Electronic Supporting Information (ESI)

A facile synthesis of cubic *Im*$\bar{3}$*m* alumina films on glass with potential catalytic activity

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Experimental Section:

Preparation of acac chelated ASB sol: A partially acetylacetonato (acac) complexed aluminium tri-sec-butoxide (ASB) stock solution was prepared following the procedure reported in our previous paper.[2] Briefly, required amounts of ASB and *n*-propanol–*iso*-butanol (3:2 w/w ratio) solution containing specific amount of acetylacetone were stirred at room temperature for 1h in a sealed container. The molar ratio of acac/ASB = 0.5 was maintained and accordingly the resultant solution is named as $ASB_{0.5acac}$.

Preparation of cubic mesostructured alumina films: Cubic alumina sol was prepared as follows: F127 (0.4 g, $EO_{106}PO_{70}EO_{106,}$ M_n = 12,600, Sigma-Aldrich) was stirred with ethanol (10.5 g, Merck) for 2 h. HNO_3 (0.7 g, 70 wt%, s.d. fine-chem. Limited) was added to it followed by a successive addition of the modified alumina precursor ($ASB_{0.5acac}$, 2.915 g). The resultant mixture was stirred for 5h and then thin films were prepared by dip-coating (Dip-master 200, Chemat Corporation) on cleaned soda lime glass, silicon wafers and silica glass substrates at a constant speed (6 in. min^{-1}) from the mesoporous alumina sol (to be referred as CMAS) composed in a molar ratio of

$ASB_{0.5acac}$: F127 : EtOH : HNO_3 : H_2O equal to 1 : 7.7 x 10^{-3} : 55.13 : 1.88 : 2.82. The as-prepared films were dried at 60 °C for 16 h followed by heat-treated at 400 °C for 1 h with a ramp of 1 °C min^{-1}. Further annealing were done cumulatively at 500, 600, 800 °C and 900 °C (1h, ramp 1 °C min^{-1}). In the sol the molar ratio of $ASB_{0.5acac}$: F127: EtOH: HNO_3: H_2O were varied as 1: 3.8–15.4 x 10^{-3}: 55.13–15.75: 1.88: 2.82 to study the effect of variation of the surfactant and ethanol on the ordered nature of the film.

Preparation of Au incorporated mesoporous alumina films: Au nanoparticles (NPs) were synthesized following a method reported by Chen et al.[9] Briefly, $HAuCl_4$ solution (0.25 mmol, s. d. fine-chem. Limited) was added to methanolic solution (50 ml, Rankem) of mercaptosuccinic acid (0.625 mmol, Sigma Aldrich) and stirred for 30 min at 0–5 °C, then an aqueous solution of $NaBH_4$ (12.5 ml, 0.2 M, Sisco Research Lab.) was added drop wise keeping the same temperature. The solution was stirred for 1h and kept overnight. The Au NPs were centrifuged and washed as usual and dispersed in ethanol under acidic pH (using 1N HNO_3). This Au solution (~1–2 nm) was kept as stock for further usage. 0.01 M solution of Au in 1-propanol was prepared from this stock and the CMAFs heat-treated at 500 °C were dipped in this solution, kept for 60 sec and lifted up at 6 in. min^{-1} using a dip-coating machine and finally washed twice with ethanol to remove any surface adhered Au NPs. The Au incorporated films were heated at 100, 300 and 500 °C (ramp 1 °C min^{-1}, 1 h) and characterised.

Characterization: The cubic mesoporous alumina films (CMAF) as well as Au incorporated CMAFs were systematically analyzed by X-ray diffraction technique by a Rigaku SmartLab X-ray diffractometer operating at 9 kW (200 mA and 45 kV) using Cu Kα (λ = 1.5406 Å) radiation. Low angle XRD was done in continuous θ/2θ scanning mode with scanning speed of 1° min^{-1} using step size 0.02° whereas for high angle XRD studies, 2θ scanning mode with same speed and step size was used maintaining the grazing incidence angle (ω) at 0.3°. Infrared absorption spectra of the films deposited on both side polished silicon wafers were recorded using Nicolet 380 FTIR spectrometer. Transmission Electron Microscopic studies of the films were done using a Tecnai G^2 30ST (FEI) operating at 300 kV. The refractive index and thickness measurements of the CMAFs (coated on one-side polished silicon wafers) were done using J. A. Woolam Co. M 2000 spectroscopic ellipsometer. The UV-visible spectra were recorded using a Cary 50 scan UV-Visible spectrophotometer.

Estimation of Au in the film by ICP-AES analysis: The concentration of Au in CMAF-Au_{100} was quantitatively estimated by inductively coupled plasma atomic-emission spectrometry (ICP-AES) using Spectro Ciiros Vision, Germany. For this purpose, 2 pieces of CMAF-Au_{100} (approximate dimensions 1.4 cm × 0.7 cm × thickness 135 nm × 2 surfaces) were dipped in aqua regia and kept under ultrasonication for 10 min to leach out the contents of the film. The process was repeated for 3 times and the leached solutions were mixed together. It was followed by evaporation to dryness thrice and the final solution was prepared in 10% HCl medium. The final solution was used to estimate the concentration of Au by ICP-AES. Similarly, two other sets were prepared and analysed.

The concentration of Au was calculated by averaging the values of three such analyses. Using the concentration of Au, the Au:Al atomic ratio present in the film was estimated to be 2.79:97.21.

Catalytic study: To study the catalytic property of the Au NPs loaded mesoporous alumina films heat-treated at different temperatures the reduction of 4-nitrophenol to 4-aminophenol was used as a model system. Two pieces of both side coated Au loaded catalytic film (dimension: 1.4 cm x 0.7 cm x 135 nm) were placed inside the cuvette cell of UV-Visible spectrometer containing 4-nitrophenol (0.1 mL; $3x10^{-4}$ M, Merck), water (2.8 mL, Mili-Q, 18.2 MΩ) and $NaBH_4$ (0.1 mL; 0.3M). The progress of the reaction was studied at 25 ºC. The reaction mixture was stirred continuously and the films were cautiously kept in such a way that they did not touch each other thereby ensuring maximum surface area for catalysis. After the reaction, the catalytic film was taken out, washed with water and dried at 60 °C for 10–15 min and reused.

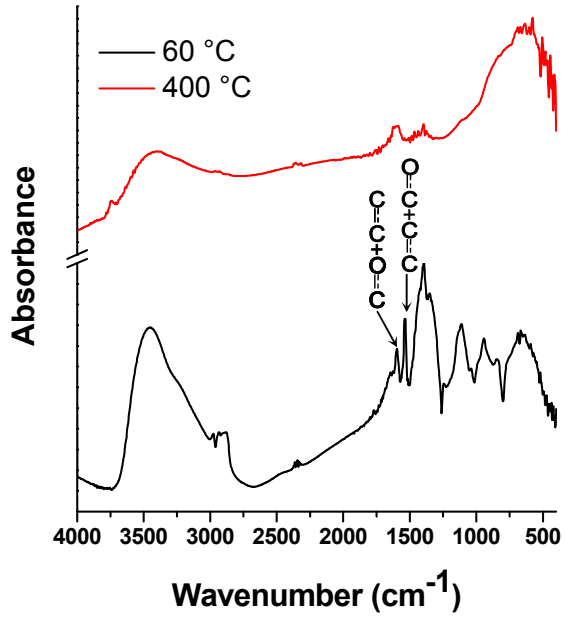

Fig. S1 FTIR spectra of the CMAFs showing the presence of the organics at 60 °C and their absence after heat-treatment at 400 °C. The 60 °C dried film shows clear (C–O+C–C) related peaks (marked in the body of the figure) due to the presence of acac in chelated fashion with Al atom.

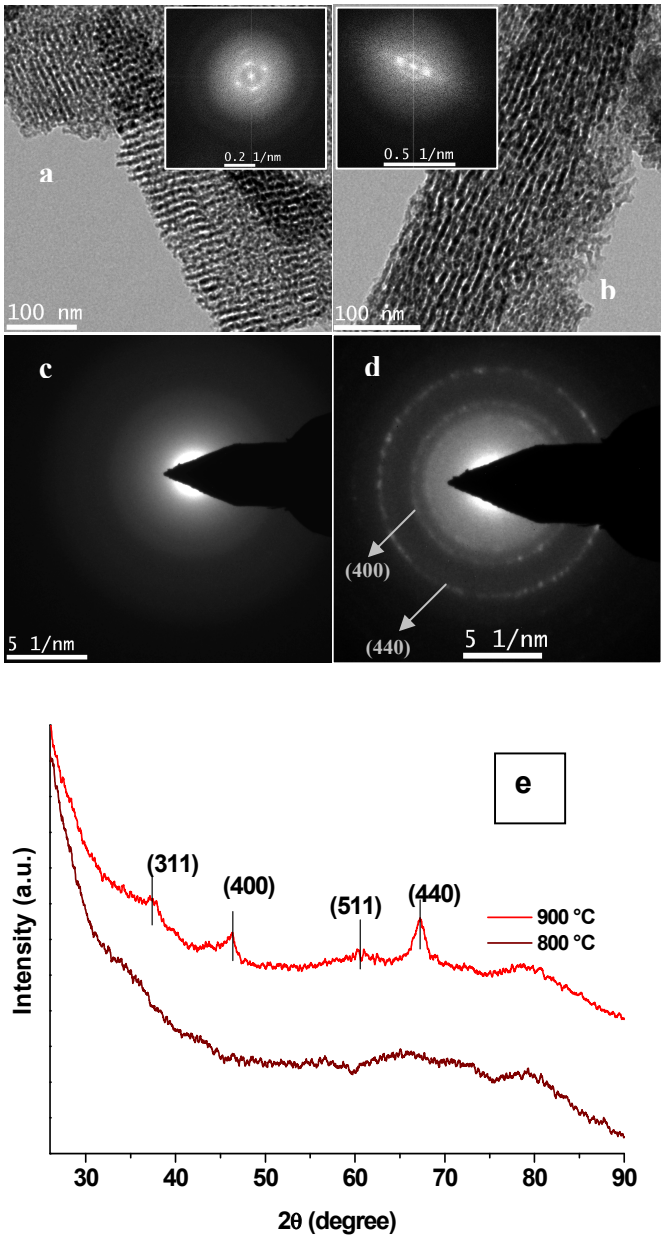

Fig. S2 Bright field TEM images of the CMAFs show the presence of ordered domains even at (a) 800 °C and (b) 900 °C. The selected area electron diffraction patterns (SAED) of the samples heated at 800 °C (c) and 900 °C (d) confirm the amorphous and crystalline nature of the films, respectively. (e) High angle XRD patterns of the films heat-treated at 800 and 900 °C reveal the phase change of the film matrix from amorphous to crystalline γ-Al_2O_3.

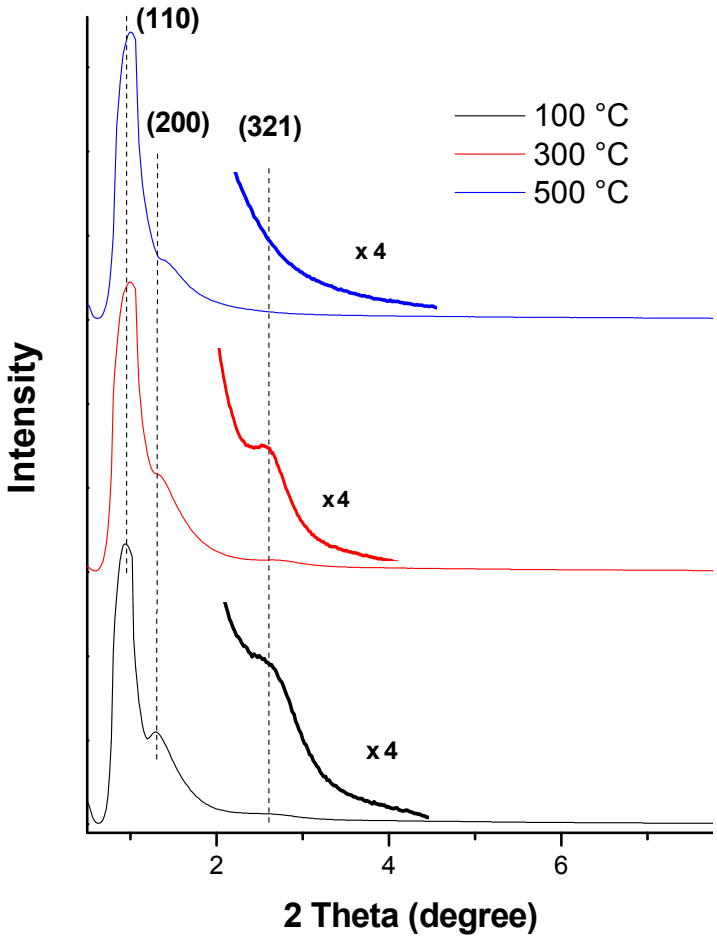

Fig. S3 Low angle XRD patterns of the Au loaded CMAFs showing the effect of thermal treatments (100 °C to 500 °C) on the mesoporous ordered structure due to the growth of the embedded Au NPs.

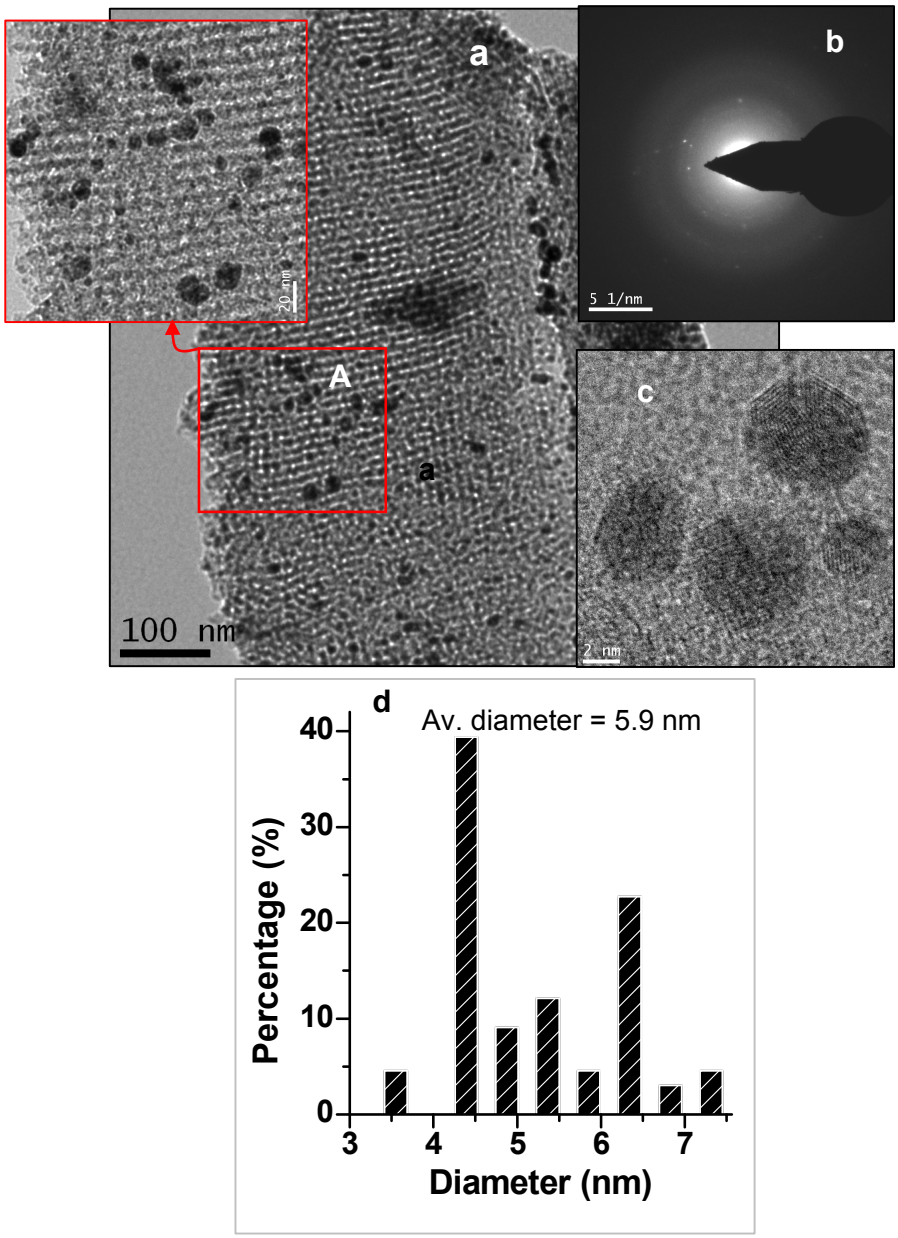

Fig. S4 (a) The bright field image of CMAF–Au_{500} showing the presence of ordered mesoporous alumina structure embedded with Au NPs (inset shows magnified view of a portion marked by A), (b) SAED taken from (a) showing the spots corresponding to the Au lattice planes, (c) HRTEM image of Au NPs and (d) the size distribution of the embedded Au NPs (average size 5.9 nm) in CMAF–Au_{500}.

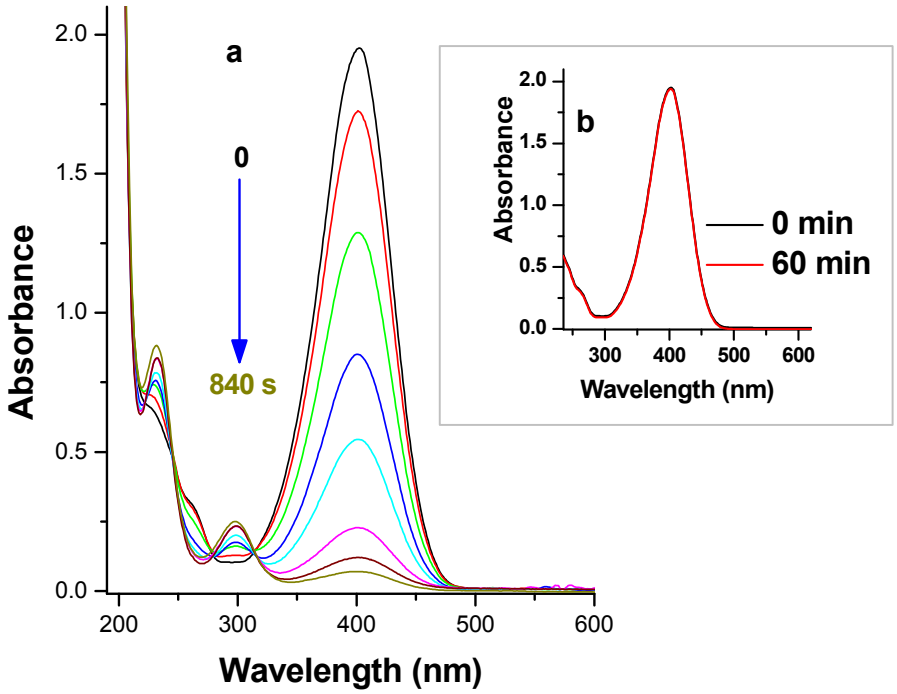

Fig. S5 (a) UV-visible spectral evolution showing the reduction of 4-nitrophenol by $NaBH_4$ at 25 °C in presence of CMAF–Au_{100}. (b) The same reaction studied with undoped CMAF of similar dimension, under identical conditions showed almost no reaction in even after 60 min.

Table S1. The d-spacings obtained from TEM and low-angle XRD studies of the cubic mesoporous alumina films (CMAFs) heated at different temperatures.

Temperature (°C)	**TEM $_d$ (nm)**	**XRD $_d$ (nm)**
400	11.8	11.1
500	11.2	10.85
800	10.3	9.74
900	9.9	9.63

Table S2. The variation of refractive index, thickness, porosity (%) and the lattice parameter (a_o) of the CMAFs with respect to the heat-treatment temperatures.

Temperature (°C)	**Refractive index (n)**	**Thickness (nm)**	**Porosity* (%)**	**a_o # (nm)**
60	1.4754	380	22.76	16.64
400	1.27695	145.5	45.40	15.69
500	1.2956	138	41.65	15.62
800	1.3046	118.5	38.61	13.78
900	1.3217	101	34.74	13.57

* Porosity has been calculated using Lorentz-Lorentz relation:

$$1-P = \frac{(n_f^2-1)}{(n_f^2+2)} \div \frac{(n_a^2-1)}{(n_a^2+2)}$$

where n_f, n_a are the refractive index values of mesoporous film and nonporous alumina film respectively. The nonporous alumina film was prepared using the same experimental method but without F127.

The lattice parameter (a_o) is evaluated from the low angle XRD data using the relation: $a_o = d_{hkl}(h^2+k^2+l^2)^{1/2}$