Electronic Supplementary Information for

Boronate self-assembles with embedded Au nanoparticles; preparation, characterization and their catalytic activities for the reduction of nitroaromatic compounds

Yusuke Matsushima,[a] Ryuhei Nishiyabu,[a] Naoto Takanashi,[a] Masatake Haruta,[a] Hideaki Kimura,[b] and Yuji Kubo*[a]

[a]*Department of Applied Chemistry, Graduate School of Urban Environmental Science, Tokyo Metropolitan University, Minami-ohsawa, Hachioji, Tokyo 192-0397, Japan*
[b]*BrukerBioSpin K. K., 3-9, Moriya-cho, Kanagawa-ku, Yokohama-shi, Kanagawa 221-0022, Japan*.

*Corresponding Author: Yuji Kubo, yujik@tmu.ac.jp

Synthesis of Au/SiO_2 hybrids

Au/SiO_2 catalysts were prepared according to the procedure reported by Corma et al..[1] 10 mL of ethanol solution containing the dispersed capped Au NPs were added to a solution formed by 1.85 mL of TEOS (tetra-ethyl-ortho-silicate) and 0.25 mL of H_2O. The hydrolysis was catalysed by 0.6 mL of an aqueous solution of NH_4F (0.045 M). The sol under continuous stirring became in tens of minutes a gel that slowly converted in a white, slightly yellow powder. The powder was finally dried overnight at 450 ºC. In this way, 474 mg of Au/SiO_2 catalysts was obtained. The amount of loaded Au was 1.6 wt%, determined by ICP-AES. For the characterization, the TEM micrograph and histogram of the particle size distribution are shown in Fig. S1.

1. G. Budroni and A. Corma, *Angew. Chem. Int. Ed.*, 2006, **45**, 3328–3331.

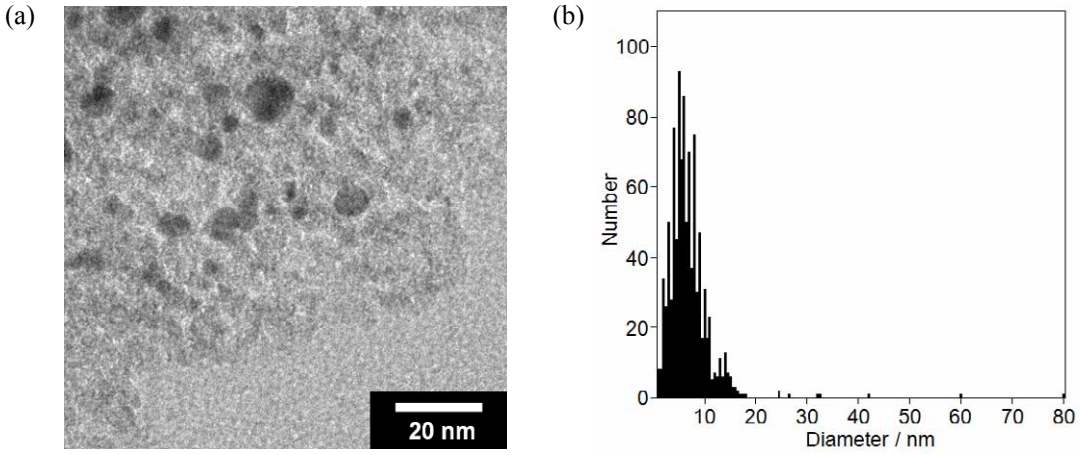

Fig. S1 (a) The TEM image and (b) the particle size distribution of Au/SiO_2.

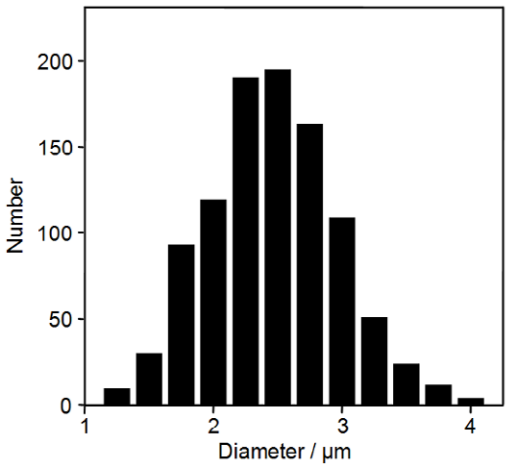

Fig. S2 The size distribution of boronate microparticles **BP**.

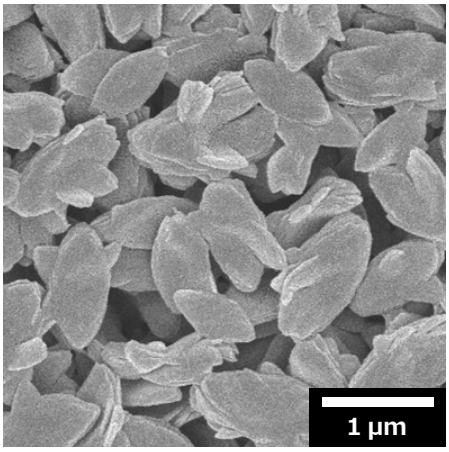

Fig. S3 FE-SEM image of boronate ester polymers prepared from **1** (5.0×10^{-2} mmol) and **2** (5.0×10^{-2} mmol) in DMSO (5 mL) at room temperature for 5h.

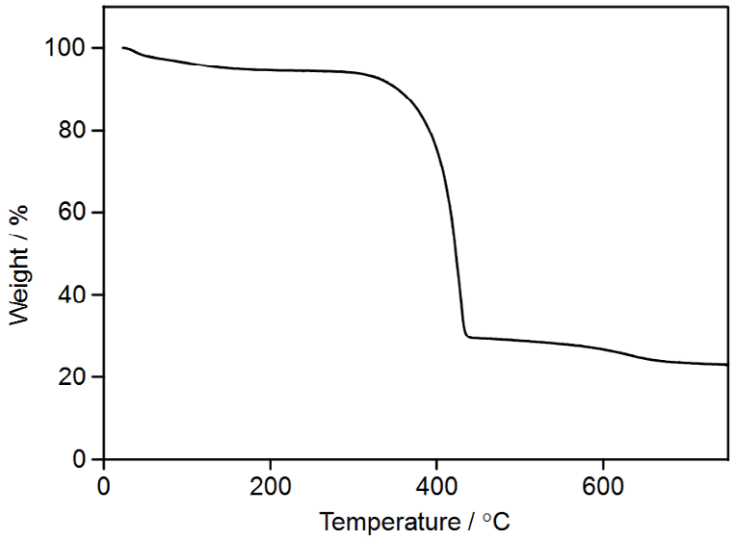

Fig. S4 Thermogravigram (TG) curve of **BP**. The graph shows the loss of mass as a function of temperature. Conditions: nitrogen atmosphere and heating rate of 5ºC min^{-1} in the temperature range of 22.7–878.2ºC.

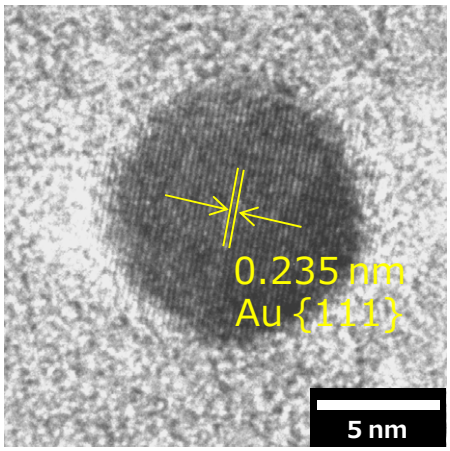

Fig. S5 HR-TEM image of Au NP deposited on **Au–BP(SG)** by solid griding (SG) method.

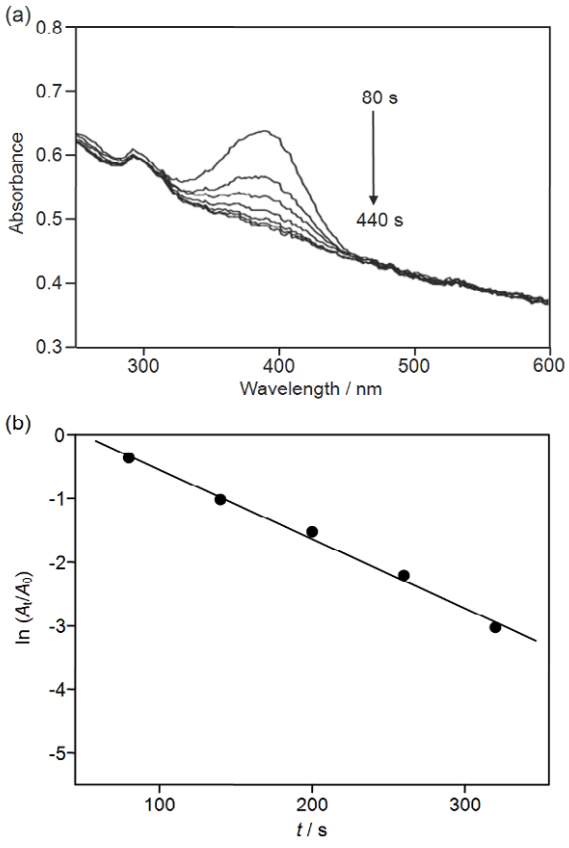

Fig. S6 (a) UV/vis absorption spectra for the reduction of 4-NP with $NaBH_4$ over **Au–BP(SG)** in methanol at 25 °C. The base line was normalized due to a slight precipitation during the reaction. (b) Plot of $\ln(A_t/A_0)$ versus time for the reduction of 4-NP. Reaction condition, [Au] = 7.1×10^{-5} M, [4-NP] = 1.3×10^{-4} M, and $[NaBH_4] = 1.8 \times 10^{-2}$ M.

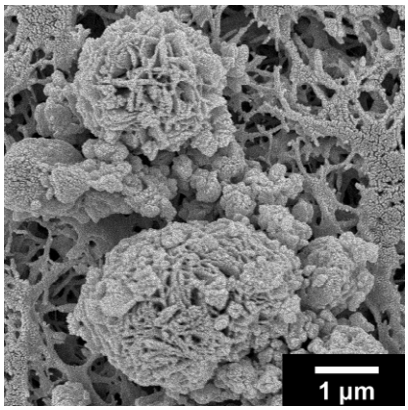

Fig. S7 FE-SEM image of **Au-BP(SG)**.

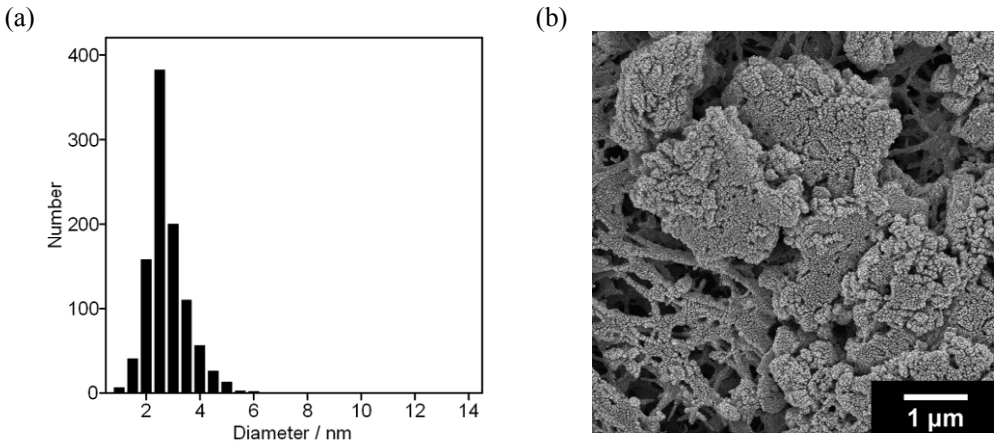

Fig. S8 (a) Size distribution of Au NPs, being based on TEM image, for **Au−BP(DR)** after the second run for the hydrogenation. The average diameter was determined to be 2.8 ± 0.6 nm. (b) FE-SEM image for **Au−BP(DR)** after the second run for the hydrogenation.

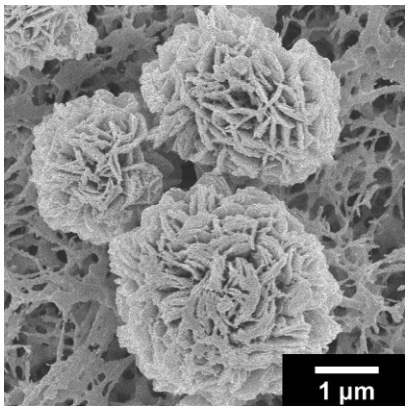

Fig. S9 FE-SEM image of **Au-BP(DR)** after five successive runs for reduction of 4-NP with $NaBH_4$ in methanol.