

Highly Ordered Cubic Mesoporous Electrospun SiO₂ Nanofibers†

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Electronic Supplementary Information (ESI)

1. Experimental:

1.1. Chemicals

Tetraethyl orthosilicate (TEOS), F127 (EO₁₀₆ PO₇₀ EO₁₀₆, M_{av} =12,600), mercaptosuccinic acid, p-nitrophenol and sodium borohydride were supplied by Sigma-Aldrich. Ethanol, methanol, HF (40 %), HClO₄ (70%), HNO₃ (65%) and HCl (35.4%) were purchased from Merck. Polyvinyl alcohol of M_{av} = 125,000 (PVA, ~80% and residual ~20% polyvinyl acetate) and gold chloride were obtained from s. d. fine chemicals Pvt Ltd. Millipore Milli-Q water (resistivity ~18.2 MΩ. cm) was used in this study.

1.2. Synthesis of SiO₂ sol

SiO₂ sol was prepared by acid hydrolysis and condensation of silicon alkoxide (TEOS) in water-ethanol mixture. In a typical synthesis 10 g TEOS was dissolved in 22 g ethanol in a round bottom flask. Thereafter 3 g water and 0.024 g concentrated HCl were added dropwise into the reaction mixture under stirring condition. Finally to ensure complete hydrolysis and condensation of TEOS, resultant mixture was refluxed at 80 °C for 1 h. The molar ratio of TEOS, ethanol, water and concentrated HCl in the SiO₂ sol was kept at 1:10:3.45:1.3x10⁻².

1.3. Preparation of PVA and F127 mixed SiO₂ sol

Aqueous PVA polymer (M_{av} = 125,000) solution (12 wt%) was prepared separately in hot water at 80 °C. First the amount of PVA was varied from 2–6 wt% with respect to the equivalent SiO₂ present in the sol. We found good fiberizability of the sol at 5.7 wt% PVA

and this optimized PVA concentration was used in the sol. Accordingly 10 g 12 wt% PVA solution and 1 g F127 were added in 10 g hydrolysed SiO₂ sol with stirring and the stirring was continued for 15 min. In the resultant sol, weight percentage of PVA was 5.7%. The corresponding molar ratio of SiO₂ : PVA : F127 in the final sol was 1 : 7.0 × 10⁻⁴ : 5.8 × 10⁻³.

1.4. Electrospinning of SiO₂ sol

PVA and F127 mixed SiO₂ sol was taken in a 1 meter long silicone rubber tube (internal diameter 0.3 cm) by attaching 20 ml sol filled plastic syringe at one end of tube. The other end of the tube was connected with a needle of diameter 0.8 mm which was placed 15 cm away from the steel collector plate. Now applying a potential difference between the needle and collector at +15 kV and setting sol release rate at 2 ml h⁻¹ from the needle (using a NEU01 Electrospinning Unit; NaBond Technologies Co., Limited, China), we obtained very fine jet of SiO₂ fibers. The as prepared fibers were dried at 60 °C for 1 h then heat-treated at 500 °C for 2 h with a ramp of 2° min⁻¹ in air atmosphere to obtain ordered mesoporous silica nanofibers (OMSNF).

1.5. Incorporation of Au NPs into the OMSNF

Au NPs were prepared using a method reported by Chen et.al.¹² In brief, 0.084 gm aqueous HAuCl₄ solution (0.25 mmol) was reacted with 0.098 gm mercaptosuccinic acid in 50 ml methanol and stirred for 30 min. Afterward, freshly prepared 12.5 ml 0.2 mmol sodium borohydride solution was added dropwise into the reaction mixture under vigorous stirring condition at 0-5 °C. The solution immediately turned into black color indicating the formation of Au NPs and then stirred for another 1 h. The reaction mixture was centrifuged at 10000 rpm for 5 min to separate the precipitate containing Au NPs. The Au NPs were washed two times in 20% (v/v) water-methanol mixture, dispersed in minimum amount of ethanol in acidic condition (0.01 g 1N HNO₃ was added). Finally 0.01 M Au solution was prepared by adding 1-propanol. Now, 50 mg of heat-treated (500 °C) OMSNF was soaked in 10 ml 0.01 M Au solution and stirred for 2 h. The Au

incorporated silica nanofibers were washed two times with ethanol to separate loosely bound surface attached NPs and finally heat-treated at 300 °C.

1.6. ICP analysis of Au NPs incorporated SiO₂ nanofiber

The Au content in Au-OMSNF has been estimated by inductively coupled plasma atomic emission spectrometry using Spectro Ciros Vision, Germany. The average Au content in the doped fiber was estimated using two different sets of Au-OMSNF samples of different weights. At first SiO₂ contents have been removed as gaseous silicic acid from the precisely weighed Au-OMSNF sample (4.80 mg) by treating with mixture of concentrated 6 ml HF (40 vol%)-HClO₄ (70 vol%) in v/v=5:1 at 50 °C in teflon containers. Thereafter, to ensure the complete removal of SiO₂ contents, the process was repeated once again using 5 ml concentrated HF (40 vol%) and kept the samples in hot condition (50 °C) until evaporated to dryness. The solid residue obtained was dissolved in 5 vol% aqueous HNO₃ in a 100 ml volumetric flask. Finally this solution was used for the estimation of Au by ICP analysis. The same experiment was repeated using 5.8 mg Au-OMSNF sample.

1.7. Catalytic study of Au NPs incorporated SiO₂ nanofiber

For catalytic study, 1 mg of Au NPs loaded nanofibers was introduced in a reaction mixture of 0.1 ml of 3.0 x 10⁻³ M p-nitrophenol, 2.8 ml of water and 0.1 ml of 3.0 x 10⁻¹ M NaBH₄ at 25 °C. The progress of the reaction (i.e. the reduction of p-nitrophenol to p-aminophenol) was monitored by the evolution of absorption spectral changes using a Cary 50 scan UV-visible spectrometer attached with a Peltier temperature controller. The apparent rate constant (k_{app}) of the reaction was evaluated from the decay of p-nitrophenol peak (400 nm) with respect to time. The same experiment was also carried out in presence of undoped nanofibers under similar conditions.

1.8. Characterization

XRD patterns were recorded using a Rigaku SmartLab diffractometer operating at 9 kW Cu K α radiation ($\lambda=1.5405$ Å). Aqueous suspension of heat-treated fiber or powder samples was drop-casted on soda lime glass substrates followed by dried at 100 °C and

used to record the low angle XRD (0.3° – 10° 2θ) patterns by maintaining a X-ray grazing incidence angle of 0.5° . The high angle XRD (20° – 90° 2θ) patterns were recorded using the powder samples. The viscosity of SiO_2 sols was measured in Rheo Stress 6000 rotational rheometer (HAAKE Co.) at room temperature. FTIR spectra of both dried (60°C) and heat-treated (500°C) samples were collected by the KBr pellet method using Nicolet 380 FTIR spectrometer. For microscopic analysis (FESEM and TEM) heat-treated samples were first ultrasonicated in water medium. In case of FESEM the suspension was deposited on the single side polished silicon wafer and analyzed by ZEISS SUPRA 35VP field-emission scanning electron microscope. For TEM study the suspension was placed on the carbon coated Cu grid, dried and analyzed with a Technai G^2 30ST (FEI) operating at 300 kV with energy dispersive X-ray analysis (EDX) facility. The nitrogen adsorption-desorption measurements of the heat-treated SiO_2 nanofiber and powder samples were performed at -196°C (77 K) using an ASAP 2020 Micromeritics instrument after degassing at 300°C for 6 h under vacuum (10^{-2} T).

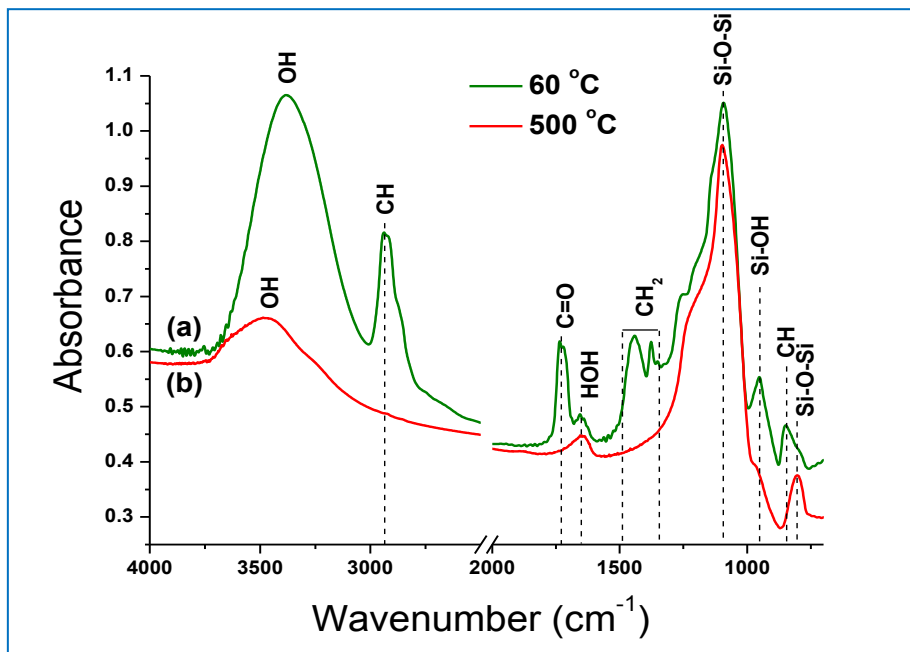


Fig. S1. FTIR spectra of (a) dried (60 °C) and (b) heat-treated (500 °C) SiO₂ fibers with peak assignments. The appearance of the C=O (1720 cm⁻¹) in case of dried fiber indicates the presence of acetic acid produced by the hydrolysis of residual polyvinyl acetate in PVA under the experimental condition. The study confirms elimination of all organics after heat-treatment at 500 °C.

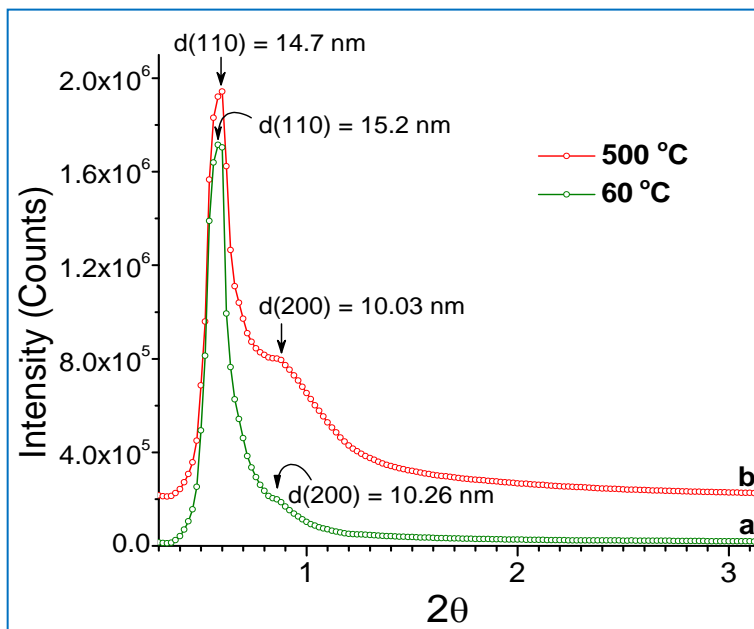


Fig. S2. Low angle XRD patterns of the 60 °C dried (a) and the corresponding heat-treated (500 °C) SiO₂ nanofibers (b). The Y axis of (b) has been shifted for clarity.

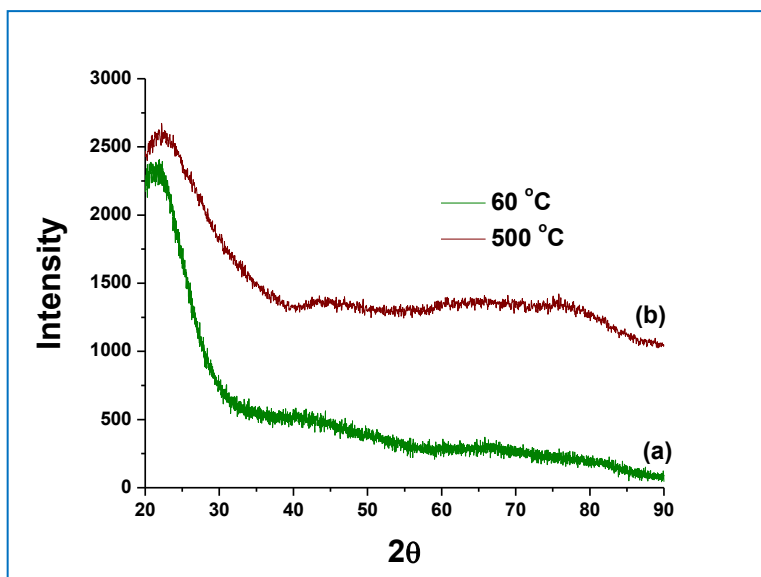


Fig. S3. High angle XRD patterns of SiO₂ silica nanofibers (a) dried (60 °C) and (b) heat-treated (500 °C). Both the patterns show amorphous characteristics of the samples.

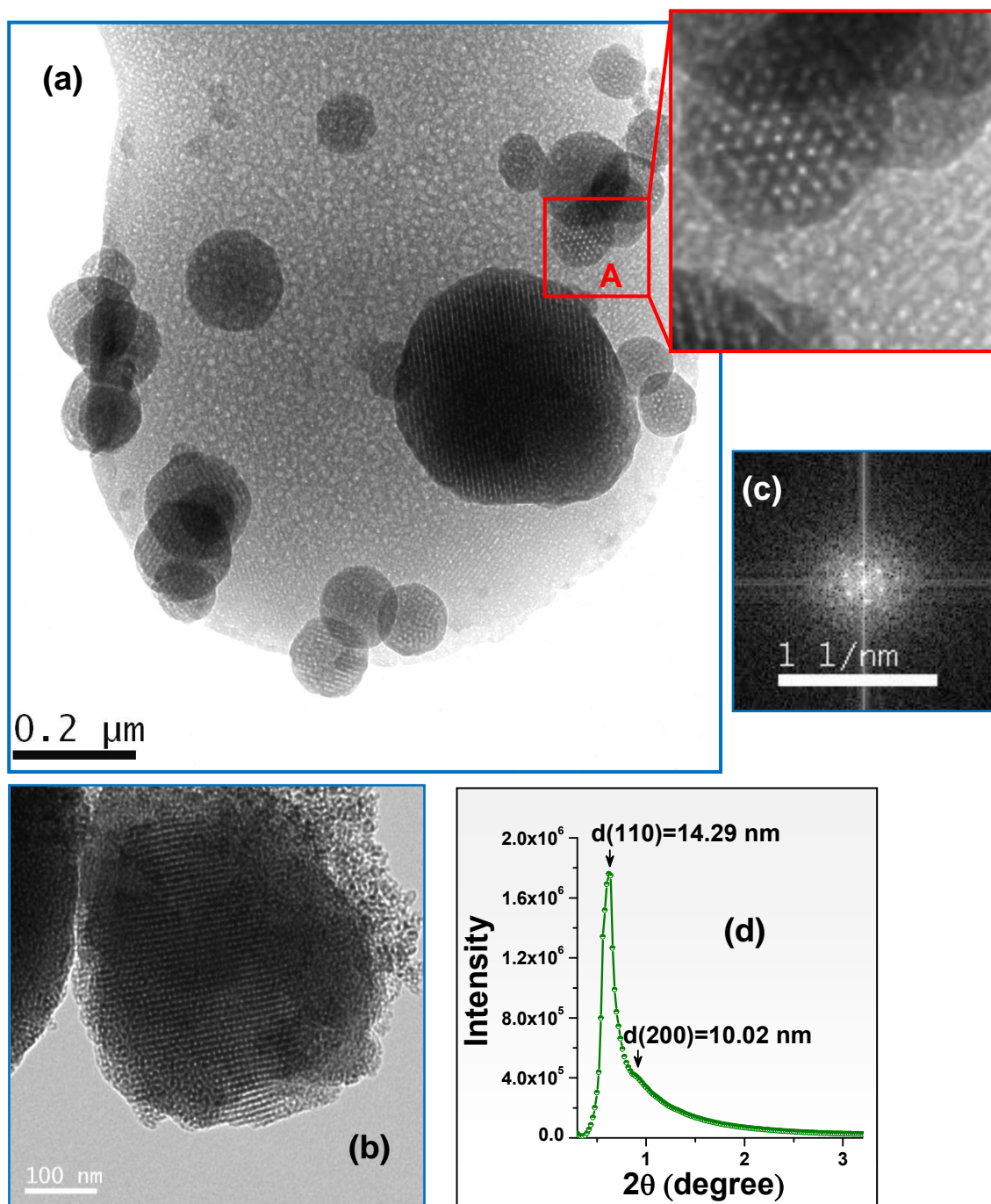


Fig. S4. (a,b) TEM images of SiO₂ powders obtained from the sol used for fiber preparation by electrospinning. The sol was aged in open condition to form gel and subsequently dried at 60 °C followed by heat-treated at 500 °C. The obtained powder sample was analysed by TEM. Existence of several spheres with cubic ordered mesopores can be observed. The area marked by 'A' in (a) is magnified to show the presence of mesoscopic orders also where the spheres are embedded. (c) FFT acquired from the sphere in 'A' shows a typical spot pattern corresponding to cubic (Im3m) symmetry. (d) Low angle XRD pattern of these SiO₂ powders.

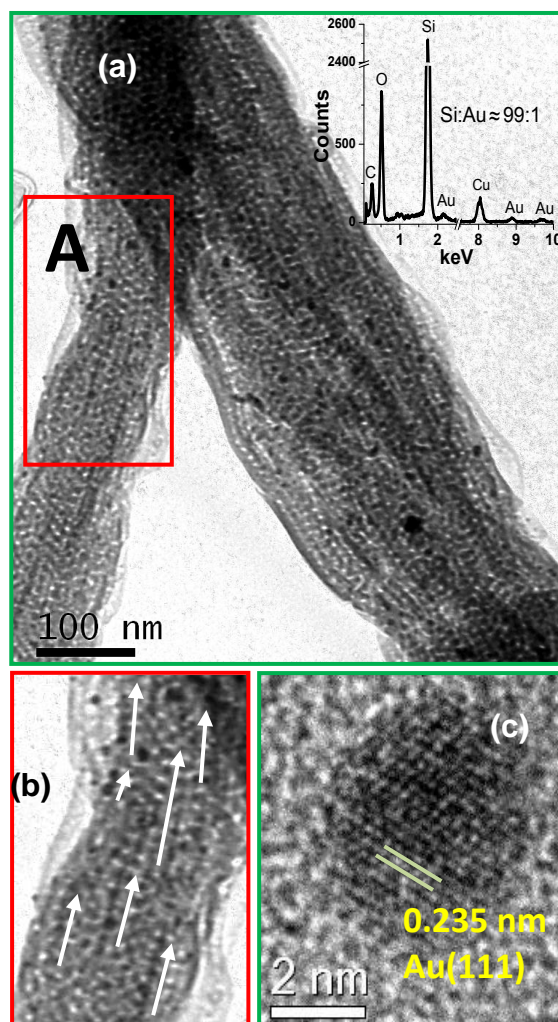


Fig. S5. TEM studies of Au NPs incorporated silica nanofibers. First, Au NPs solution was soaked into the heat-treated mesoporous SiO₂ nanofibers and the resultant fibers were washed with ethanol for two times and heat-treated at 300 °C. (a) TEM image of Au NPs incorporated nanofibers and the corresponding EDX pattern (shown in the inset). EDX shows presence of about 1 at% Au with respect to equivalent SiO₂. (b) Magnified image of the portion of (a) marked by 'A' to show the presence of Au NPs in the pores. Au NPs residing in the pores are shown along the white arrows. (c) High resolution image of one Au NP showing the lattice spacing of 0.235 nm corresponding to Au (111) plane.

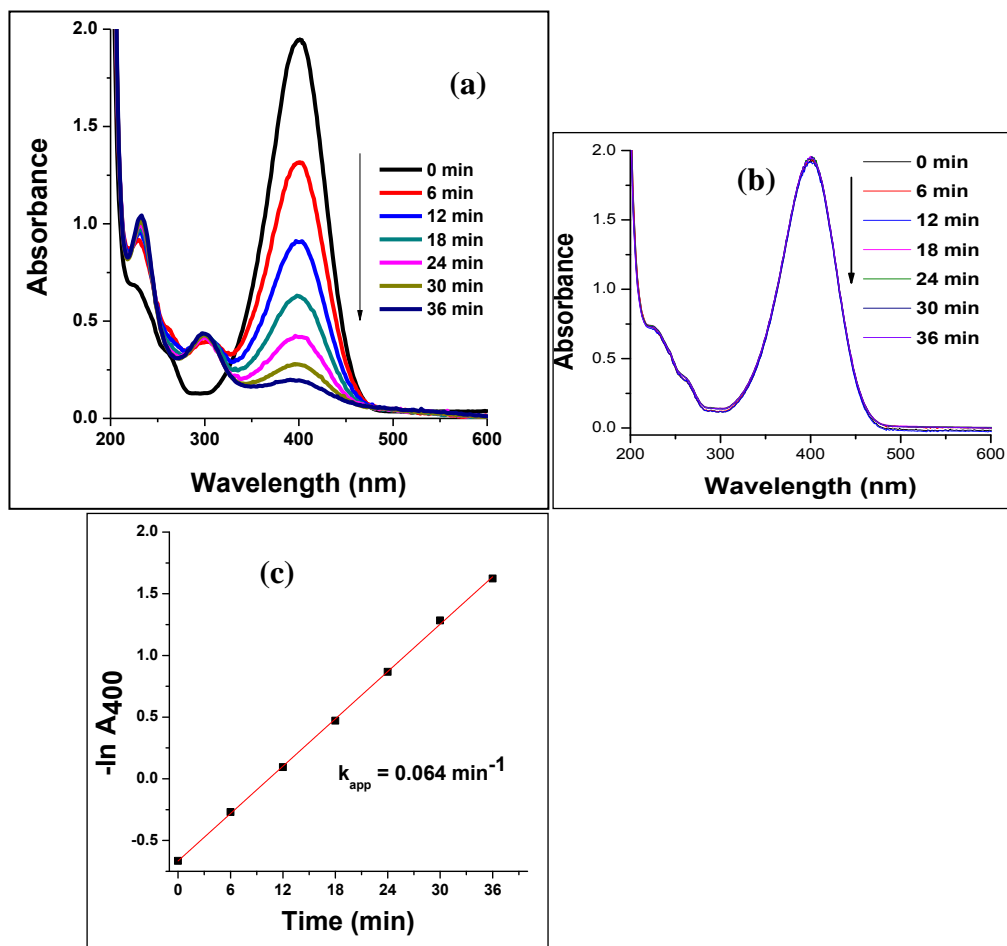


Fig. S6. (a) UV-Vis spectral evolution showing the reduction of p-nitrophenol to p-aminophenol by NaBH_4 in presence of the catalyst Au doped nanofibers at 25 °C. (b) The same reaction in presence of undoped nanofibers shows no reduction. (c) The pseudo first order plot of $-\ln A_{400}$ against time for the reaction evaluated from (a). It is clear from (a) that in presence of Au loaded nanofibers, the reduction of p-nitrophenol to p-aminophenol proceeds smoothly with an apparent rate constant (k_{app}) value of $6.4 \times 10^{-2} \text{ min}^{-1}$. See section 1.7 (submitted with this ESI) for experimental details.