Supplementary information for

Photocatalytic reduction of benzonitrile to benzylamine in aqueous suspension of palladium-loaded titanium(IV) oxide

Experimental

Preparation of metal-loaded TiO₂ samples

All reagents were purchased from Wako Pure Chemical Industries, Ltd. and used without further purification. Three kinds of TiO₂, MT-150A (Tayca, Osaka), P 25 (Degussa) and ST-01 (Ishihara), were used as photocatalysts. Photodeposition was used to load metal co-catalysts (0.3 wt%) (platinum (Pt), silver (Ag), copper (Cu), gold (Au) and palladium (Pd)) on TiO₂ using hexachloroplatinic(IV) acid, silver nitrate, copper chloride, tetrachloroauric(III) acid and palladium(II) chloride as starting sources. In a 50 vol% methanol aqueous solution (10 cm³) containing a metal source, TiO_2 particles were suspended, and the solution was photoirradiated for 120 min with a 400 W high-pressure mercury arc ($\lambda > 300$ nm, Eiko-sha) with magnetic stirring under argon (Ar) or the atmosphere at 298 K. Analysis of the liquid phase after photoirradiation revealed that the metal co-catalysts had been almost completely deposited on the TiO₂ particles. After photoirradiation, the metal-loaded TiO₂ particles were recovered, washed repeatedly with water, and dried at 293 K in vacuo for 120 min.

Typical procedure of photocatalytic reaction

Metal-loaded TiO₂ powder (50 mg) was suspended in a 0.1-mol dm⁻³ aqueous hydrochloric acid (HCl) solution containing PhCN (50 µmol) and oxalic acid (oxalic acid, 200 µmol) as a hole scavenger. The tube was sealed with a rubber septum and then photoirradiated by a 400 W high-pressure mercury arc ($\lambda > 300$ nm, Eiko-sha) under Ar with magnetic stirring at 298 K. After the reaction, the gas phase was analyzed by a gas chromatograph (Shimadzu, GC-8A equipped with MS-5A columns for H₂ and equipped with porapak QS for carbon dioxide (CO₂)). After the suspension had been filtered to remove the particles, the amounts of PhCN remaining and product(s) were determined by a gas chromatograph (Shimadzu GC-2025 equipped with DB-1 columns).

Results



Fig. S1 X-ray diffraction patterns of Pd-TiO₂ prepared by photodeposition method, TiO₂ (rutile, JCPDS 21-1276), Pd (JCPDS 46-1043) and palladium oxide (PdO, JCPDS 41-1107).