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LETTER

Synthesis of silicon carbide nanorods from mixture of polymer and sol–gel silica

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Silicon carbide possesses many unique properties like superior strength, corrosion and oxidation resistance at elevated temperature [1]. Silicon carbide in the fibrous form is employed for the development of ceramic-matrix and metal- matrix composites (CMCs and MMCs) [2, 3]. Recently there is growing interest in the synthesis of nanofibres, which could be used for the development of nanocomposites, solid-state lubricants, catalysts and components of magnetic devices [4]. Nano silicon carbides are synthesized as nanorods, nanowires, nanotubes and nanofibres [5–8]. Silicon carbide nanomaterials which can be used as reinforcing material are generally prepared by chemical vapor deposition (CVD) [9], arc-discharge [10], polymer blend technique [11] and by reaction between carbon nanotubes and silicon monoxide [12]. The authors had also employed and reported polymer blend technique for the development of pitch based carbon fibres [13, 14]. It was seen by the authors during their efforts to develop carbon fibres from pitches modified with polymers that polyphenylene oxide–polystyrene (PPO–PS) blend does not give fibres on spinning and gives rod like materials [13]. Based on the results of the above studies, attempts have been made in the present investigation to synthesize SiC nanorods by blending sol–gel derived silica with PPO–PS polymer.

Commercially available PPO–PS was used as carbon source and methyltriethoxysilane [(MTEOS) Lancaster, 98%] and tetraethoxysilane [(TEOS) E'Merck, 98%] are used as silica source. PPO–PS was carbonized at 1000 °C in inert atmosphere to determine carbon residue. PPO–PS was dissolved in dichloromethane and was mixed with MTEOS sol, which was prepared by hydrolyzing a mixture of MTEOS, water and dichloromethane. The mixture was stirred well for about 2 h. The sol-containing polymer was then allowed to gel at room temperature and dried at 60 °C to obtain polymer incorporated with sol–gel derived silica, which is the silicon carbide nanorods precursor. The same experiment was repeated with TEOS sol.

The SiC precursor prepared as above was carbonized at 1000 °C and analyzed for carbon and silica contents. The carbonized product was further heated at 1400 °C under argon atmosphere to get a mixture of SiC, carbon and silica.

The pyrolysed products (Heat treatment temperature = 1400 °C) were oxidised in air at 800 °C to remove the free carbon. The carbonized, pyrolysed and oxidized products of PPO–PS + MTEOS and PPO–PS + TEOS were characterized by scanning electron microscopy (SEM, LEO-440). The oxidized sample derived from PPO–PS + MTEOS derived silica was also characterized by transmission electron microscopy (TEM, Jeol JEM 2000 CX). The FTIR spectra of the precursor (PPO–PS + MTEOS derived SiO_2) and the pyrolysed sample (heat treatment temperature = 1400 °C) were recorded by KBr pellet method using Perkin Elmer FTIR 2000. X-ray diffraction

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studies were carried out employing D-8 Advanced Bruker Powder X-ray diffractometer using CuK$_\alpha$ radiation (λ = 1.5418 Å) and Scanning Electron Microscope (SEM, LEO-440).

The carbon residue of PPO–PS was found to be around 23% and hence it can be employed as the carbon source in the synthesis of SiC. The SiC precursor (PPO–PS with sol–gel silica) on carbonisation at 1000 °C yielded carbon residue incorporated with silica. The carbonised product (carbon residue derived from PPO–PS + silica) on oxidation at 700 °C gave silica as residue. The results of the above studies are given in Table 1. It is seen from the values listed in Table 1 that carbon to silica ratio (mole ratio) is $>$ 4.0. According to the reaction $SiO_2 + 3\,C \rightarrow SiC + 2\,CO\uparrow$, the carbon content in the SiC precursor is sufficient for the carbothermal reduction of silica in the proposed method.

The X-ray studies showed that the pyrolysed samples are amorphous in nature. The FTIR spectrum of the precursor (MTEOS derived sol–gel silica incorporated PPO–PS) is given in Fig. 1. The absorption peaks noticed at 1020, 1190 and 1310 cm^{-1} are characteristic of PPO (aromatic ether in PPO–PS) while the absorption band at 1020 cm^{-1} is also assigned to Si–O–Si [15–18]. The absorption peak at 1270, 1385 and 800 cm^{-1} are assigned to Si–C of Si–CH_3 [17, 18]. The peaks noticed around 1470 and 1610 cm^{-1} is due to aromatic C = C and peaks appearing at 2920, 825 and 855 cm^{-1} are assigned to C–H stretching and aromatic C–H bending in PPO–PS [15–19]. The peak around 860 cm^{-1} is characteristic of PPO in PPO–PS while the peak appearing at 720 cm^{-1} is the characteristic of PS in the polymer blend [20]. The sharp absorption band appearing at 3440 cm^{-1} is characteristic of hydrogen bonding.

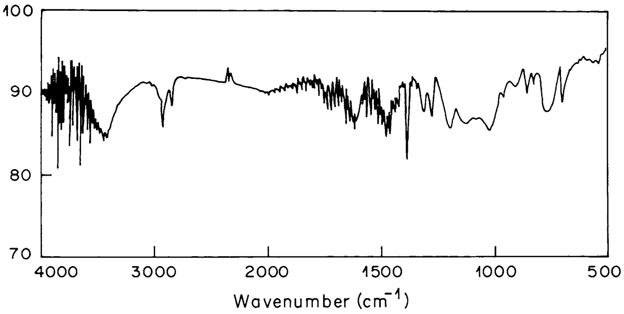


Fig. 1 FTIR spectrum of PPO–PS + MTEOS derived silica

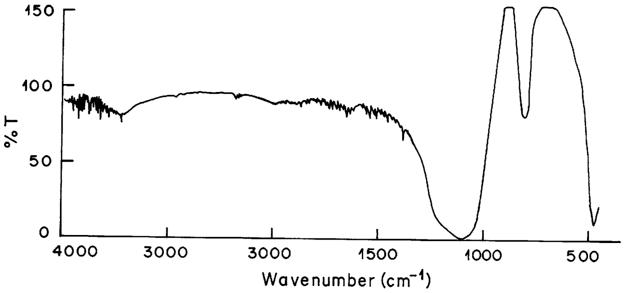


Fig. 2 FTIR spectrum of pyrolysed PPO–PS + MTEOS derived silica (HTT = 1400 °C)

The FTIR spectrum of the pyrolysed sample given in Fig. 2 shows characteristic vibration of Si–C bond of silicon carbide around 800 cm^{-1} and is sharp as compared to Si–C of Si–CH_3 observed in the FTIR spectrum of the precursor. The peaks appearing at 470 and 1100 cm^{-1} are attributed to Si–O–Si and O–Si–O of silica, which is present as unreacted material in the pyrolysed product along with excess carbon [17, 18].

Table 1 Analysis of the SiC precursor (pitch incorporated with sol–gel silica)

Sample details	Heat treatment temperature of carbonisation (°C)	Silica (wt %)	Carbon (wt %)	Carbon: silica (mole ratio)
PPO–PS + MTEOS	1000	48.90	51.10	5.21:1
PPO–PS + TEOS	1000	38.0	62.0	8.15:1

The scanning electron micrographs are illustrated in Fig. 3a–g. It is seen from these micrographs that silicon carbide nanorods are formed in the pyrolysed products of PPO–PS + MTEOS derived silica heated to 1400 °C (Fig 3a, b) with the diameter ranging from 40 to 50 nm. The micrograph also shows nodules in the fibres attributable to unreacted silica. The oxidized product given in Fig. 3b shows nanorods in the diameter range of 60–80 nm. The SEM micrographs given in Fig 3c, d show that SiC nanorods formation is better in the pyrolysed (HTT 1400 °C) and oxidised products (HTT 800 °C) derived from PPO–PS + TEOS derived silica. The unreacted silica is also seen on the tip of the rods in the pyrolysed product of PPO–PS + TEOS derived silica shown in Fig 3c. The diameter of the SiC nanorods in the pyrolysed product of PPO–PS + TEOS derived silica is in the diameter range 75–200 nm (Fig 3c) while the diameter of the oxidised rods is in the range of 150–400 nm (Fig 3d). The SEM photograph of the precursor (Fig. 3e) shows the polymer incorporated with silica as single phase. On carbonization the polymer melts and carries the silica nanoparticles formed through sol–gel process as seen in Fig. 3f, g. The SEM photographs of the carbonized products (Fig 3f, g) also show the formation of the carbonized rods of PPO–PS containing silica, and the diameter of these rods were found to be more than

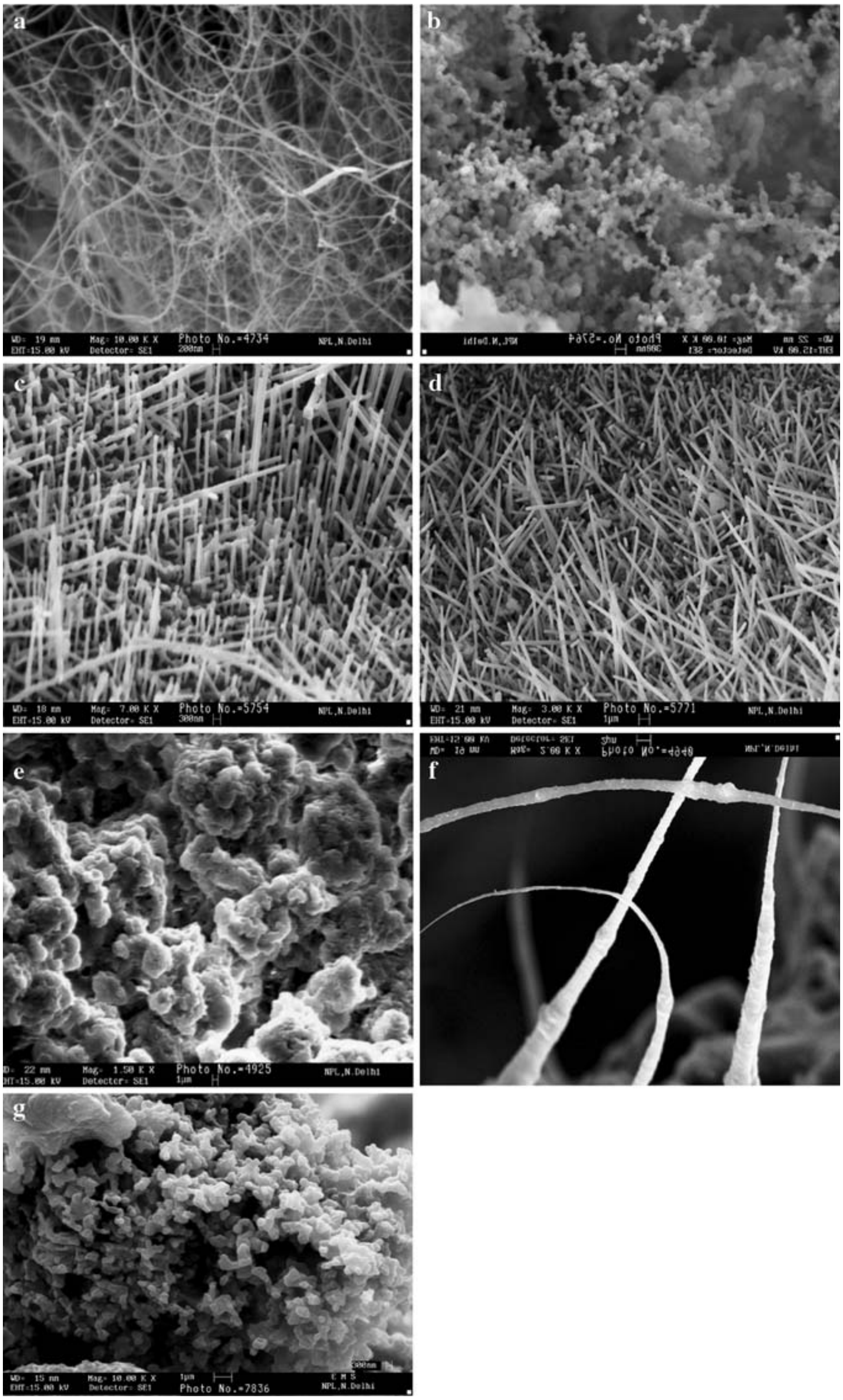


Fig. 3 Scanning electron micrographs of (**a**) pyrolyzed product (HTT = 1400 °C) synthesised from PPO–PS incorporated with MTEOS derived silica (**b**) pyrolyzed and oxidized product (HTT = 800 °C) of PPO–PS + MTEOS (**c**) pyrolyzed product (HTT = 1400 °C) synthesised from PPO–PS incorporated with TEOS derived silica (**d**) pyrolyzed and oxidized product (HTT = 800 °C) of PPO–PS + TEOS. (**e**) PPO–PS incorporated with MTEOS derived silica precursor (**f**) carbonised (HTT = 1000 °C) product of PPO–PS + M TEOS derived silica. (**g**) carbonised (HTT = 1000 °C) product of PPO–PS + TEOS derived silica

300 nm (Fig. 3f, g), which is due to the incorporation of silica in the interior of the polymeric rods, which on carbothermal reduction yielded SiC nanorods.

The TEM micrographs of the oxidized sample synthesised from PPO–PS + MTEOS derived silica given in Fig. 4a–c show the formation of the SiC nanorods. The high magnification TEM photographs given in Fig. 4b, c show the formation of the nanorods with the diameter ranging from 10 to 60 nm. It is also seen in Fig. 4c that the nanorods contain agglomerated nanoparticles along the growth axis.

The formation of SiC nanorods was made easy in the present investigation due to the proximity of sol–gel derived silica and carbon residue of the polymer. The

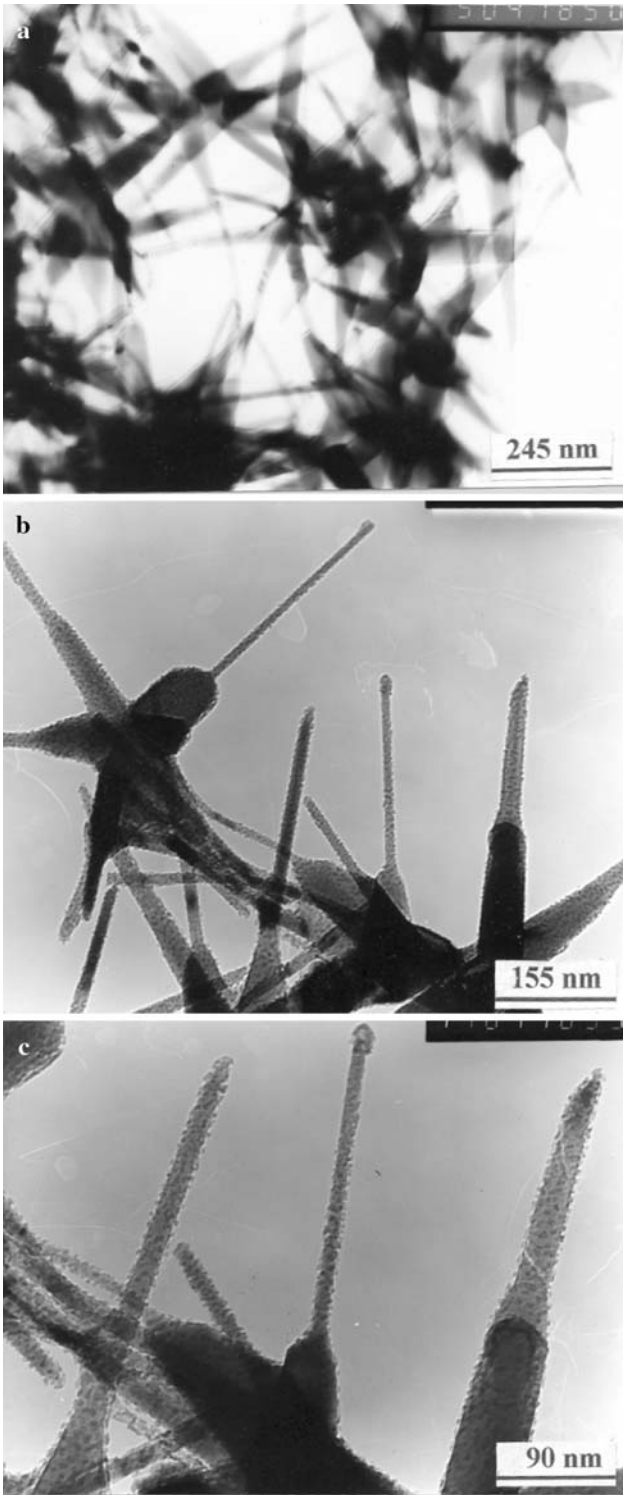


Fig. 4 **(a–c)** Transmission electron micrographs of the oxidised (HTT = 700 °C) product of PPO–PS + MTEOS derived silica

sol–gel process yielded sol, which is in liquid form which, could be effectively mixed with the polymer solution. On drying, the mixture yielded the homogeneous solid product (PPO–PS incorporated with silica). On carbonization the polymer in the precursor melted to give polymer rods containing the nano silica. The silica nanoparticles embedded in the carbon residue of the polymer could react faster when compared to the macro/ micro sized silica particles to give SiO and CO as per the reaction

$$SiO_2(s) + C(s) \longrightarrow SiO(g) + CO(g) \qquad (1)$$

and this step is the initiation reaction for carbothermal reduction of silica which proceeds as follows.

$$SiO(g) + 2C(s) \longrightarrow SiC(s) + CO(g) \qquad (2)$$

$$SiO(g) + 3CO(g) \longrightarrow SiC(s) + 2CO_2(g) \qquad (3)$$

$$3SiO(g) + CO(g) \longrightarrow SiC(s) + 2SiO_2(s) \qquad (4)$$

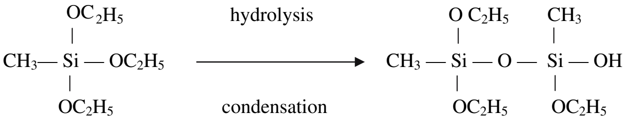
$$CO_2(g) + C(s) \longrightarrow 2CO(g) \qquad (5)$$

The overall reaction is

$$SiO_2(s) + 3C(s) \longrightarrow SiC(s) + 2CO(g) \qquad (6)$$

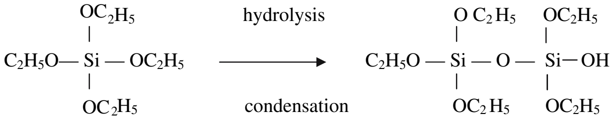
The excess carbon residue obtained from the polymer could also help in the formation of carbon monoxide which reacts with SiO to give SiC [15]. Further, the supersaturated condition of CO vapour formed through the reactions (3) and (5) only initiates the growth of SiC nano rods [21].

The formation of silicon carbide precursor is probably through hydrogen bonding between OH of hydrolyzed MTEOS (I)/ TEOS (II) and the oxygen of PPO in PPO–PS resulting in the hybrid formation (III/IV) between organic (polymer) and inorganic (sol–gel silica) compound [22–25]. The hybrid thus formed gave silicon carbide on heat treatment to 1400 °C.



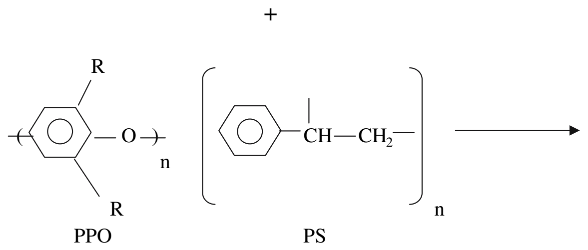
$$CH_3-\overset{\overset{OC_2H_5}{|}}{\underset{\underset{OC_2H_5}{|}}{Si}}-OC_2H_5 \xrightarrow[\text{condensation}]{\text{hydrolysis}} CH_3-\overset{\overset{O\,C_2H_5}{|}}{\underset{\underset{OC_2H_5}{|}}{Si}}-O-\overset{\overset{CH_3}{|}}{\underset{\underset{OC_2H_5}{|}}{Si}}-OH$$

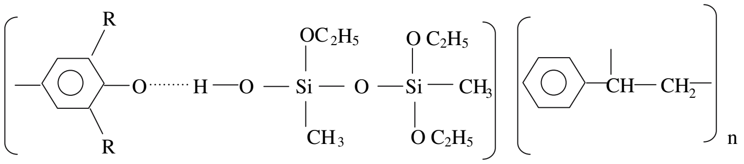
MTEOS (I)



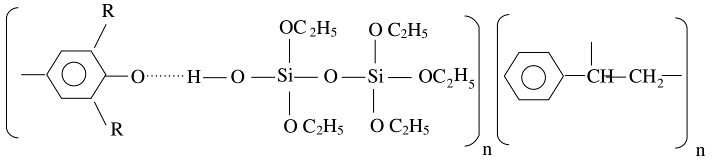
$$C_2H_5O-\overset{\overset{OC_2H_5}{|}}{\underset{\underset{OC_2H_5}{|}}{Si}}-OC_2H_5 \xrightarrow[\text{condensation}]{\text{hydrolysis}} C_2H_5O-\overset{\overset{O\,C_2H_5}{|}}{\underset{\underset{OC_2H_5}{|}}{Si}}-O-\overset{\overset{OC_2H_5}{|}}{\underset{\underset{OC_2H_5}{|}}{Si}}-OH$$

TEOS (II)





(III)



(IV)

The present investigation shows that blending the thermoplastic material (PPO–PS), with silica sol led to the formation of the hybrid through hydrogen bonding to give silicon carbide precursor. The precursor material on heating in inert gas atmosphere melted along with silica nanoparticles to give rod shaped carbon residue incorporated with silica, which on further heating in argon gave SiC nanorods through carbothermal reduction of silica.

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