

Photocatalytic hydrogenation of azobenzene to hydrazobenzene on cadmium sulfide under visible light irradiation

Yasuhiro Shiraishi,^{a,b*} Miyu Katayama,^a Masaki Hashimoto^a and Takayuki Hirai^a

^a Research Center for Solar Energy Chemistry, and Division of Chemical Engineering, Graduate School of Engineering Science, Osaka University, Toyonaka 560-8531, Japan

^b Precursory Research for Embryonic Science and Technology (PRESTO), Japan Science and Technology Agency (JST), Saitama 332-0012, Japan

shiraish@cheng.es.osaka-u.ac.jp

Electronic Supplementary Information (ESI†)

CONTENTS

	Page
Experimental methods	2
Fig. S1 SEM images of the CdS used	3
Fig. S2 Time course of hydrazobenzene photoreaction on CdS	4
Fig. S3 XPS (S 2p level) of CdS	4
Fig. S4 Absorption spectra of some catalysts	5
Fig. S5 Effect of water addition on photoreaction and adsorption.....	6

Experimental methods

Catalyst Preparation

BiVO₄,^[1] Ag₃PO₄,^[2] and g-C₃N₄^[3] were prepared according to literature procedure. CdS loaded with 0.5 and 1.0 wt % Pt (Pt/CdS) were prepared as follows:^[4] CdS (200 mg) and different amount of H₂PtCl₆·6H₂O (2.7 or 5.3 mg) were added to a 2-PrOH/water mixture (30 mL) within a borosilicate glass bottle (\varnothing 35 mm; capacity, 50 mL). The bottle was sealed with a rubber septum cap. The catalyst was dispersed well by ultrasonication for 5 min, and Ar gas was bubbled through the solution for 5 min. The bottle was photoirradiated at $\lambda > 420$ nm with magnetic stirring using a 2 kW Xe lamp (USHIO Inc.) at 303 K.^[5] The resultant was recovered by filtration, washed with water, and dried in vacuo, affording grey powders of Pt/CdS.

Photoreaction

Azobenzene or hydrazobenzene (50 μ mol) were dissolved in a 2-PrOH solution (5 mL). The solution and catalyst were added to a Pyrex glass tube (\varnothing 12 mm; capacity, 20 mL). The solution and catalyst were added to a Pyrex glass tube (\varnothing 12 mm; capacity, 20 mL). The tube was sealed with a rubber septum cap. The catalyst was dispersed well by ultrasonication for 5 min, and Ar gas was bubbled through the solution for 7 min. The tube was photoirradiated with magnetic stirring using a 2 kW Xe lamp.^[5] The temperature of solution during photoirradiation was ca. 303 K. After the reaction, the catalyst was recovered by centrifugation, and the resulting solution was analyzed by GC-FID (Shimadzu GC-2010 system). The substrate and product concentrations were calibrated with authentic samples. Analysis was performed at least three times and the errors were $\pm 0.2\%$. For action spectrum analysis, photoreactions were carried out using a 2-PrOH/water (9/1 v/v) mixture (2 mL) containing azobenzene (20 μ mol) and CdS (10 mg) for 2 h, where the incident light was monochromated by band-pass glass filters.^[6]

Analysis

Diffuse-reflectance UV-vis, XPS,^[7] and ICP analysis^[8] were performed according to literature procedure.

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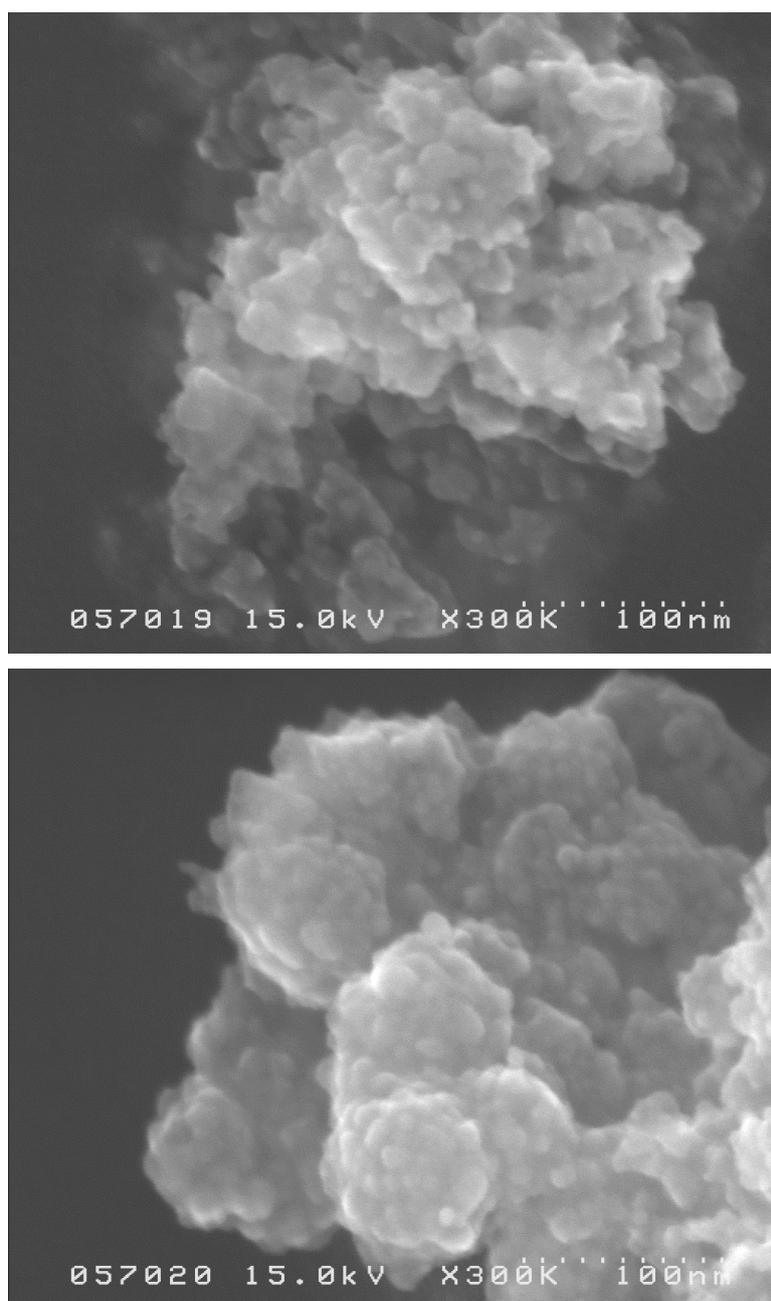


Fig. S1 Typical SEM images of the CdS used.

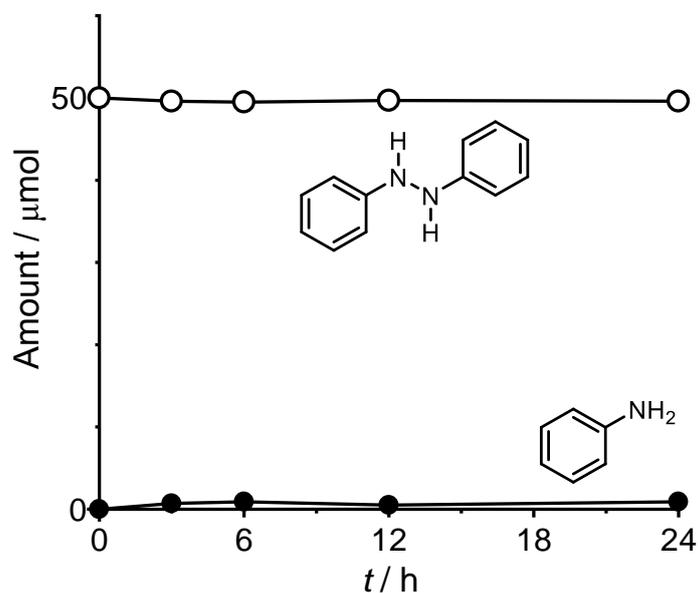


Fig. S2 Time-dependent change in the amounts of substrate and product during photoreaction of hydrazobenzene on CdS. The reaction conditions are identical to those in Fig. 1 (manuscript).

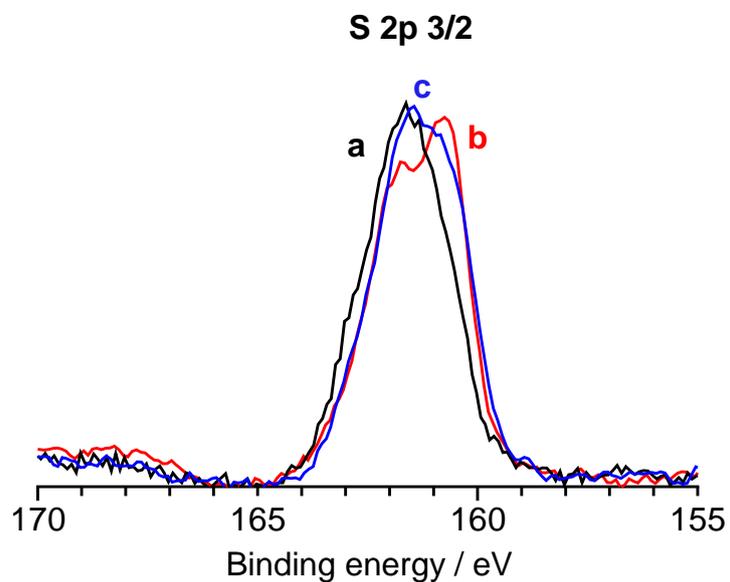


Fig. S3 XPS chart (S 2p region) of (a) CdS, (b) CdS obtained after visible light irradiation in a 2-PrOH/water mixture, and (c) the sample obtained after adsorption of azobenzene onto the photoirradiated CdS (b).

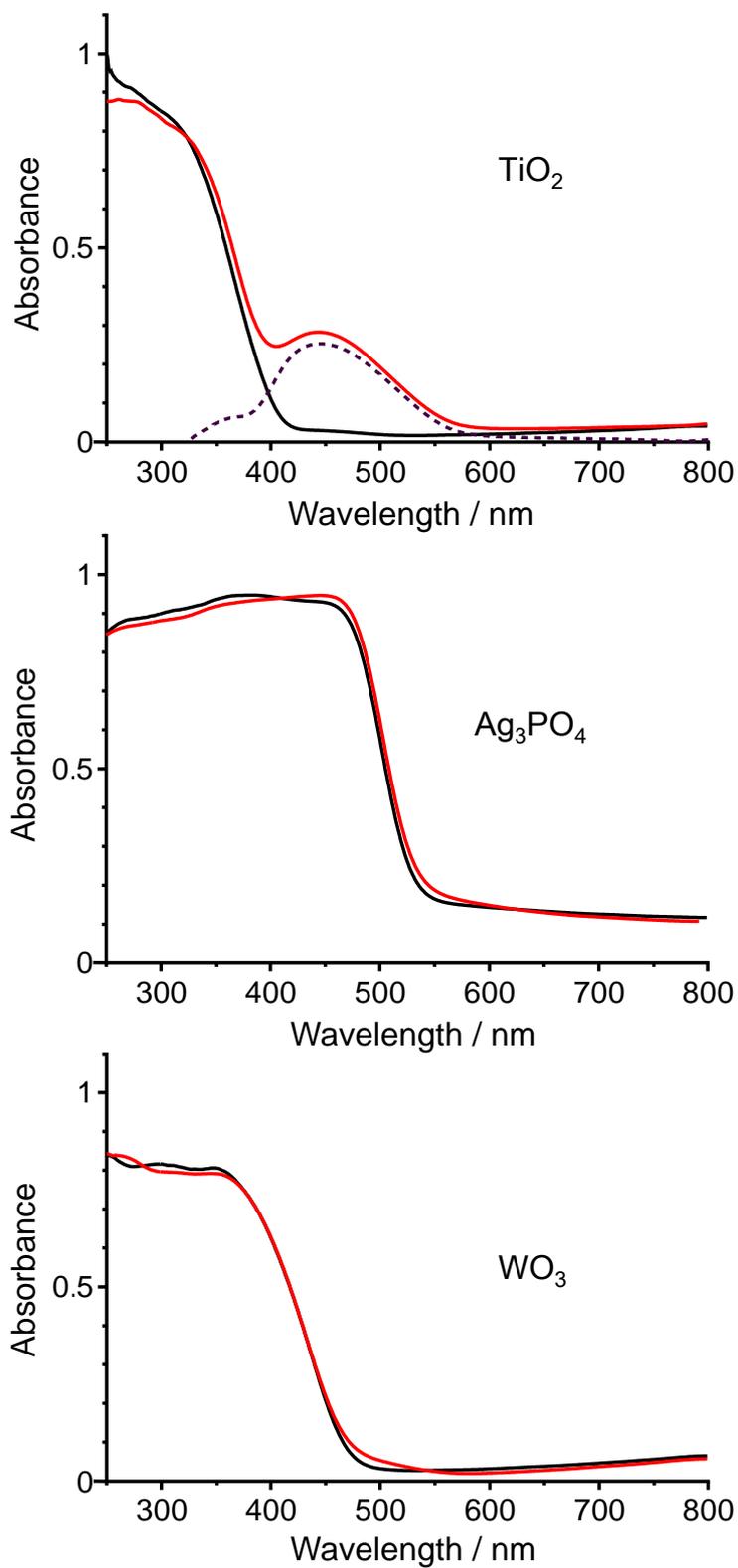


Fig. S4 UV-vis absorption spectra of (black) some catalysts and (red) the catalysts obtained after photoirradiation in a 2-PrOH/water mixture under Ar followed by adsorption of azobenzene under Ar.

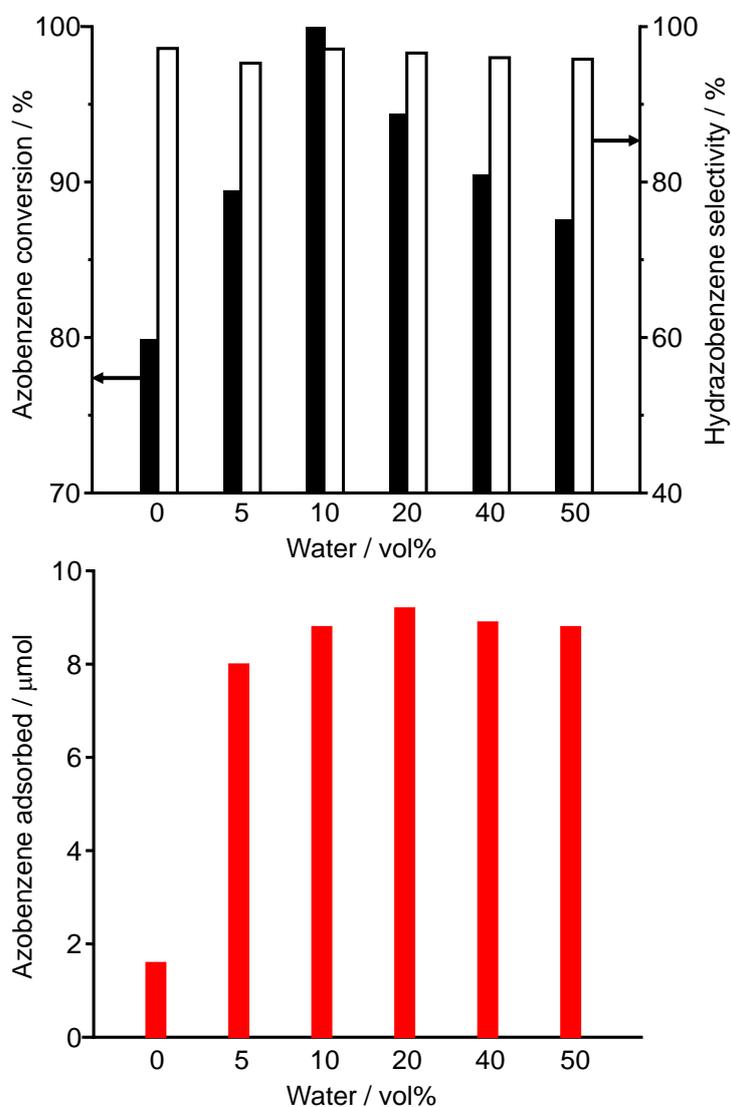


Fig. S5 (Top) Effect of water added on the conversion of azobenzene and the hydrazobenzene selectivity by photoreaction of azobenzene on CdS for 5 h. Reaction conditions are identical to those in Fig. 1 (manuscript). (Bottom) Effect of water added on the amount of azobenzene adsorbed onto CdS by stirring in the dark condition for 5 h.