (5)$$

Among them, t, P, S, λ, h, c and N_A are reaction time, optical power density, irradiation area, the wavelength of incident light, Planck's constant, the speed of light and Avogadro's constant.

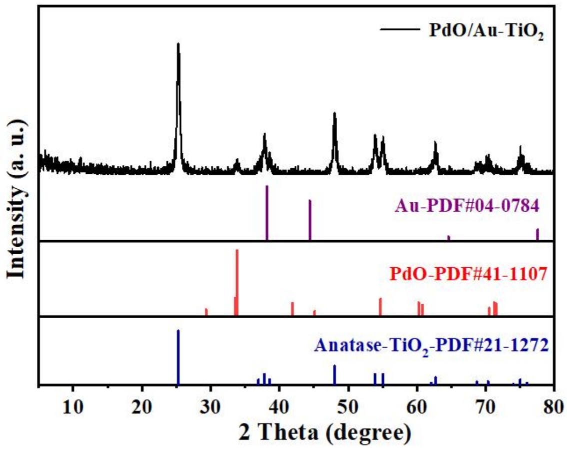

Fig. S1. The standard XRD cards of TiO_2, Au and PdO.

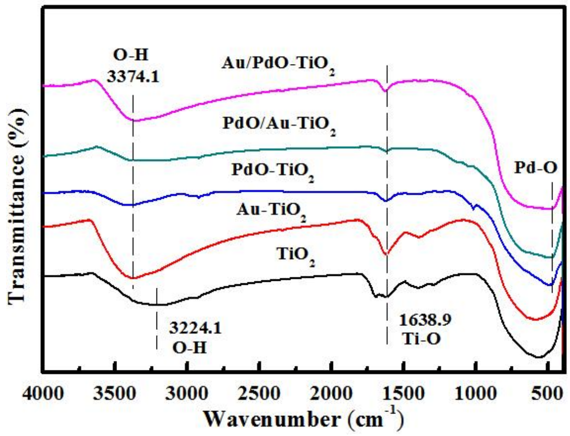

Fig. S2. FT-IR spectra of TiO_2, Au-TiO_2, PdO-TiO_2, PdO/Au-TiO_2 and Au/PdO-TiO_2.

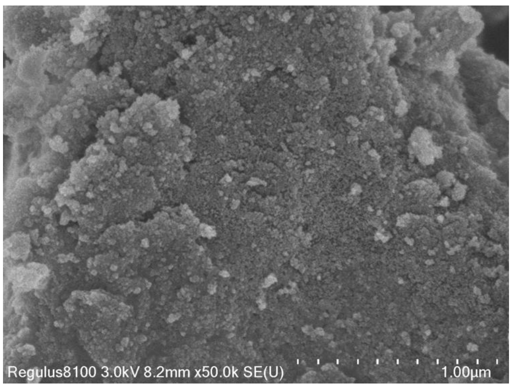

Fig. S3. SEM images of pure TiO_2.

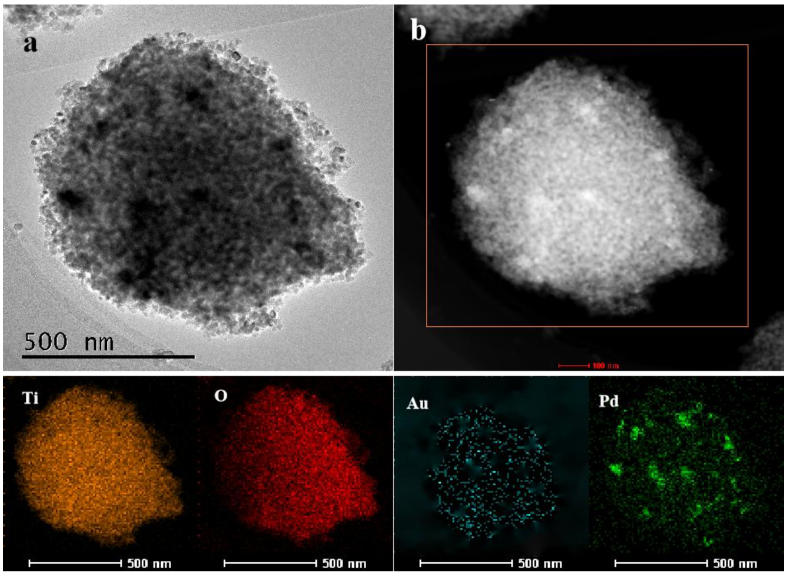

Fig. S4. TEM of Au/PdO-TiO_2 catalysts (a), elemental mapping images showing Ti, O, Au, and Pd elements in the PdO/Au-TiO_2 (b).

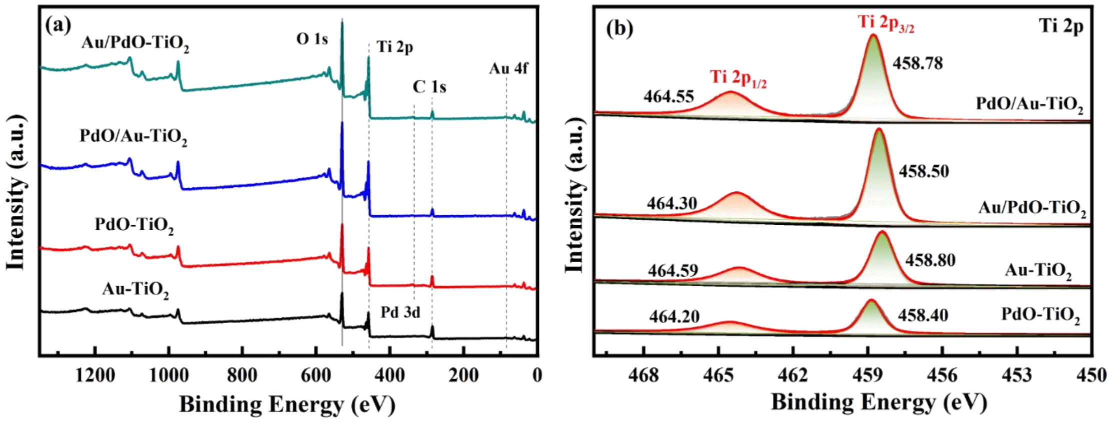

Fig. S5. The XPS Survey of Au-TiO_2, PdO-TiO_2, PdO/Au-TiO_2 and Au/PdO-TiO_2 (a), and the high-resolution XPS spectra of Ti 2p (b).

Table S1. The actual load content of PdO and Au in PdO/Au-TiO_2 was measured by ICP-OES.

Sample	m (g)	V_0 (mL)	Test elements	C_0 (mg/L)	f	C_1 (mg/L)	C_x (mg/kg)	W
PdO/Au-TiO_2	0.0494	10	Au	6.29	10	62.91	12735.04	1.2735
	0.0494	10	Pd	4.56	10	45.58	9225.77	0.9226

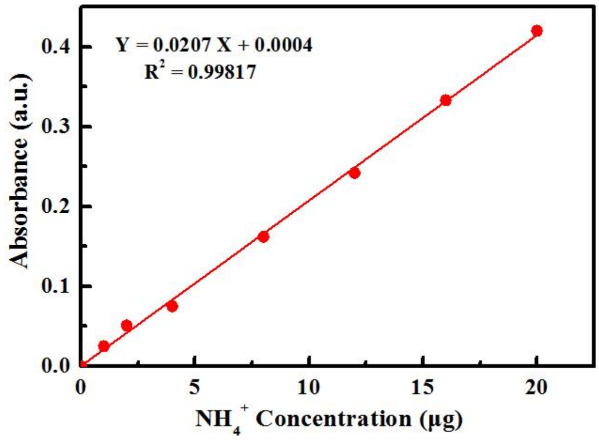

Fig. S6. Ammonia nitrogen standard curve.

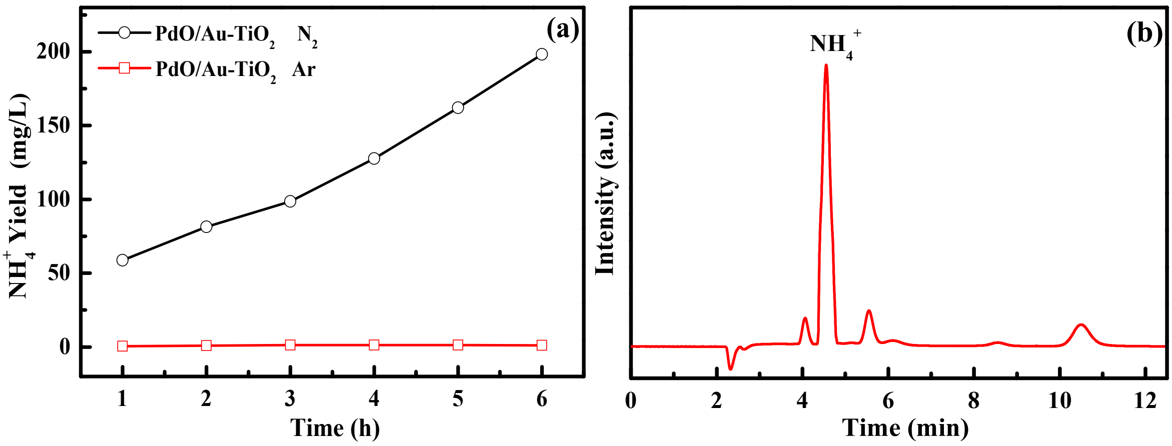

Fig. S7. The ammonia yield of PdO/Au-TiO2 with N2 and Ar atmosphere (a); the ion chromatographic peaks of NH_4^+ (b).

Table S2. The apparent quantum yields of the PdO/Au-TiO2 composites.

Wavelengh (nm)	365	400	500	550	600
AQEs (%)	20.6	3.2	0	0	0

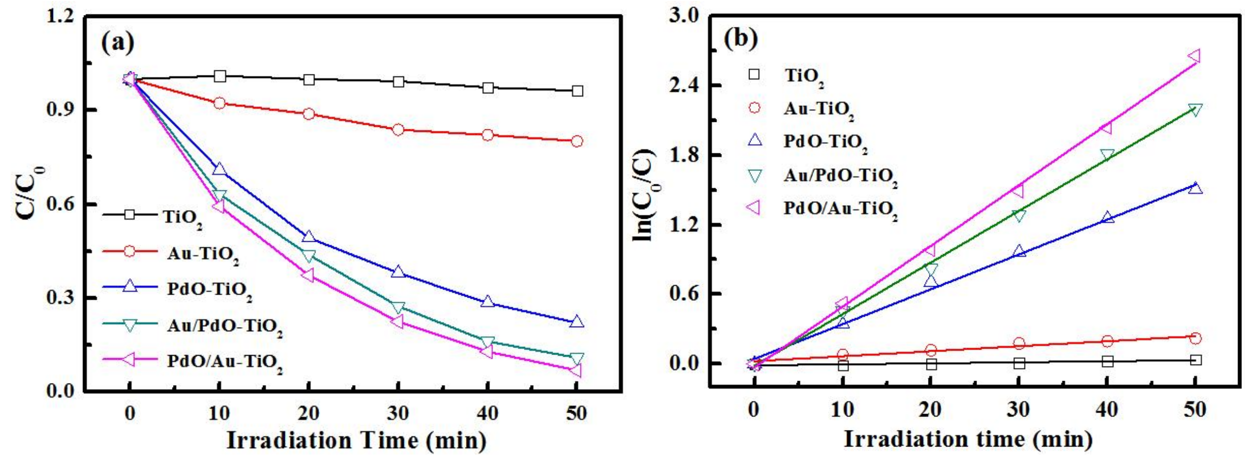

Fig. S8. Trends of ciprofloxacin (10 mg/L) photocatalytic degradation and first order kinetic constant fitting diagram of photocatalytic rate of TiO_2, Au-TiO_2, PdO-TiO_2, Au/PdO-TiO_2 and PdO/Au-TiO_2.

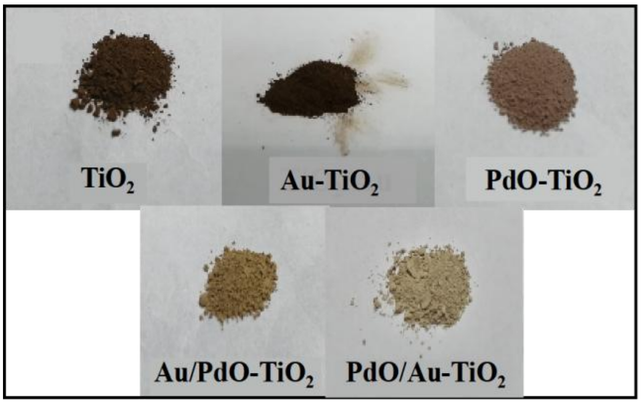

Fig. S9. The color difference map of TiO_2, Au-TiO_2, PdO-TiO_2, Au/PdO-TiO_2 and PdO/Au-TiO_2.

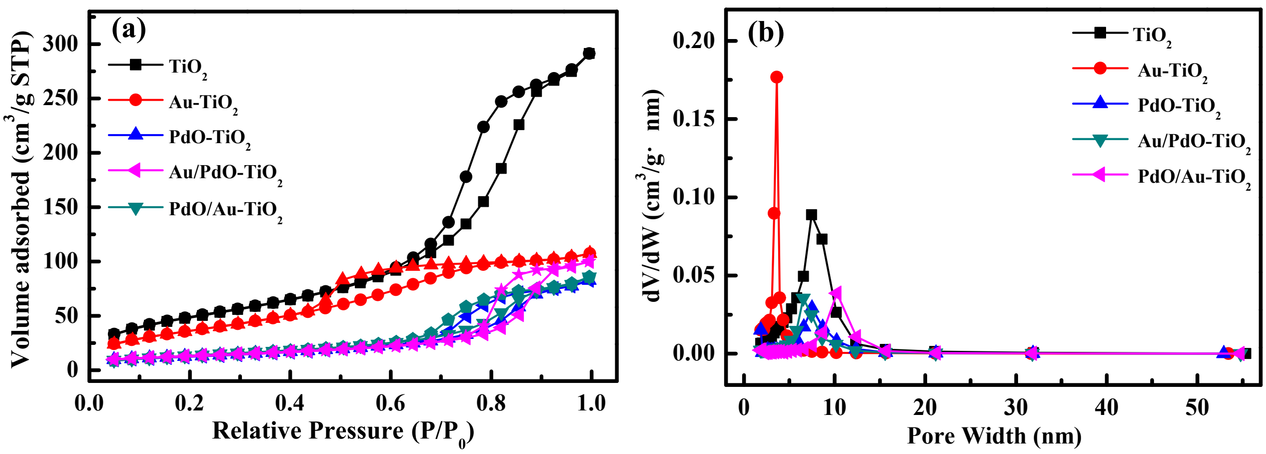

Fig. S10. The nitrogen adsorption and desorption curves (a) and pore size distribution (b) of the TiO_2, Au-TiO_2, PdO-TiO_2, PdO/Au-TiO_2 and Au/PdO-TiO_2.

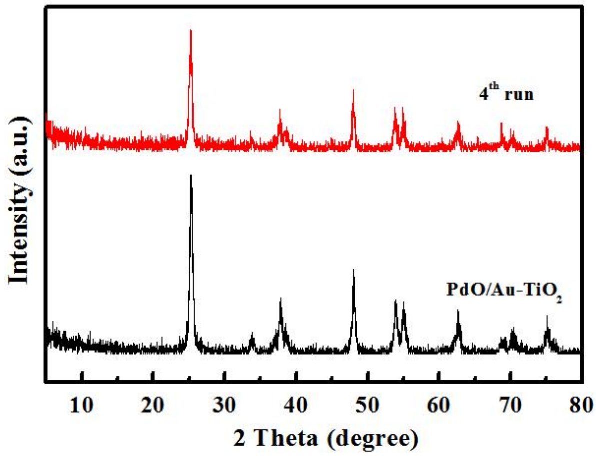

Fig. S11. XRD patterns of PdO/Au-TiO_2 after 4 cycles of experiments.

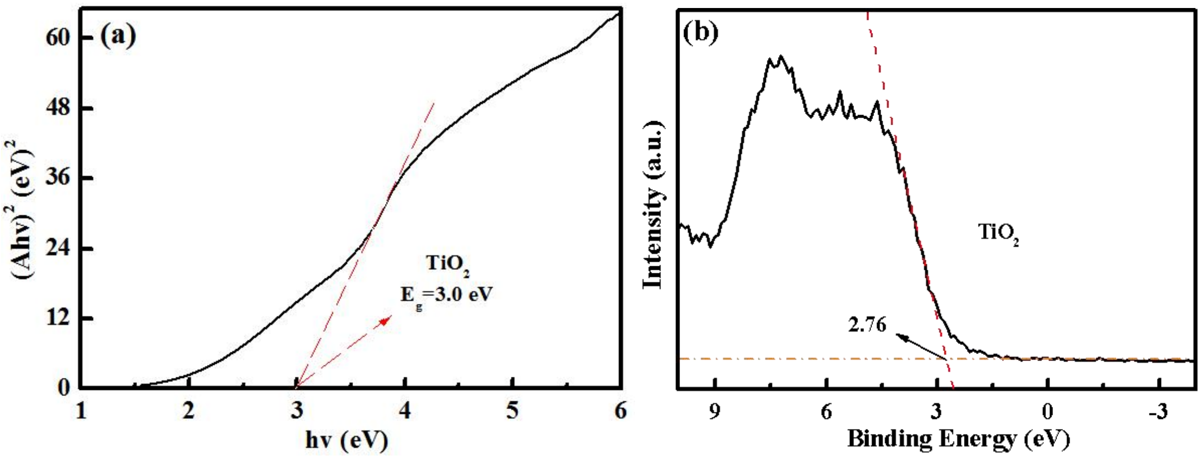

Fig. S12. Tauc curve of TiO_2 (a) and Valence band XPS spectra (b).

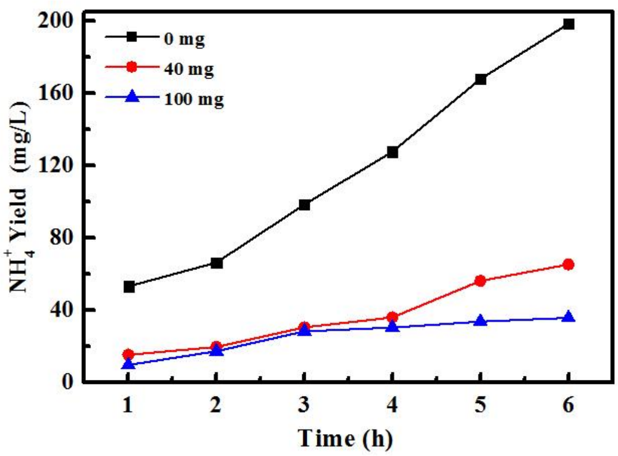

Fig. S13. The effects of electron sacrificial agent ($AgNO_3$) on the photocatalytic nitrogen fixation activity of PdO/Au-TiO_2 composites.