Supplementary information

Direct C–N coupling of aniline to aminodiphenylamines with platinum-loaded titanium oxide photocatalyst

Kexin Zou, Akira Yamamoto, and Hisao Yoshida

Graduate School of Human and Environmental Studies, Kyoto University,
Yoshida-nihonmatsu-cho, Sakyo-ku, Kyoto, 606-8501, Japan

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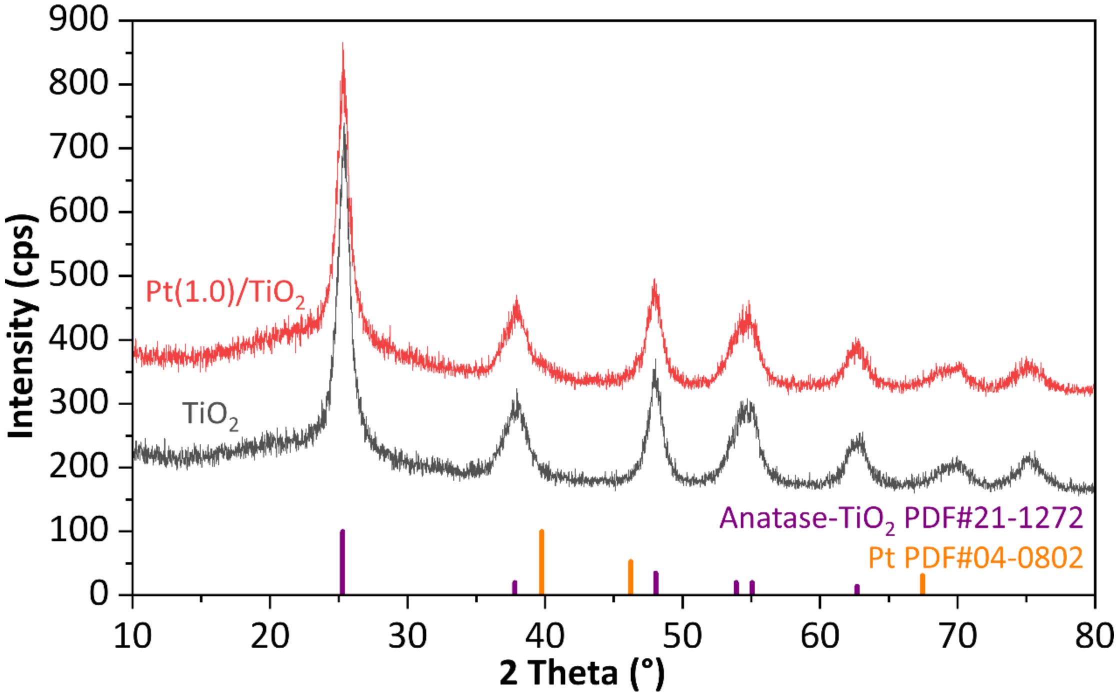

Fig. S1 XRD pattern of the Pt(1.0)/TiO$_2$ and TiO$_2$ samples with the reference data for anatase TiO$_2$ (PDF#21-1272) and Pt (PDF#04-0802). The TiO$_2$ phase of the Pt(0.1)/TiO$_2$ sample did not change after Pt loading. No characteristic peaks of Pt were observed for the Pt(0.1)/TiO$_2$ sample, which would be due to a small loading amount and a small size of Pt species.

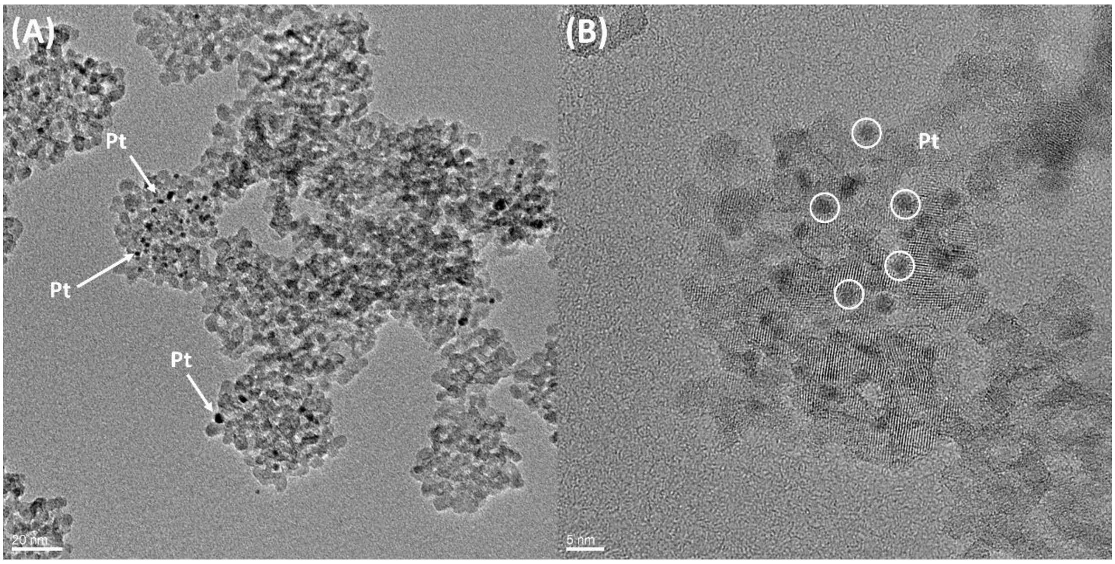

Fig. S2 (A) The TEM image of the Pt(1.0)/TiO_2 sample and (B) the enlarged TEM image showing Pt nanoparticles. The average size of Pt nanoparticles was 2.06 nm.

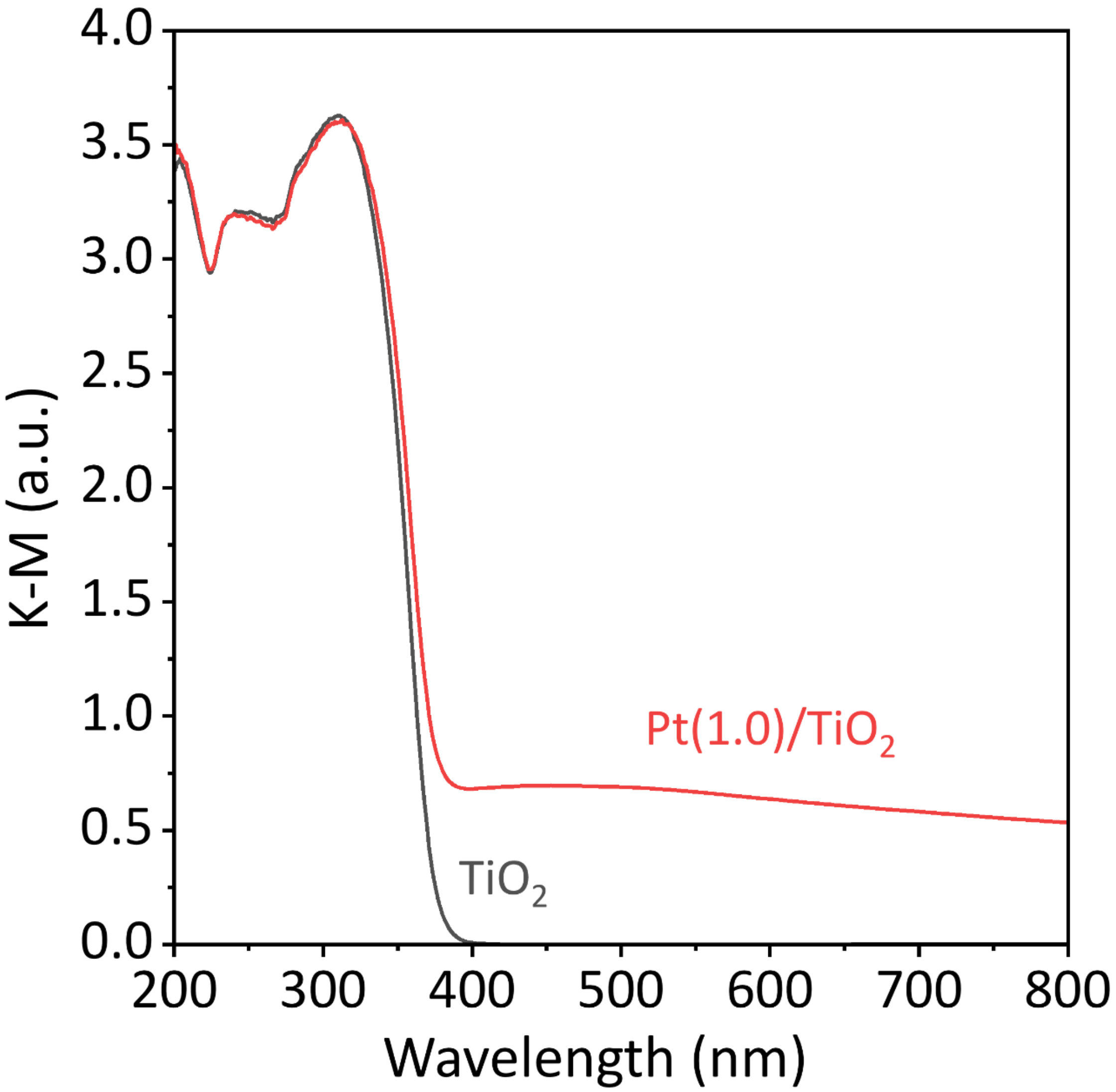

Fig. S3 DR UV-Vis spectra of the bare TiO_2 and Pt(1.0)/TiO_2 samples. The Pt(1.0)/TiO_2 sample shows a similar light absorption as bare TiO_2 sample in UV region with an enhanced absorption in visible light range due to the loaded platinum on the TiO_2 surface, which gave the catalyst a greyish color.

Table S1 The results of some blank tests. [a]

Entry	Photoirradiation	Photocatalyst	*C* (%) [b]	*Y* (%) [c]		
				AZB	2-ADPA	4-ADPA
1	No	No	0	n.d. [d]	n.d.	n.d.
2	No	Yes	0	n.d.	n.d.	n.d.
3	Yes	No	0	n.d.	n.d.	n.d.

[a] Reaction conditions: 50 mg of Pt(1.0)/TiO_2 photocatalyst was used (**entry 2**); 4.6 μL (50 μmol) of aniline was introduced as the reactant; 4 mL of 0.1 mol L^{-1} of NaOH (*aq*, pH = 12.70) was applied; Reaction time was 30 min; The incident UV-LED light wavelength was around 365 ± 5 nm, the irradiated light intensity was 1035 mW cm^{-2} when measured at 360 ± 20 nm in wavelength (**entry 3**); [b] Conversion of aniline, *C*(%)= 100 × (introduced aniline – aniline remnant after reaction)/(introduced aniline); [c] Yield of detectable products, *Y*(%) = 100 × $A_{(2\text{-ADPA, 4-ADPA, AZB})}$ × 2/(introduced aniline), where $A_{(2\text{-ADPA, 4-ADPA, AZB})}$ stand for the yielded amount of 2-ADPA, 4-ADPA, and AZB, respectively; [d] n.d. = not detected.

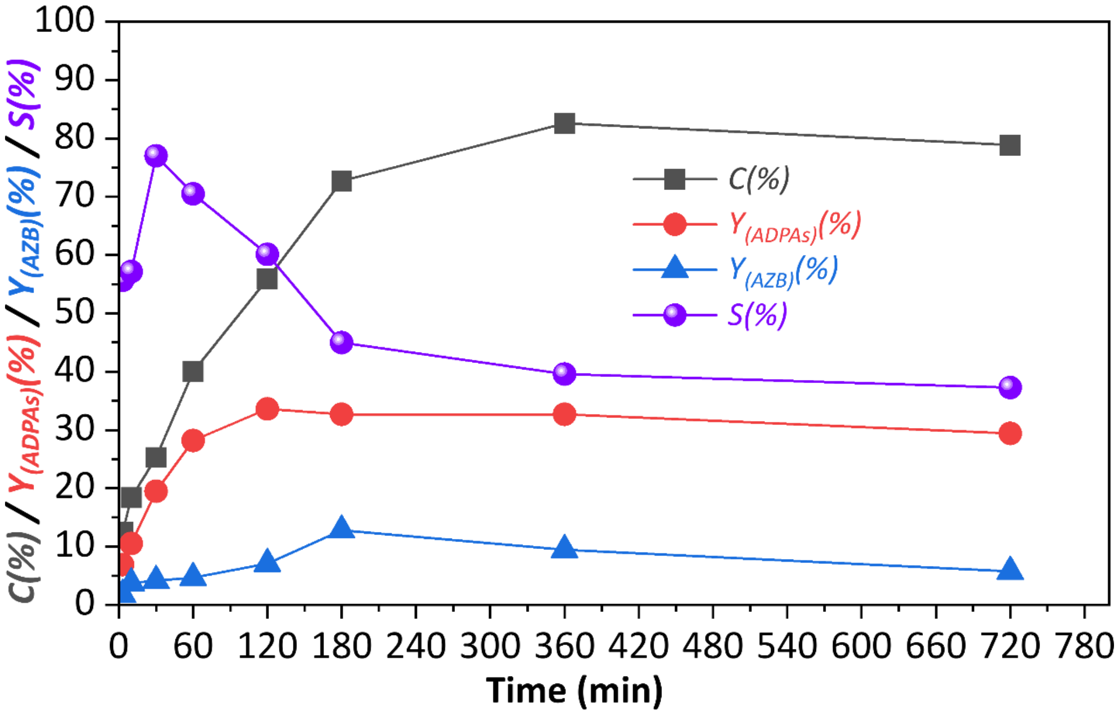

Fig. S4 Results of the photocatalytic reaction test with various reaction times. Reaction conditions: 50 mg of Pt(1.0)/TiO_2 photocatalyst was used; 4.6 µL (50 µmol) of aniline was introduced as the reactant; 4 mL of 0.1 mol L^{-1} NaOH (*aq*, pH = 12.70) was applied; The incident UV-LED light wavelength was around 365 ± 5 nm, the irradiated light intensity was 1035 mW cm^{-2} when measured at 360 ± 20 nm in wavelength; C (%) = 100 × (introduced aniline – remained aniline after reaction)/(introduced aniline); $Y_{(ADPAs)}$ (%) = 100 × ($A_{(2\text{-}ADPA)}$ + $A_{(4\text{-}ADPA)}$)× 2/(introduced aniline), $Y_{(AZB)}$ (%) = 100 × $A_{(AZB)}$× 2/(introduced aniline), where $A_{(2\text{-}ADPA,\ 4\text{-}ADPA,\ AZB)}$ stand for the yielded amount of 2-ADPA, 4-ADPA, and AZB, respectively; S (%) = 100 × ($A_{(2\text{-}ADPA)}$ +$A_{(4\text{-}ADPA)}$) × 2/(introduced aniline – remained aniline). The highest $Y_{(ADPAs)}$ was observed at 120 min with a yield of 33.6%. The highest S (%) was found at 30 min with a selectivity of 77.0%.

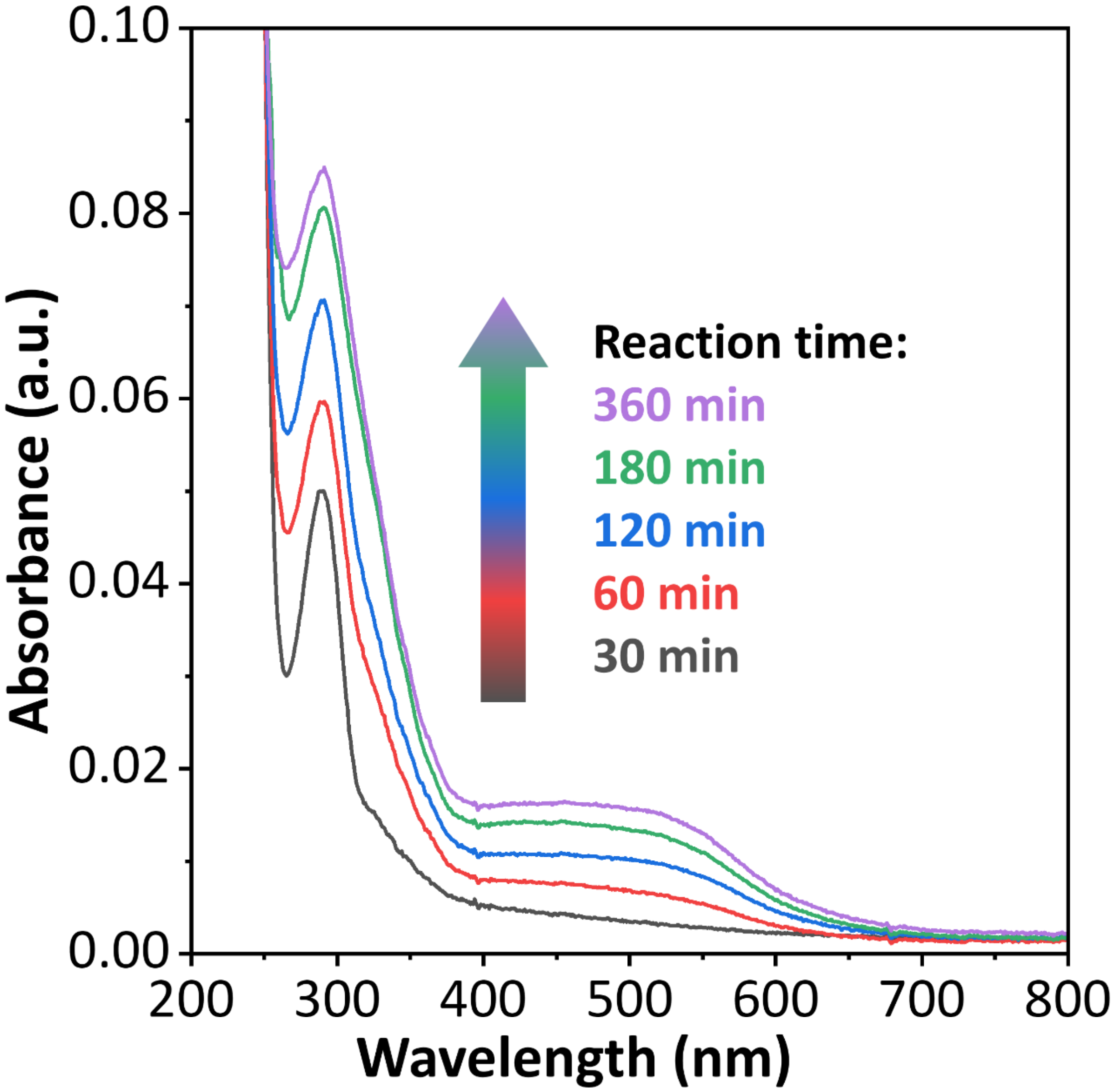

Fig. S5 Transmitted UV-vis spectra of the after-reaction solutions with various reaction times. All the solution samples were diluted 150 times with acetonitrile to avoid saturated light absorption in UV region. Other reaction conditions are given in the footnote of **Fig. S4**.

Table S2 The photocatalytic reaction tests with different concentrations of aniline. [a]

Entry	c_0 [b] (mmol L^{-1})	r [c] (μmol min^{-1})	*C* (%) [d]	*Y* (%) [e] 2-ADPA	4-ADPA	AZB	*S* (%) [f]
1	0.859	0.0815	71.1	tr. [g]	tr.	tr.	0
2	5.10	0.223	32.7	5.15	5.86	1.09	33.6
3	12.5	0.435	25.3	8.99	10.5	4.16	77.0
4	41.1	0.490	8.89	2.46	3.45	0.763	66.6
5	128	0.803	4.67	1.16	1.46	0.414	56.2

[a] Reaction conditions: 50 mg of the Pt(1.0)/TiO_2 photocatalyst was used; Different amount of aniline was introduced as the reactant; 4 mL of 0.1 mol L^{-1} NaOH (*aq*, pH = 12.70) was applied; The incident UV-LED light wavelength was around 365 ± 5 nm, the irradiated light intensity was 1035 mW cm^{-2} when measured at 360 ± 20 nm in wavelength; Reaction time was 30 min. [b] initial concentration of aniline, *c* = (introduced amount of aniline)/(introduced volume of aniline and NaOH (*aq*)); [c] consumption rate of aniline, *r* = (introduced aniline – remained aniline after reaction)/(reaction time); [d] Conversion of aniline, *C* (%) = 100 × (introduced aniline – remained aniline after reaction)/(introduced aniline); [e] Yield of detectable products, *Y* (%) = 100 × $A_{(2\text{-ADPA, 4-ADPA, AZB})}$ × 2/(introduced aniline), where $A_{(2\text{-ADPA, 4-ADPA, AZB})}$ stand for the yielded amount of 2-ADPA, 4-ADPA, and AZB, respectively. [f] Selectivity to 2-ADPA and 4-ADPA based on consumed aniline, *S* (%) = 100 × ($A_{(2\text{-ADPA})}$ +$A_{(4\text{-ADPA})}$) × 2/ (introduced aniline – remained aniline); [g] tr. = not detected in GC-FID, but appeared characteristic mass peak in GC-MS.

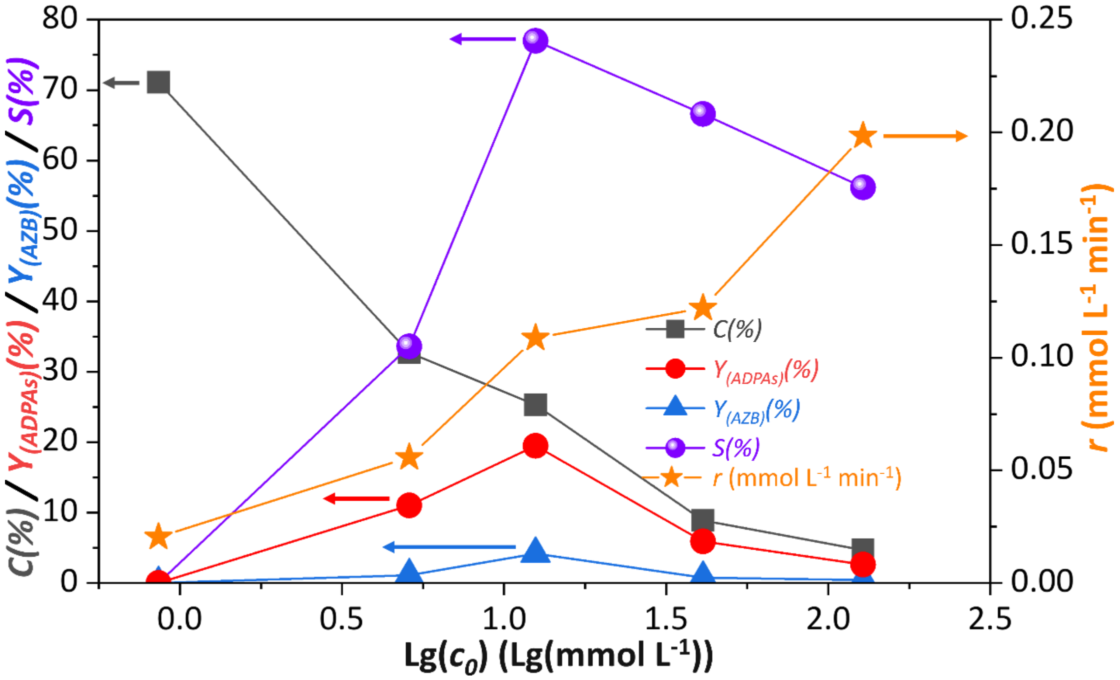

Fig. S6 Results of the photocatalytic reaction test with different concentrations of aniline. The reaction conditions were described in **Table S2**.

Table S3 Photocatalytic conversion of aniline under various aqueous solutions with different pH [a]

Entry	pH [b]	*C* (%) [c]	*Y* (%) [d]			*S* (%) [e]	H_2 (μmol)
			2-ADPA	4-ADPA	AZB		
1	3.29	0	n.d. [f]	n.d.	n.d.	/	0.844
2	5.62	0	n.d.	n.d.	n.d.	/	1.11
3	6.58	0	n.d.	n.d.	n.d.	/	0.916
4	7.74	0	n.d.	n.d.	n.d.	/	1.11
5	10.35	0	n.d.	n.d.	n.d.	/	1.47
6	11.79	1.82	n.d.	n.d.	n.d.	/	2.13
7	12.01	30.5	7.40	10.1	0.488	57.4	n.m. [g]
8	12.21	30.1	9.65	11.7	1.84	70.9	6.94
9	12.70	25.3	8.99	10.5	4.16	77.0	6.09
10	13.01	25.8	8.36	9.06	3.72	67.5	5.92
11	13.43	24.9	4.57	5.21	3.17	39.3	5.62

[a] Reaction conditions: 50 mg of the Pt(1.0)/TiO_2 photocatalyst was used; 4.6 μL (50 μmol) of aniline was introduced as the reactant; 4 mL of different aqueous solvents with different pH were applied; The incident UV-LED light wavelength was around 365 ± 5 nm, the irradiated light intensity was 1035 mW cm^{-2} when measured at 360 ± 20 nm in wavelength; Reaction time was 30 min; [b] The exact pH was measured by a pH meter. For acidic solutions, HCl (*aq*) with different concentration (**entries 1** and **2**) and ion-changed water were used; For basic solutions, NaOH (*aq*) with different concentration (**entries 4–11**) were added; [c] Conversion of aniline, *C* (%) = 100 × (introduced aniline – remained aniline after reaction)/(introduced aniline); [d] Yield of detectable products, *Y* (%) = 100 × $A_{(2\text{-ADPA, 4-ADPA, AZB})}$ × 2/(introduced aniline), where $A_{(2\text{-ADPA, 4-ADPA, AZB})}$ stand for the yielded amount of 2-ADPA, 4-ADPA, and AZB, respectively. [e] Selectivity to 2-ADPA and 4-ADPA based on consumed aniline, *S* (%) = 100 × ($A_{(2\text{-ADPA})}$ +$A_{(4\text{-ADPA})}$) × 2/ (introduced aniline – remained aniline); [f] n.d. = not detected in GC-MS and GC-FID; [g] n.m. = not measured.

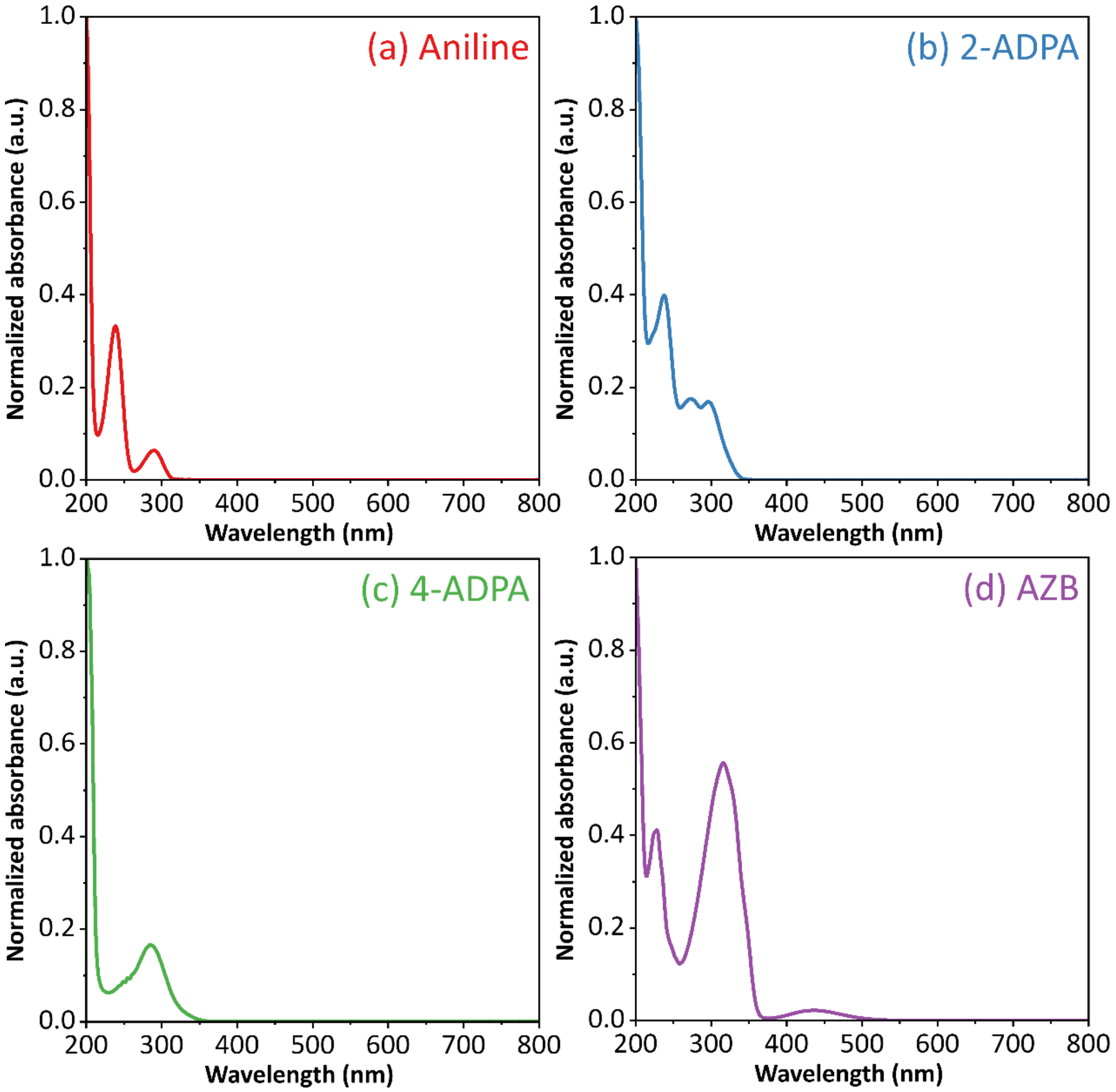

Fig. S7 Transmitted UV-vis spectra of aniline, 2-ADPA, 4-ADPA, and AZB samples. All the samples were prepared as acetonitrile solutions to avoid the saturated absorbance in UV region. Each spectrum was normalized to its maximum absorbance.