

Supplementary information for

**Chemoselective reduction of nitrobenzenes to aminobenzenes having
reducible groups by titanium(IV) oxide photocatalyst under gas- and
metal- free conditions**

Introduction

Table S1 Chemoselective reduction of NVB to AVB by various catalytic methods

Catalyst	Temp. /K	Solvent	Gas phase	Pressure /atm	Time /h	Conversion /%	Selectivity /%	References
TiO ₂	298	10% Water-ACN	Ar	1.0	2	100	93	This work
Pt/C-H ₃ PO ₂ -VO(acac) ₂	373	Toluene	H ₂	4.9	-	95 ^a		1.9
0.23 mol%-Au/TiO ₂	393	Toluene	H ₂	8.9	6	99	96	10-12
0.39 mol%-Au/Fe ₂ O ₃	403	Toluene	H ₂	11.8	9.5	95	95	10
0.2 wt%-Pt/C	313	Toluene	H ₂	3.0	-	95	90	11
0.2 wt% Pt/TiO ₂	313	Toluene	H ₂	3.0	6.5	95	93	11,12
5 wt%-Ni/TiO ₂	393	Toluene	H ₂	15	3	93	90	11
1wt%-Ru/TiO ₂	393	Toluene	H ₂	15	1.5	95	96	11
0.2 mol%-Au/Al ₂ O ₃	393	THF	H ₂	30	2	>99	99	13
2 mol%-Ag/Al ₂ O ₃	433	THF	H ₂	30	1	>99	92	12,15
14 mol%-Ag/HT	423	DMA ^b	CO	9.0	3	>99	>99	16
Rh ₆ (CO) ₁₆	353	2-Ethoxyethanol ^c	CO	4.0	5	91 ^a		17
MoO ₂ Cl ₂	393	Ethanol	H ₂	50	48	>99	>99	18
Ag@CeO ₂	383	Dodecane	H ₂	6	6	>99	98	19

^a Yield of AVB. No data for conversion and selectivity were presented.

^b *N,N*-Dimethylacetamide

^c Water and *N,N,N',N'*-tetramethyl-1,3-propanediamine were added.

Experimental

Bare TiO₂ powder (Degussa P 25, 50 mg) was suspended in a mixture of acetonitrile (ACN, Wako Pure Chemical Industries, Osaka) and water (5 cm³) containing *m*-nitrovinylbenzene (NVB, 50 μmol, Sigma-Aldrich Japan, Tokyo) and oxalic acid (OA, 200 μmol, Wako Pure Chemical Industries, Osaka) in a test tube. The tube was sealed with a rubber septum and then photoirradiated at a wavelength >300 nm by a high-pressure mercury arc (400 W, Eiko-sha, Osaka) under argon (Ar) with magnetic stirring at 298 K. After the reaction, gas phase was analyzed by a gas chromatograph (Shimadzu, GC-8A equipped with MS-5A columns). After the suspension had been filtered to remove the particles, the amounts of NVB and product(s) were determined by high-performance liquid chromatography (Jasco, UV-2075Plus detector, PU-2089Plus pump, equipped with an Inertsil ODS-3 column, eluent: aqueous sodium borate buffer/ACN = 50/50, flow rate: 0.5 cm³ min⁻¹ at r.t). To obtain apparent quantum efficiency (AQE), a UV light-emitting diode (UV-LED, PJ-1505-2CA, CCS Inc, Kyoto, 927 μW cm⁻², maximum energy at λ = 366 nm) was also used as a light source. A spectrum and light intensity of the UV-LED were determined using a spectroradiometer USR-45D (Ushio, Tokyo).

Results

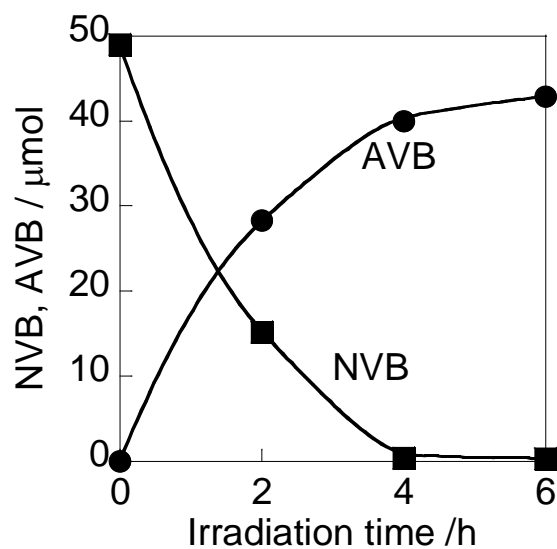


Figure S1 Time courses of amount of NVB remaining (squares) and amount of *m*-aminovinylbenzene (AVB) formed (circles) in an ACN suspension of TiO₂ (50 mg) in the presence of OA (200 μmol) as a hole scavenger under deaerated conditions.

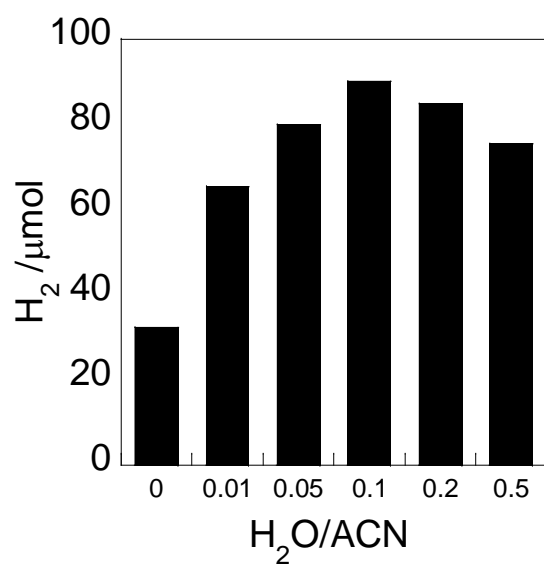


Figure S2 Effect of water content of solvents (water-ACN) on decomposition of OA (H₂ evolution) in the suspensions of platinized TiO₂ for 2 h.

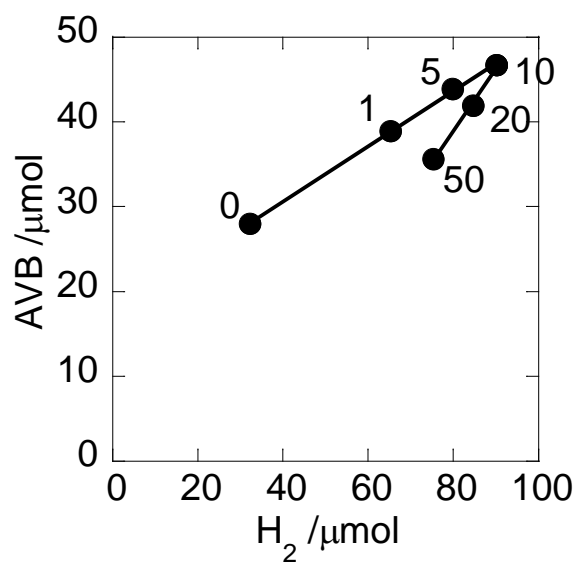


Figure S3 Correlations between amount of AVB formed and H₂ evolved after 2-h and 30-min photoirradiation. Values in the figure indicate the content of water in reaction mixtures.