Photocatalytic hydrogenolysis of epoxides with alcohol as a reducing agent on TiO_2 loaded with Pt nanoparticles

Hiroaki Hirakawa,[a] Yasuhiro Shiraishi,*[a,b] Hirokatsu Sakamoto,[a] Satoshi Ichikawa,[c] Shunsuke Tanaka,[d] 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] *PRESTO, JST, Saitama 332-0012, Japan*
[c] *Institute for NanoScience Design Center, Osaka University, Toyonaka 560-8531, Japan*
[d] *Department of Chemical, Energy and Environmental Engineering, Kansai University, Suita 564-8680, Japan*
E-mail: shiraish@cheng.es.osaka-u.ac.jp

Electronic Supplementary Information (ESI†)

Photoreaction

Each of the respective epoxides was dissolved in an alcohol solution (5 mL). The solution and catalyst were added to a Pyrex glass tube (φ 12 mm; capacity, 20 mL), and the tube was sealed with a rubber septum cap. The catalyst was dispersed well by ultrasonication for 5 min, and N_2 was bubbled through the solution for 5 min. The tube was photoirradiated with magnetic stirring using a 2 kW Xe lamp (USHIO Inc.; λ >300 nm).[1] The temperature of solution during photoirradiation was ca. 303 K. After the reactions, the catalyst was recovered by centrifugation, and the solution was analyzed by GC−FID (Shimadzu GC-2040 system) equipped with a DB-17 capillary column (Agilent Technologies, 30 m × 0.250 mm × 0.25 μm). The substrate and product concentrations were calibrated with authentic samples. The analysis was performed at least three times, where the errors were ±0.2%. Products were identified using a GC−MS system (Shimadzu GCMS-QP5050A).

Analysis

TEM observations were performed using an FEI Tecnai G2 20ST analytical electron microscope operated at 200 kV.[2] XRD patterns were measured on a Philips X′Pert-MPD spectrometer. Diffuse-reflectance (DR) UV-vis spectra were measured on an UV-vis spectrophotometer (JASCO Corp.; V-550) equipped with Integrated Sphere Apparatus ISV-469, using $BaSO_4$ as a reference.[3] DRIFT analysis was carried out on a FT/IR 610 system,[4] equipped with an in-situ DR cell (Heat Chamber HC-500, ST Japan, Inc.). Monochromatic light (360 nm) was irradiated by a Xe lamp (300 W; Asahi Spectra Co. Ltd.; Max-302) equipped with 360 nm band-pass filter.

References

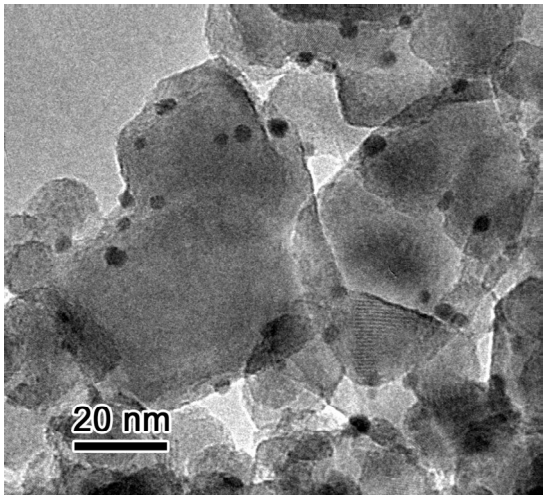
[1] Y. Shiraishi, Y. Sugano, S. Tanaka and T. Hirai, *Angew. Chem., Int. Ed.*, 2010, **49**, 1656−1660.

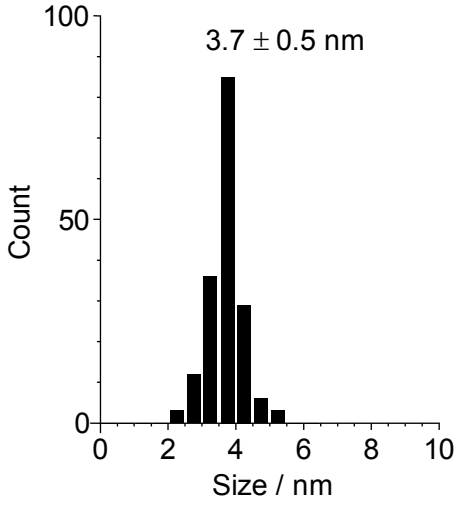
[2] Y. Shiraishi, K. Tanaka, E. Shirakawa, Y. Sugano, S. Ichikawa, S. Tanaka and T. Hirai, *Angew. Chem. Int. Ed.*, 2013, **52**, 8304−8308.

[3] Y. Shiraishi, S. Kanazawa, Y. Kofuji, H. Sakamoto, S. Ichikawa, S. Tanaka and T. Hirai, *Angew. Chem. Int. Ed.*, 2014, **53**, 13454−13459.

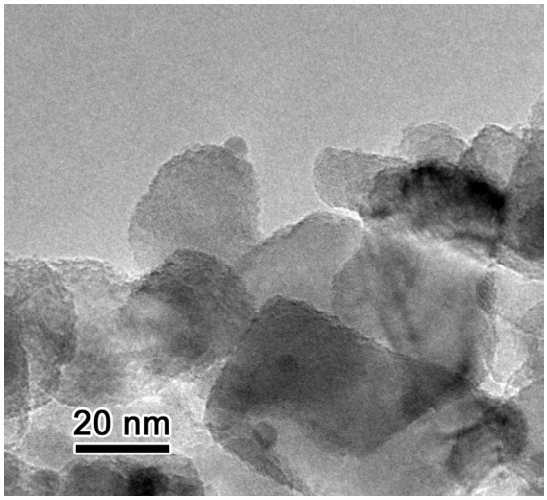
[4] Y. Shiraishi, H. Hirakawa, Y. Togawa and T. Hirai, *ACS Catal.*, 2014, **4**, 1642−1649.

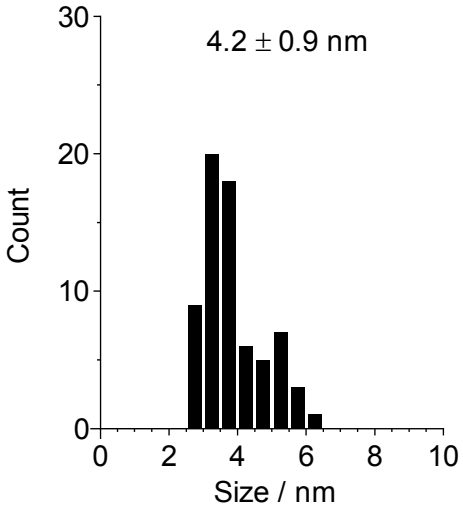
Au_2/TiO_2 (prepared by deposition-precipitation method)



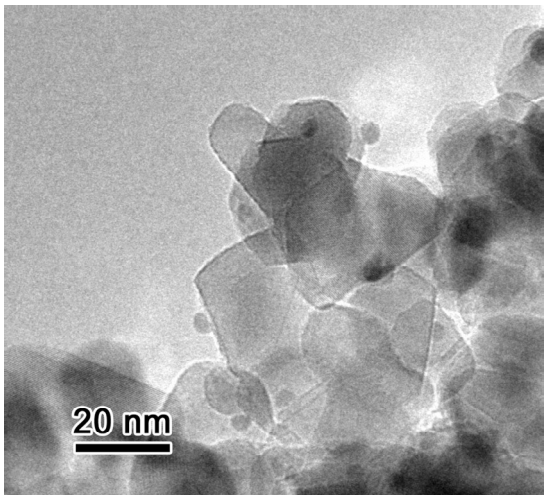


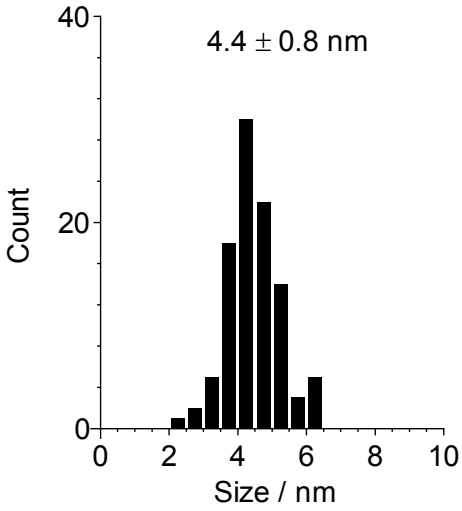
Ag_2/TiO_2 (prepared by H_2 reduction at 673 K)



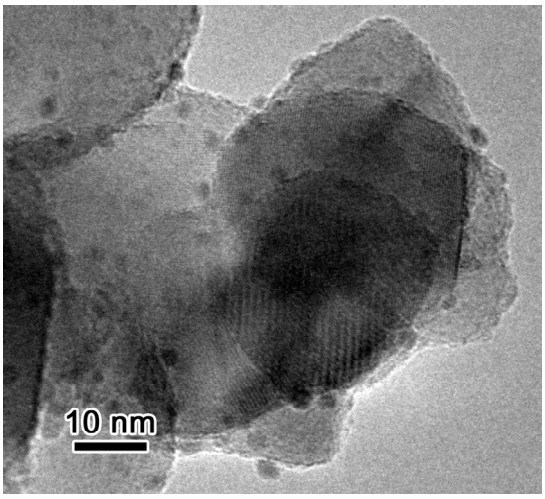


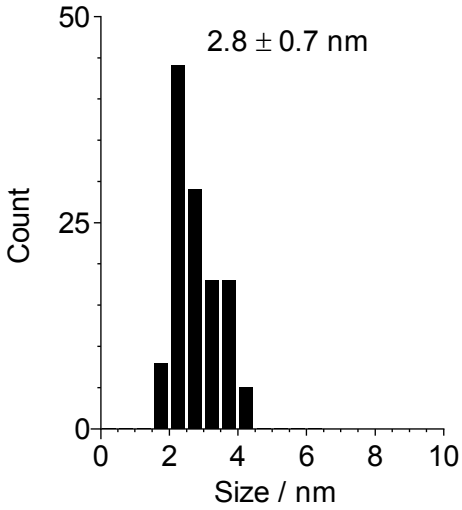
Pd_2/TiO_2 (prepared by H_2 reduction at 673 K)



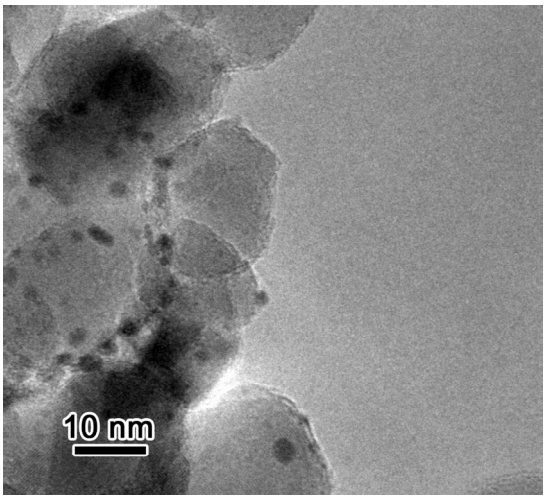


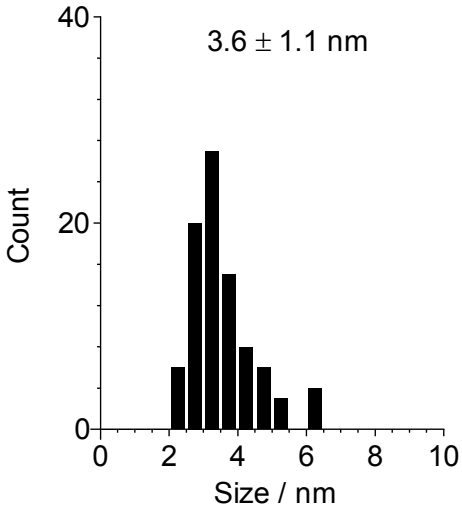
Pt_2/TiO_2 (prepared by H_2 reduction at 573 K)



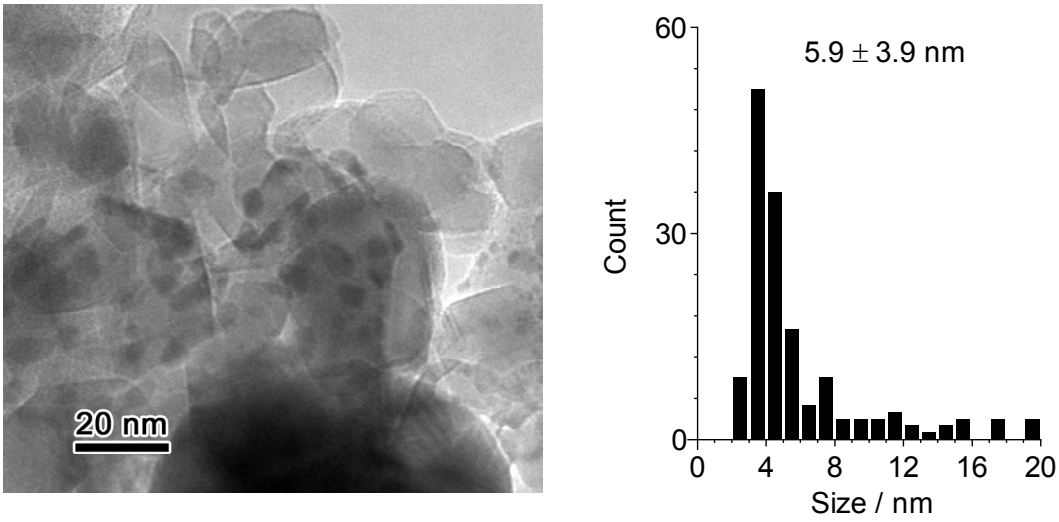


Pt_2/TiO_2 (prepared by H_2 reduction at 773 K)

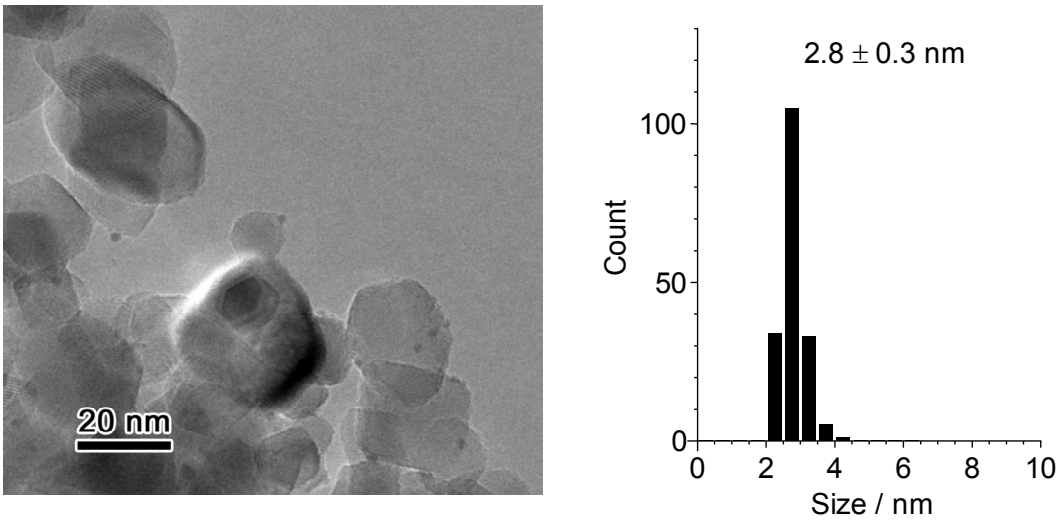




Pt_2/TiO_2 (prepared by H_2 reduction at 873 K)



$Pt_{0.5}/TiO_2$ (prepared by H_2 reduction at 673 K)



Pt_4/TiO_2 (prepared by H_2 reduction at 673 K)

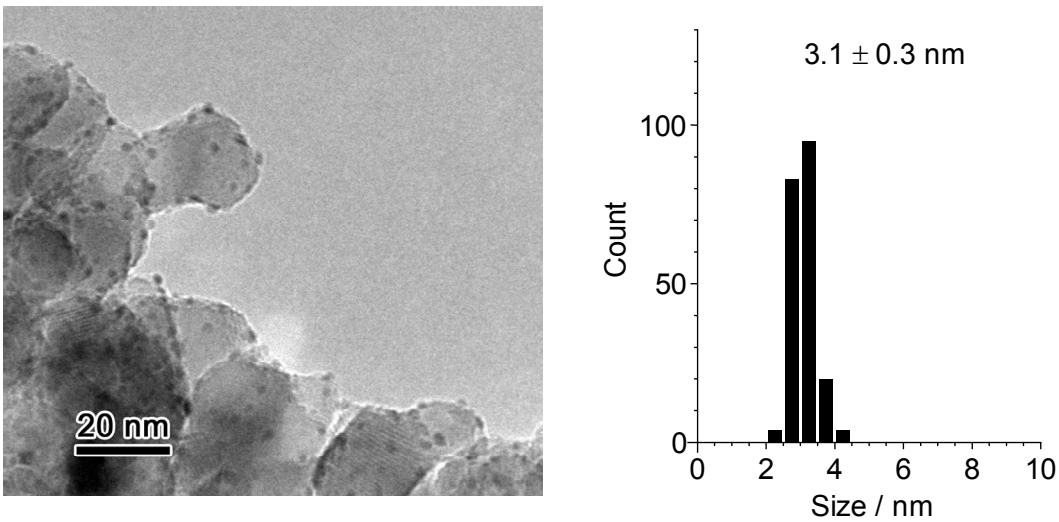


Fig. S1 Typical TEM images of M_x/TiO_2 catalysts and size distributions of metal particles.

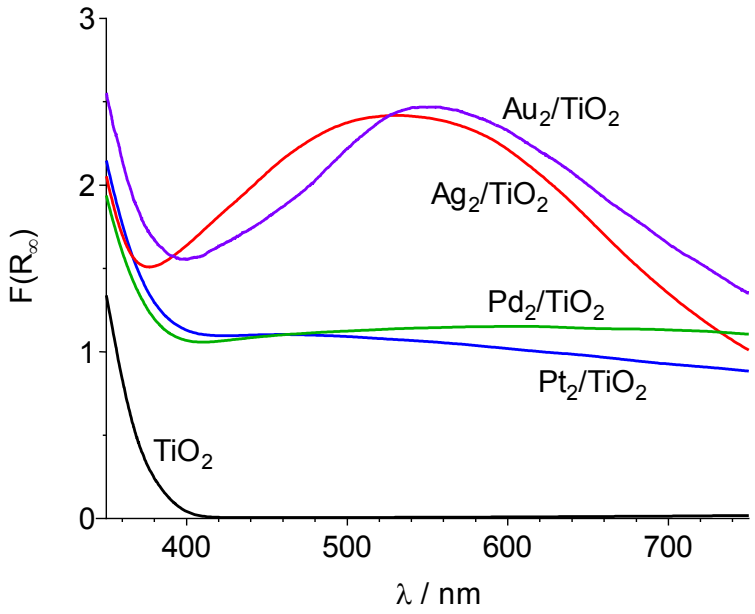


Fig. S2 Diffuse reflectance UV-vis spectra of the catalysts.

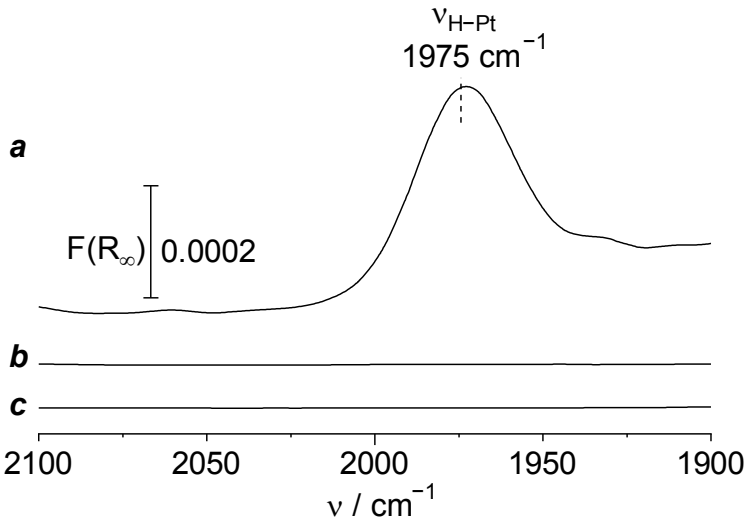


Fig. S3 (a) DRIFT spectrum measured on Pt_2/TiO_2 with 2-PrOH under 360 nm light irradiation. The spectrum was measured as follows: Pt_2/TiO_2 (20 mg) was placed in a DR cell and evacuated (5.5 Pa) at 423 K for 3 h. 2-PrOH (42 μmol) was introduced to the cell at 303 K and left for 5 min under photoirradiation. The measurement was started with continued photoirradiation. Attenuated total reflection (ATR) spectra of (b) acetone and (c) 2-PrOH measured at 303 K are also shown.

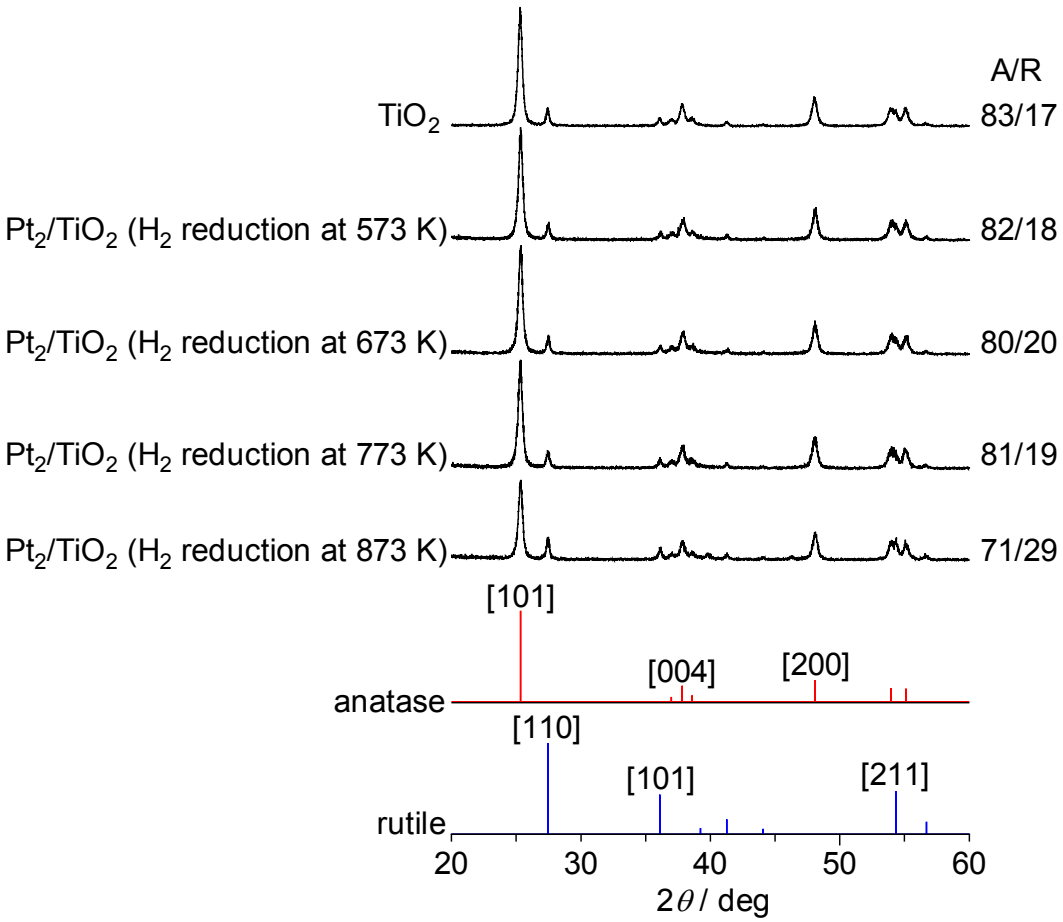


Fig. S4 XRD patterns of Pt_2/TiO_2 prepared at different H_2 reduction temperature. The anatase (A) and rutile (R) contents were determined with the equation: A (%) = $I_{A(101)}$ / [$I_{A(101)}$ + 1.4$I_{R(110)}$] × 100 (G. Ramis, G. Busca, C. Cristiani, L. Lietti, P. Forzatti and F. Bregani, *Langmuir*, 1992, **8**, 1744–1749).