Supplementary Material (ESI) for Journal of Materials Chemistry

Transformation of Pd → $PdH_{0.7}$ nanoparticles inside the mesoporous Zr-modified SiO_2 films in ambient conditions†

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Electronic Supplementary Information (ESI)

Expreimental Section:

Chemicals:

Tetraethyl orthosilicate (TEOS), (3-glycidoxy propyl)-trimethoxy silane (GLYMO), pluronic P123 (PEO_{20} PPO_{70} PEO_{20}, M_{av} = 5800) (P123), methyl triethoxy silane (MTES), sodium borohydride, zirconium isopropoxide (70% in propanol) and palladium acetate were supplied by Sigma-Aldrich. HCl (35.4%), n-butanol and methanol were obtained from Ranbaxy. Palladium chloride was purchased from S. D. Fine-chem. Ltd. N, N-dimethylformamide and acetylacetone were supplied by Merck. Millipore water (18.2 MΩ) was used although the work.

Synthesis of Zr-modified SiO_2 and Pd doped sols:

Three different silicon alkoxides (TEOS, GLYMO and MTES) were dissolved in 1-butanol and stirred for 15 min. To hydrolyse the alkoxy groups, a mixture of water and catalytic amount of HCl in methanol was added. This resultant mixture was stirred for 30 min and refluxed at 80 °C for 90 min. The molar ratio of TEOS, GLYMO, MTES, 1-butanol, HCl, H_2O and MeOH in the reaction mixture was $1:1:1.3:3.4:1.9\times10^{-2}:14.8:3.4$. The required amount of P123 (0.005 mol P123/mole of equivalent SiO_2) was dissolved in minimum amount of 1-butanol and mixed with silica sol (15.16 wt% equivalent SiO_2) with stirring for 1 h. A partial acetylacetonato Zr-propoxide solution was prepared separately by mixing Zr-propoxide and acetylacetone (0.5 mol per mol of Zr-propoxide) in n-butanol.[13] Zr-modified SiO_2 sol (3 equivalent mol% zirconia with respect to silica) was prepared by mixing the proportionate amount of the partial acetylacetonato Zr-propoxide solution to the above SiO_2 sol containing P123. The mixture was stirred for 2 h at room temperature. For the preparation of Pd doped sol a calculated amount of $PdCl_2$ (3 mol% with respect to SiO_2) was dissolved in minimum amount of 1N HCl and added to the Zr-modified SiO_2 sol with stirring.

Preparation of films:

Coatings (both undoped and Pd doped) were prepared on cleaned soda-lime glass slides by single dipping technique using a Dip-master 200 (Chemat Corporation, USA) dip-coating machine. A withdrawal velocity of 13 in. min^{-1} was used. Both sides of the substrates were coated simultaneously. The undoped (Zr-modified SiO_2) films were first dried at 90 °C (1 h) and then heat-treated at 400 °C for 2 h (ramp 0.7 °C min^{-1}) in air. The Pd doped films were also dried (90 °C) and heat-treated in air at 400 °C in a similar way. These films were finally heat-treated at 400 °C in 10% H_2–90% Ar (henceforth will be designated as H_2) atmosphere to obtain Pd nanoparticles (NPs) doped films.

Conversion of Pd → PdH_x NPs inside the films:

The Pd doped films on glass substrate (film dimension: 2 cm x 0.5 cm x 1 μm thickness; both sides of the glass were coated) were dipped into 5 ml aqueous 0.019 (M) $NaBH_4$ solution. After every 30 min of time interval (up to 4 h), the films were taken out, washed thoroughly by millipore water (18.2 MΩ) and dried at room temperature for 24 h. The films were dried finally at 40 °C for 2 h in an air oven prior to XRD measurements.

Synthesis of bare Pd NPs and its reaction with aqueous $NaBH_4$:

Pd NPs were synthesized using a method by Omole et al.[19] 0.15 gm palladium acetate in 50 ml N, N-dimethylformamide was reacted with 50 ml 0.05 (N) aqueous $NaBH_4$ at room temperature for 30 min. As prepared palladium NPs were filtered and dried at 37 °C for overnight. This dried Pd NPs were mixed with excess amount of 0.019 (M) aqueous $NaBH_4$ solution with stirring at room temperature and the stirring was continued for 4 h. Finally the NPs were centrifuged, washed thoroughly with millipore water and dried at room temperature for 24 h.

Characterization of the Film:

The film thickness was measured by surfcorder SE-2300 profilometer (Kosaka Laboratory Ltd., Japan). For profilometric measurements the as-prepared films were first scratched with a sharp plastic knife and then heat-treated at 400 °C. The scratched portions were then scanned by the profilometer. Low angle and high angle XRD patterns of films and powders were obtained by Rigaku SmartLab operating at 200 mA and 45 kV (9 kW) grazing incidence x-ray diffractometer using Cu Kα (λ = 1.54059 Å) radiation. A grazing incidence X-ray angle of 0.3° was maintained for all film samples. Transmission electron microscopic (TEM) measurements were carried out using Tecnai G^2 30ST (FEI) operating at 300 kV attached with EDX facility.

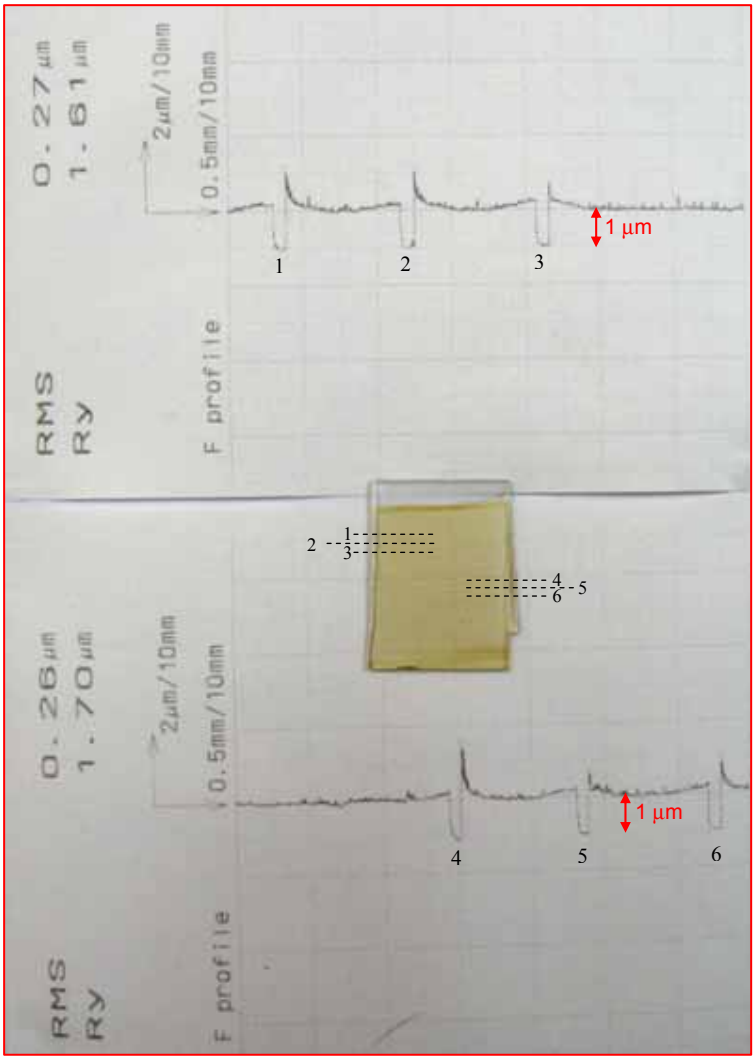

Fig. S1. Profilometric traces at 6 different places of one representative Pd doped Zr-modified mesoporous SiO_2 film deposited on glass substrate. One surface of the as-prepared film (dried at room temperature) was first scratched with a sharp plastic knife and followed by dried (90 °C) and heat-treated at 400 °C in air. The depth of scratches (marked by 1–6) along the thickness are estimated to be ~1 µm. The photo of the film is also shown in the figure. The scratches are not clearly visible because of the presence of film on the other side.

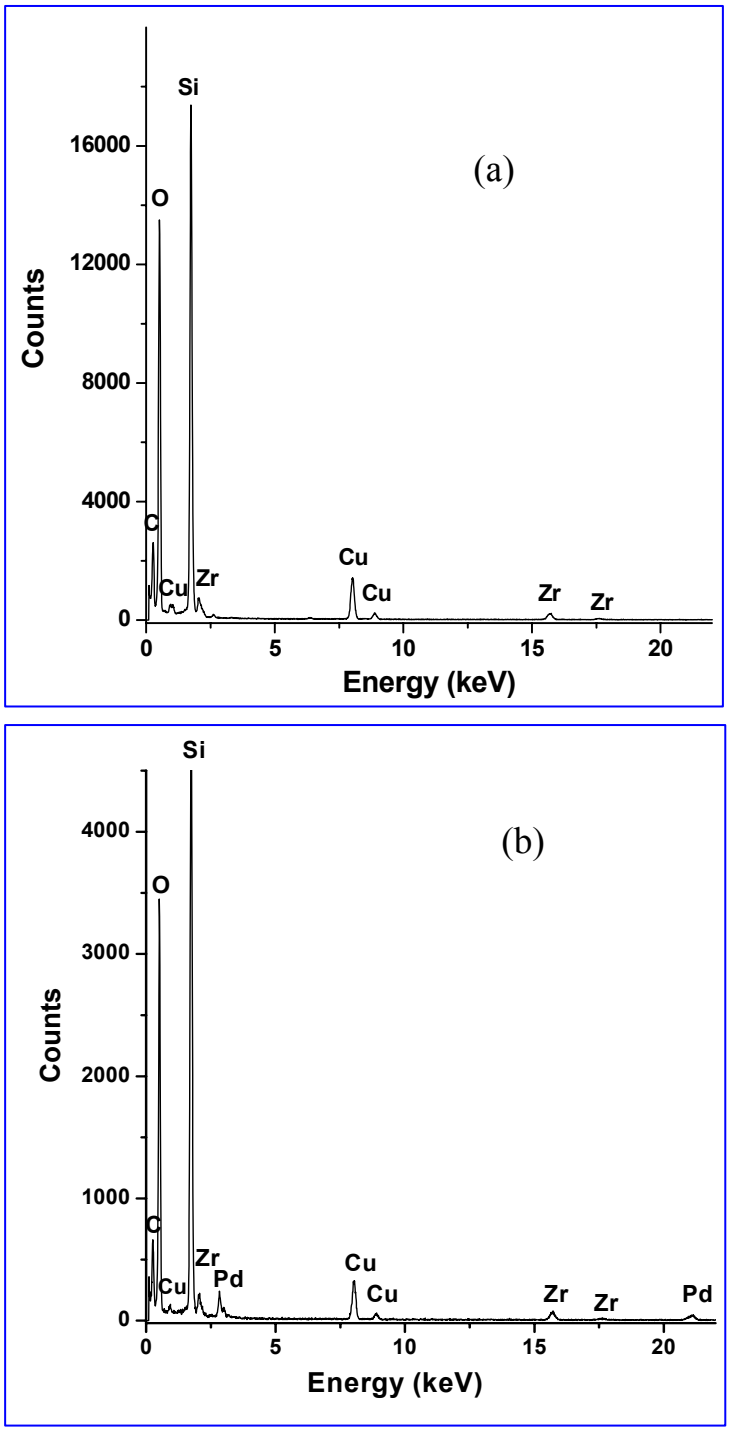

Fig. S2. TEM-EDX patterns obtained from the undoped and Pd-doped Zr-modified SiO_2 films. Cu peaks are from the copper grid used for TEM study.

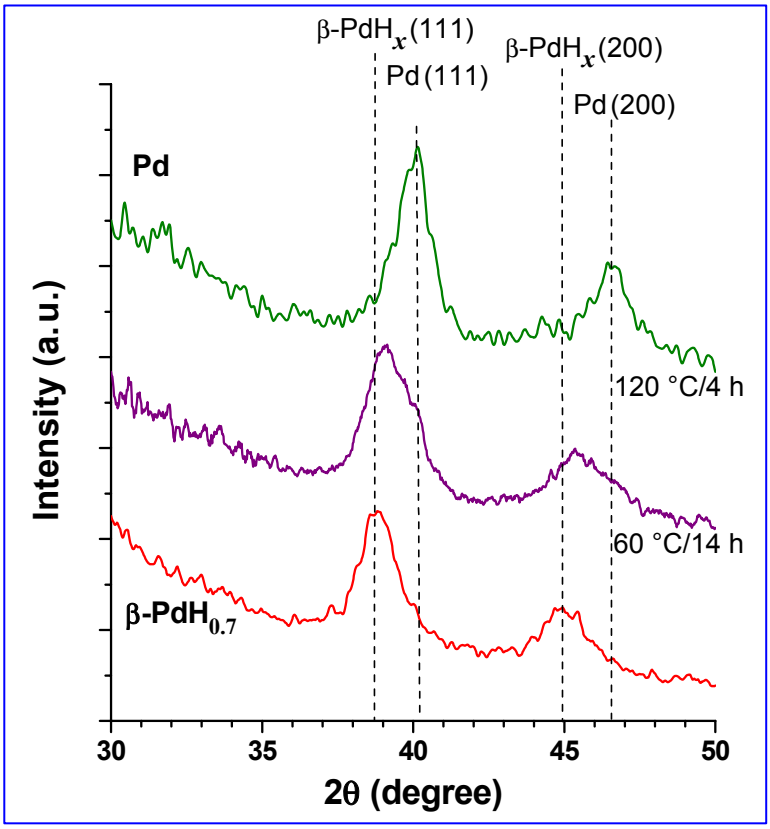

Fig. S3. Release of adsorbed hydrogen from the embedded $PdH_{0.7}$ NPs and regeneration of original Pd NPs.

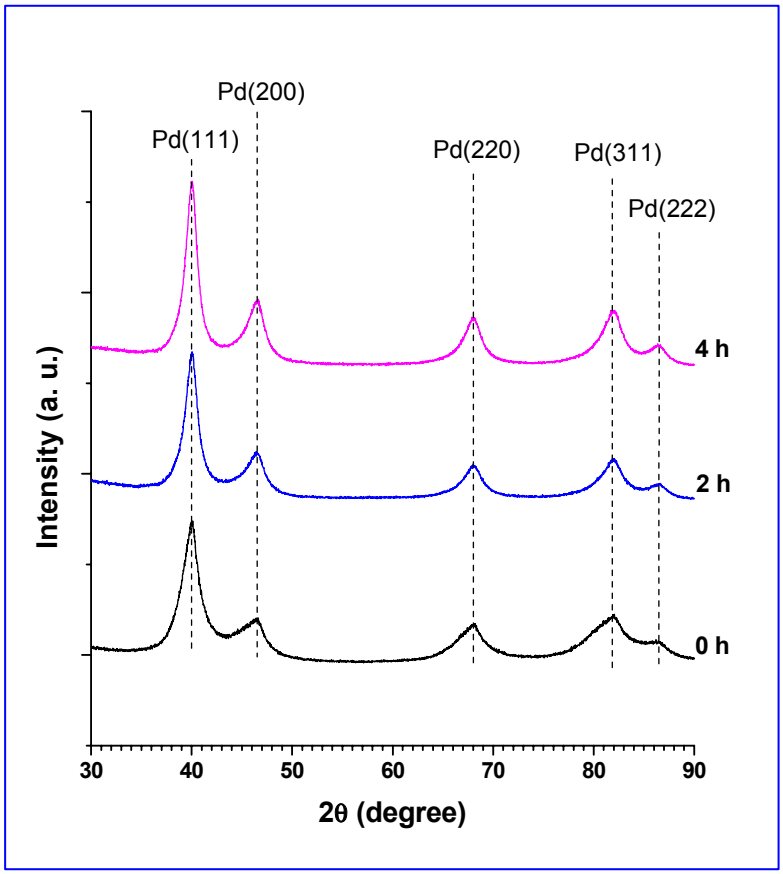

Fig. S4. Powder XRD patterns of the Pd NPs reacted with aqueous $NaBH_4$ solution for 0 (as-synthesized), 2 and 4 h.