Electronic Supplementary Information

Hydrogen- and noble metal-free conversion of nitro aromatics to amino aromatics having reducible groups over an organically modified TiO_2 photocatalyst under visible light irradiation

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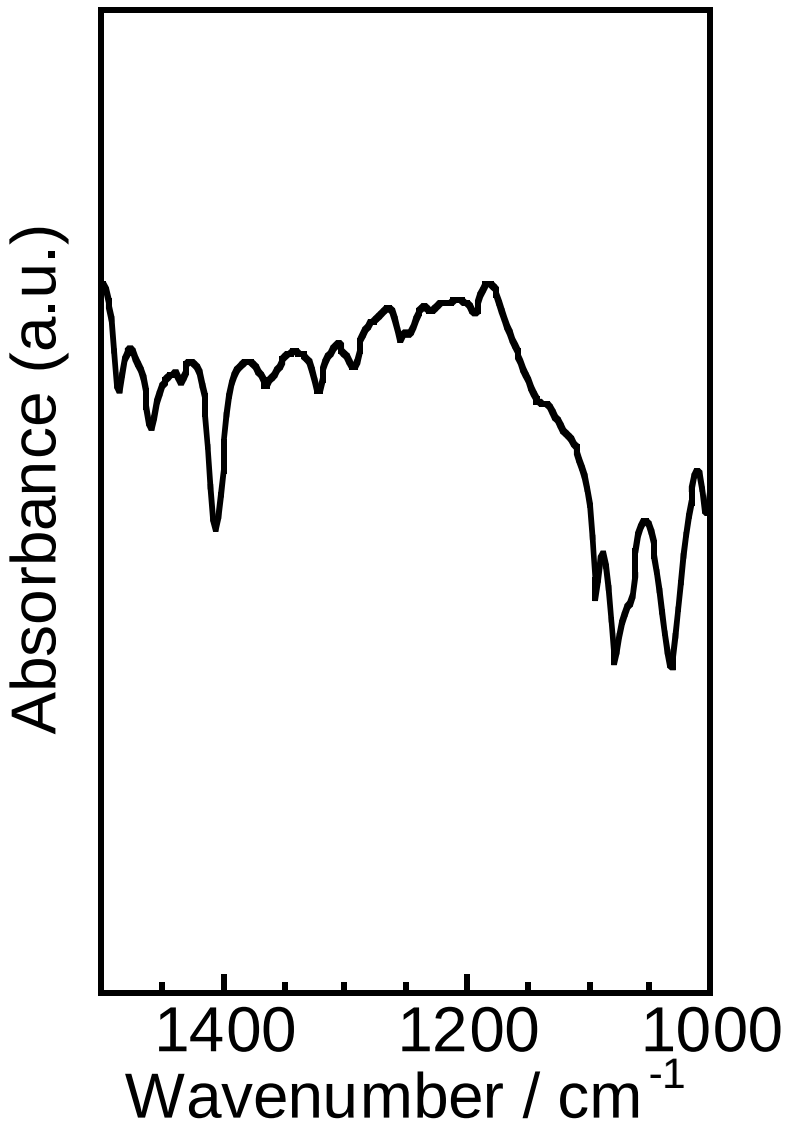

Fig. S1 FT-IR spectrum of TEOA-loaded TiO_2.

Table S1 summary of various reduction of nitrobenzenes to anilines.

Entry	reference	Catal.	R	Solvent	Initial	Irradiation	Hole scavenger	Temp.	Atm.	Time / h	Conv. / %	Sel. / %
1	10	AgNPs@CeO_2, 25 mg	vinyl	dodecane	0.5 mmol	×	×	110	H_2 (6 atm)	6	99[a]	99
2	11	Au/Al-2.5, 0.2 mol%	vinyl	THF	2 mmol	×	×	120	H_2 (3 MPa)	2	100	99
3	11	Au/Al-2.5, 0.2 mol%	Acetyl	THF	2 mmol	×	×	65	H_2 (3 MPa)	4	100	99
4	9	Au/TiO_2, 0.23×10^{2}, [b]	Vinyl	Toluene	[b]	×	×	120	H_2 (15 bar)	6.5	98.5	95.9
5	9	Pt/TiO_2, 0.75×10^{2}, [b]	Chloro	THF	[b]	×	×	45	H_2 (4 bar)	1	99	99.6
6	9	Pt/TiO_2, 0.24×10^{2}, [b]	Acetyl	Toluene	[b]	×	×	40	H_2 (3 bar)	5.6	98.9	90.1
7	2	TiO_2, 50 mg	vinyl	Water	50 μmol	Hg lamp (> 300 nm)	Oxalic acid, 200 μmol	25	Ar (1 atm)	6	>99	88
8	2	TiO_2, 50 mg	Chloro	Water	50 μmol	Hg lamp (> 300 nm)	Oxalic acid, 200 μmol	25	Ar (1 atm)	2	>99	>99
9	2	TiO_2, 50 mg	Bromo	Water	50 μmol	Hg lamp (> 300 nm)	Oxalic acid, 200 μmol	25	Ar (1 atm)	2	>99	>99
10	2	TiO_2, 50 mg	Acetyl	Water	50 μmol	Hg lamp (> 300 nm)	Oxalic acid, 200 μmol	25	Ar (1 atm)	2	>99	91
11	I	CdS/g-C_3N_4, 0.1 g	H	Benzotrifuloride	127.5 μmol	300 W Xe lamp (> 420 nm)	p-Methoxybenzyl alcohol, 382.5 μmol	60	N_2 (0.5 MPa)	4	70	57.1
12	34	DHN/1 wt%Pt-TiO_2, 50 mg	H	Acetonitrile	0.1 mmol	500 W Xe lamp (> 420 nm)	TEOA, 1 mmol	R. T.[c]	Ar (1 atm)	4	42.7	*ca*. 75
13	II	Fe(bpy)$_3$@rGO, 25 mg	Chloro	Acetonitrile	0.1 mmol	20 W LED (> 400 nm)	hydrazine monohydrate 1 mmol	R. T.[c]	1 atm[c]	10	86	97[d]
14	II	Fe(bpy)$_3$@rGO, 25 mg	Bromo	Acetonitrile	0.1 mmol	20 W LED (> 400 nm)	hydrazine monohydrate 1 mmol	R. T.[c]	1 atm[c]	12	80	94[d]
15	III	CdS, 20 mg	Chloro	*i*-PrOH	50 μmol	3 W Blue LED (> 420 nm)	*i*-PrOH, solvent	R. T.[c]	Ar (1 atm)	20	100	90
16	III	CdS, 20 mg	Acetyl	*i*-PrOH	50 μmol	3 W Blue LED (> 420 nm)	*i*-PrOH, solvent	R. T.[c]	Ar (1 atm)	20	100	98
17	This study	DHN/TiO_2, 50 mg	Vinyl	Acetonitrile	50 μmol	Blue LED (λ_{max} = 467 nm)	TEOA, 300 μmol	R. T.	Ar (1 atm)	10	>99	97
18	This study	DHN/TiO_2, 50 mg	Chloro	Acetonitrile	50 μmol	Blue LED (λ_{max} = 467 nm)	TEOA, 300 μmol	R. T.	Ar (1 atm)	10	>99	98
19	This study	DHN/TiO_2, 50 mg	Bromo	Acetonitrile	50 μmol	Blue LED (λ_{max} = 467 nm)	TEOA, 300 μmol	R. T.	Ar (1 atm)	18	>99	>99
20	This study	DHN/TiO_2, 50 mg	Acetyl	Acetonitrile	50 μmol	Blue LED (λ_{max} = 467 nm)	TEOA, 300 μmol	R. T.	Ar (1 atm)	15	>99	>99

[a] Conv. = (Yield / Sel.) ×100, [b] Pt/nitro (mol), [c] No description, [d] Sel. = (Yield / Conv.) ×100, [e] Numbers in parentheses represent results in the presence of 50 mg of the HCO_2NH_4.

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