



HAL
open science

Disordered mesoporous polymer derived N-doped TiO₂/Si-O-C-N nanocomposites with nanoscaled heterojunctions towards enhanced adsorption and harnessing of visible light

Eranezhuth Wasan Awin, Abhijeet Lale, K.C. Hari Kumar, Samuel Bernard,
Ravi Kumar

► To cite this version:

Eranezhuth Wasan Awin, Abhijeet Lale, K.C. Hari Kumar, Samuel Bernard, Ravi Kumar. Disordered mesoporous polymer derived N-doped TiO₂/Si-O-C-N nanocomposites with nanoscaled heterojunctions towards enhanced adsorption and harnessing of visible light. *Applied Surface Science*, 2020, 508, pp.144953-144961. 10.1016/j.apsusc.2019.144953 . hal-02487237

HAL Id: hal-02487237

<https://unilim.hal.science/hal-02487237>

Submitted on 12 Dec 2020

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Disordered mesoporous polymer derived N-doped TiO₂/Si-O-C-N

nanocomposites with nanoscaled heterojunctions towards enhanced adsorption and harnessing of visible light

Eranezhuth Wasan Awin^a, Abhijeet Lale^b, K.C. Hari Kumar^a, Samuel Bernard^b, Ravi Kumar^a,

^a Laboratory for High Performance Ceramics, Department of Metallurgical and Materials Engineering, Indian Institute of Technology-Madras (IIT Madras), Chennai 600036, India

^b Univ. Limoges, CNRS, IRCER, UMR 7315, F-87000 Limoges, France

ABSTRACT

Keywords:
Mesoporous
Nanocomposite
Photocatalysis

Adsorption
Heterojunction

The mesoporous N-doped TiO₂/Si-O-C-N ceramic nanocomposites has been revealed to be a potential candidate towards visible light photocatalytic degradation of organic dyes. The polymer-derived ceramic route was implemented to prepare uniformly distributed in-situ crystallized N-doped TiO₂ nanocrystals in a mesoporous

amorphous siliconoxycarbonitride matrix. This chemical approach assisted by the hard template pathway resulted in a high surface area (186 m²/g) nanocomposite exhibiting predominantly mesoporous structure with an average pore size of 11 nm. The two-step process involved pyrolysis of the polyhydromethylsiloxane impregnated in CMK3 (hard template) under argon generating SiOC-C composites and functionalizing it with titanium n-tetrabutoxide to be pyrolyzed under ammonia to form the titled nanocomposite. Interestingly, pyrolysis in a reactive ammonia atmosphere resulted in the incorporation of nitrogen in the titania lattice while decomposing the template. The Si-O-C-N support on which N-doped TiO₂ exhibited superior adsorption of organic dye molecules and photocatalytically active in the visible wavelength. The nanoscaled heterojunctions reduced the recombination rate and the presence of superoxide anions/hydroxyl radicals was found to be responsible for the dye degradation.

1. Introduction

Titania (TiO₂), known for its photocatalytic applications ever since its discovery by Fujishima and Honda [1] has attracted a lot of interest in the research community ranging its application from hydrogen production and water purification to solar cells [2–5]. The low cost, oxidizing power and durability of TiO₂ has made it a material of interest. However, the band gap of TiO₂ of 3.2 eV restricts itself from harnessing of light in the visible wavelength thereby limiting its photocatalytic activity in the UV region [6]. Several methods have been explored towards the reduction of band gap of TiO₂ which includes doping of TiO₂ with non-metals such as C, N, F, P and S [7–10]. The introduction of dopants generates an impurity state above the valence band of TiO₂, hence raising the valence band edge, resulting in the absorption of visible light. Ever since Asahi et al. reported the reduction of band gap in nitrogen-doped TiO₂ (N-TiO₂) and improved absorption of solar light [11], various approaches have been adopted towards synthesis of N-doped TiO₂ photocatalysts. This includes sol-gel reaction [12],

solvothermal reaction [13,14] and hydrothermal reaction [15]. Recently, titanium oxynitride (Ti-O-N) microspheres were synthesized by ammonolysis of TiO₂ microspheres and were reported to exhibit visible light photocatalytic activity [15]. Visible light photocatalytic activity of mesoporous N-TiO₂ possessing high surface area was also reported to absorb light in the visible light regime [15].

The retrieval of dispersed photocatalysts from aqueous solution as well as the agglomeration of TiO₂ nanoparticles hinders the implementation of the material for water purification applications. Anchoring/immobilizing the photocatalysts on a suitable substrate is an alternative way to overcome the above mentioned disadvantage. TiO₂ immobilized on high surface area mesoporous SBA-15 was shown to act as an active photocatalyst [16]. The mesoporous substrate with high surface area plays a prominent role in determining the adsorption characteristics, thereby influencing the overall reaction rate. Precursor routes such as the Polymer-Derived Ceramics (PDCs) approach enable controlling the size, composition, porosity and shape of the final product [17–19]. The amorphous Si-O-C-N possess enhanced properties

Corresponding author.

E-mail address: nvrk@iitm.ac.in (R. Kumar).

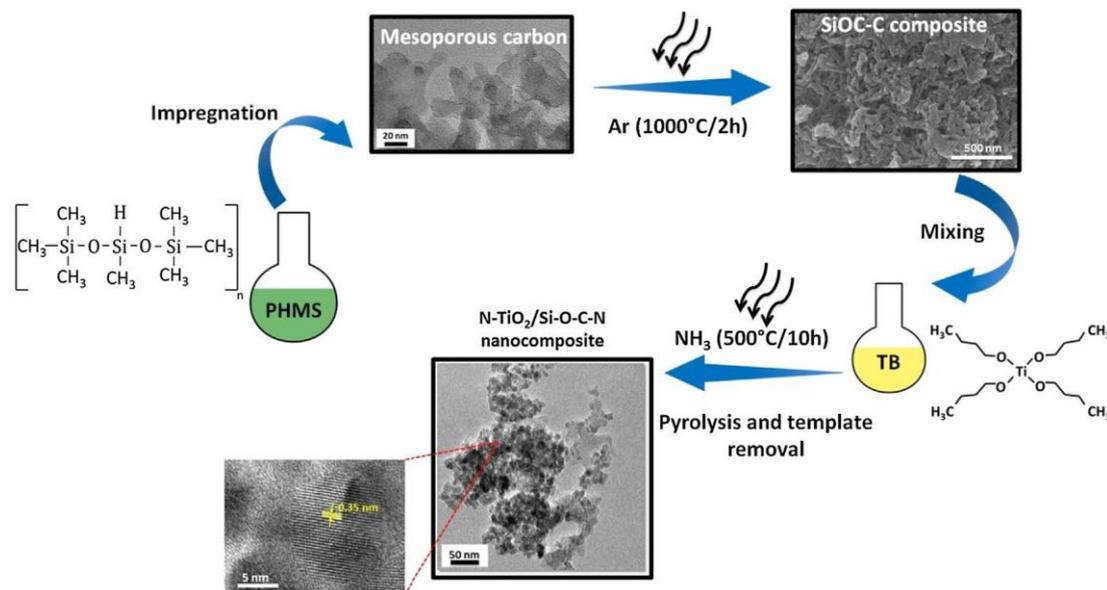


Fig. 1. Schematic representing the generalized processing route for the synthesis of the mesoporous nanocomposite.

such as thermal stability, creep resistance, chemical stability and oxidation resistance [20–22]. Hence, Si-O-C-N ceramics in the form of composites, fibers, coatings and membranes offers to be a potential candidate in extreme/harsh operating conditions. For instance, excellent adsorption capacity was shown by hierarchically porous silicon-carbon-nitrogen (Si-C-N) ceramics prepared from preceramic polymers in contrast to its bulk counterparts [23]. Such materials were shown to be highly efficient in removing organic pollutants. The template assisted PDCs approach results in porous structures with high stability, surface area and tailorable pore size [24]. In the current study, a two-step template assisted PDCs approach has been adopted to synthesize uniformly distributed N-doped TiO₂ anchored on an amorphous Si-O-C-N matrix possessing high surface area and disordered mesoporous structure, especially by tailoring the chemistry of precursors and using their reactivity with ammonia as a reactive atmosphere. The resulting material was evaluated for its photocatalytic activity towards degradation of methylene blue in visible light.

2. Experimental section

2.1. Synthesis of the mesoporous nanocomposite

0.2 g of mesoporous carbon (Sigma-Aldrich, Bangalore, India) was kept at 100 °C overnight to remove the moisture present in the pores. Subsequently 1 ml of polyhydridomethylsiloxane (PHMS, Sigma-Aldrich, Bangalore, India) was impregnated into mesoporous carbon by stirring the mixture in vacuum for 24 h. The mixture was then transferred to an alumina crucible and pyrolyzed at 1000 °C in argon atmosphere at a heating rate of 2 °C/min and held for 2 h. The pyrolyzed product, SiOC-C composite was then mixed with 1 ml of titanium n-tetrabutoxide (TB, Sigma-Aldrich, Bangalore, India) stirred overnight and subsequently pyrolyzed in ammonia atmosphere at 500 °C for 10 h maintaining a heating rate of 5 °C/min.

2.2. Characterization

The powder X-ray diffraction (XRD, D8 Discover, Bruker AXS X-ray diffractometer, USA) was carried out to understand the phase evolution. The Raman spectrum (Labram HR800, Horiba, Japan) was recorded in the range of 100 and 2000 cm⁻¹ using a He-Ne laser source. The surface morphology as well as the size distribution of the particles was studied in assistance with scanning electron microscopy (SEM, Hitachi

S-4800, Japan) and transmission electron microscopy (TEM, JEOL 3010, Japan). The sample was sputter coated for 80 s prior to SEM analysis so as to avoid the charging effects. To perform the TEM analysis, the sample was dissolved in acetone, ultrasonicated for 15 min and a couple of drops were poured on the copper grid. In order to quantify the porosity, the sample was degassed at 150 °C for 6 h and adsorption-desorption isotherm was obtained at -196 °C using BET analyzer (TriStar 3020, Micromeritics, USA). The pore size distribution was determined using Barrett-Joyner-Halenda (BJH) method. The XPS measurements (Omicron nanotechnology, ESCA-14, Germany) were carried out using Al K_α (1486.6 eV) as radiation source. The deconvolution of the spectra was done using CASA XPS software. The calibration of the spectra was done with respect to C1s peak at a binding energy value of 284.8 eV. The bonding characteristics were studied with the aid of FTIR spectroscopy (Perkin Elmer Spectrum, USA). The solid state ²⁹Si NMR was recorded using Bruker AV III, Germany spectrometer operating at 500 MHz.

2.3. Photocatalytic studies

To evaluate the photocatalytic activity of the nanocomposite, methylene blue (0.06 and 0.12 mM) was chosen as the representative dye and 50 mg of the catalyst was added to 100 ml of the solution. The mixed solution was then kept for 12 h in dark to achieve adsorption-desorption equilibrium. Subsequently, the solution was stirred and subjected to visible light exposure (500 W tungsten halogen lamp). At regular time intervals, 2 ml of the solution was taken out and centrifuged, to remove the catalyst. The concentration of the MB was measured using UV-vis spectrophotometer (ThermoFisher Scientific, Evolution 220, USA).

3. Results and discussion

PHMS, with a chemical structure of (CH₃)₃SiO[(CH₃)HSiO]_nSi(CH₃)₃ was used as the molecular precursor for the synthesis of silicon oxycarbide (SiOC) matrix. The pyrolysis of PHMS in an inert atmosphere leads to amorphous SiOC. Herein, PHMS was infiltrated into CMK3 to replicate the nanostructured mesoporous structure by nano-casting. The functionalization of the composite with titanium was done using TB (Ti(OCH₂CH₂CH₂CH₃)₄) and the template was reduced by pyrolyzing in a reactive ammonia atmosphere. The overall reaction procedure is shown in Fig. 1.

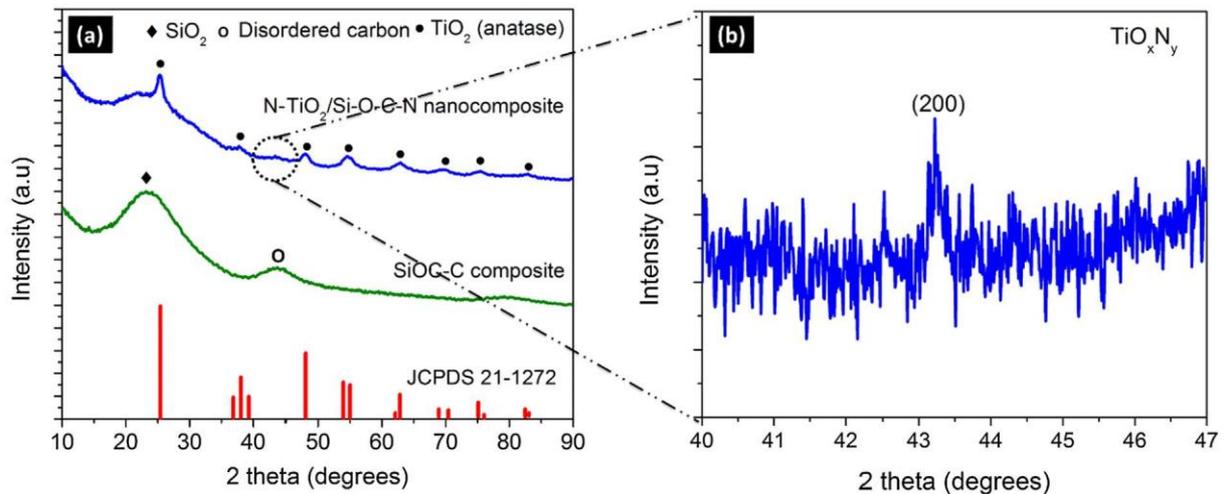


Fig. 2. (a) X-ray diffractograms revealing the amorphous and crystalline phases of the nanocomposite before and after functionalization with TB and (b) The slow scan XRD of N-TiO₂/Si-O-C-N exemplifying the TiO_xN_y phase.

The XRD pattern of SiOC-C composite before functionalization with TB was characteristic of an amorphous compound with broad peaks at $2\theta \sim 23^\circ$ and 43.8° . The broad hump at 23° corresponds to either amorphous SiO₂ [25] or the presence of SiOC [26]. The peak at $2\theta \sim 43.8^\circ$ corresponds to the characteristic amorphous disordered carbons [27]. The XRD of N-TiO₂/Si-O-C-N nanocomposite (after functionalization with TB and ammonia treatment) clearly reveals the crystallization of anatase phase with major peaks at $2\theta = 25.3^\circ, 37.8^\circ$ and 48.0° corresponding to (1 0 1), (0 0 4) and (2 0 0) planes of anatase, respectively (Fig. 2a). Interestingly, an additional peak was observed at $2\theta \sim 43^\circ$ and has been assigned to the (2 0 0) plane of titanium oxy-nitride (TiO_xN_y) phase (Fig. 2b). The initiation of the crystallization of TiO_xN_y phase is an indication of gradual transformation of anatase phase with prolonged holding hours in ammonia atmosphere. The Scherrer equation was used to calculate the crystallite size of anatase and was found to have an average size of 5 nm.

The analysis of Raman spectra (Fig. 3) indicated the presence of six bands at 151 cm^{-1} (E_g), 201 cm^{-1} (E_g), 399 cm^{-1} (B_{1g}), 505 cm^{-1} (A_{1g}), 519 cm^{-1} (B_{1g}) and 630 cm^{-1} (E_g) confirming the presence of anatase phase. This is in good agreement with the XRD result. The inset image shows the presence of D and G peaks at 1348 cm^{-1} and 1588 cm^{-1} respectively attributing to the existence of free carbon. The

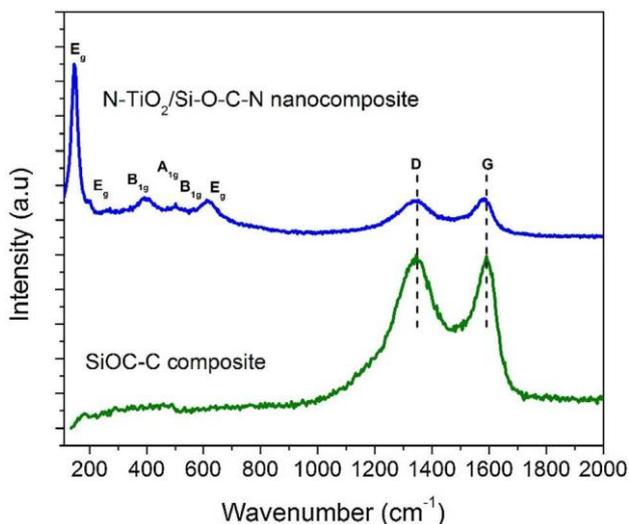


Fig. 3. Raman spectra of the nanocomposite before and after functionalization with TB implying the presence of anatase phase and free carbon.

pyrolysis in reactive atmosphere such as ammonia is known to reduce the carbon entities via transamination reactions during the initial stages of polymer to ceramic conversion [28,29]. However, the high affinity of titanium atoms towards nitrogen could hinder this reaction. This could result in the formation of free carbon by the phase separation of SiOC at higher temperatures. The Raman spectra of SiOC-C composite (i.e., before functionalization with TB) clearly revealed the formation of free carbon as a result of the phase separation of SiOC. Nevertheless, the carbon template is believed to be reduced because of its decomposition under ammonia.

The scanning electron micrographs of mesoporous carbon (CMK-3) and the TiO_xN_y-derived materials are shown in Fig. 4a and b respectively. This clearly indicates that the structure of the hard template is indeed retained in the nanocomposite after nitridation process which highlight Raman discussion on the identification of carbon in our materials. This also displays the fact that the polymer impregnated well in to the pores of the carbon template. The EDS spectrum of the nano-composite is shown in Fig. 4c. The EDS spectra clearly reveals the presence of silicon, oxygen, carbon, titanium and nitrogen.

The structural organization of the sample was analyzed using transmission electron microscopy (TEM). The micrograph clearly reveals the presence of well-defined crystals that are uniformly distributed on a support matrix (Fig. 5a). At higher magnification, the lattice fringe interplanar spacing of 0.35 nm represents the (1 0 1) plane of anatase (Fig. 5b). The crystals exhibit a spherical morphology with an average crystal size of 5–10 nm, which substantiated the XRD re-sults.

The nitrogen adsorption-desorption isotherm exhibit a typical type IV curve with a H2 hysteresis loop revealing the mesoporous nature of the nanocomposite as exemplified in Fig. 6. The impregnation/pyrolysis process resulted in the reduction of BET surface area from $478 \text{ m}^2/\text{g}$ for CMK-3 to $186 \text{ m}^2/\text{g}$ for the nanocomposite. The Barrett-Joyner-Halenda (BJH) pore size distribution profile is presented as an inset image and the mean pore size was found to be 11 nm. The pore volume was found to be $0.29 \text{ cm}^3/\text{g}$. The surface area, pore volume and pore size of SiOC-C composite was revealed to be $350 \text{ m}^2/\text{g}$, $0.45 \text{ cm}^3/\text{g}$ and 19 nm respectively. The decrease in pore volume and surface area of the mesoporous SiOC-C composite after functionalization with TB then annealing under ammonia confirms SEM observation and most probably the presence of the TiO₂ phase as nanocrystals identified by TEM in the porous structure of the pristine SiOC-C composite.

The incorporation of nitrogen in the material was confirmed by XPS as observed in Fig. 7. The deconvolution of N1s peak (Fig. 7b) resulted in three peaks at 397.2, 399.4 and 402.2 eV. The peak at 397.2 eV could

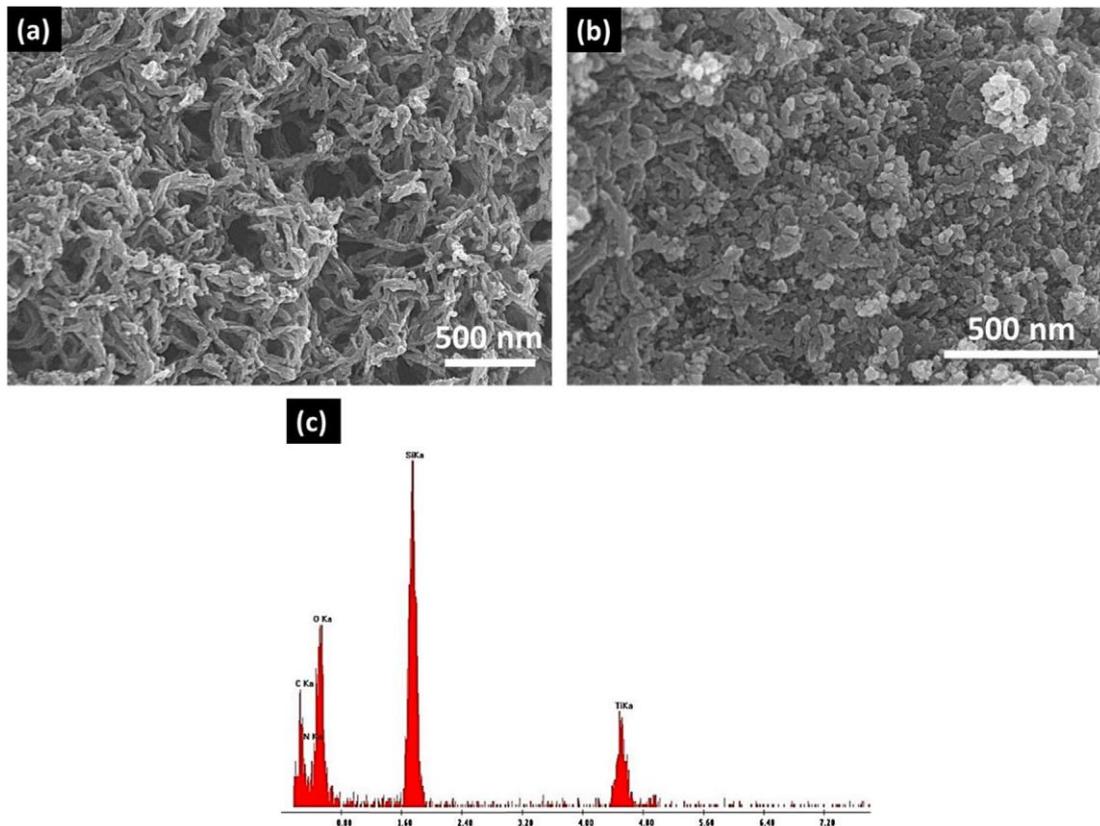


Fig. 4. Scanning electron micrograph exhibiting the porous nature of (a) CMK-3 (b) the TiO_xN_y -derived materials and (c) EDS spectrum of the nanocomposite.

be assigned to the $\text{N}\text{eTi}\text{eN}$ bonds implying the nitrogen ions occupying the substitutional sites and is close enough to the reported values of TiN [11,30]. The peak at 399.4 eV corresponds to the $\text{Ti}\text{eN}\text{eO}$ and $\text{Ti}\text{eO}\text{eN}$ linkage which could be ascribed to the positively charged N^+ ions located at the interstitial site of TiO_2 lattice [31]. The substitution of N_2 in OeTieO structure results in reduced electron density around N and increase in binding energy of N1s peak in OeTieN environment in contrast to that of $\text{N}\text{eTi}\text{eN}$. Reports suggest that both substitutional and interstitial type N evokes visible light photocatalytic activity. The presence of signal at 402 eV could be attributed to the NH_3 chemisorbed or molecular N_2 onto TiO_2 [31].

The XPS spectra of Ti 2p spectra resulted in peaks at binding energies of 459.8 eV and 465.5 eV corresponding to $\text{Ti } 2p_{3/2}$ and $\text{Ti } 2p_{1/2}$ respectively (Fig. 7a). The difference in binding energy of 5.7 eV between the doublets confirmed that titanium exists in $\text{Ti } 4+$ oxidation state. This indicates that there is negligible amount of transfer of electron from oxygen vacancies to titanium atoms [32]. The $\text{Si } 2p_{1/2}$ peak (Fig. 7d) exhibited a signal at binding energy 103.5 eV indicating the presence of SiO_4 units on the surface of the nanocomposite [33]. Fig. 7c shows the C1s spectra of the mesoporous nanocomposite. The main peak at 284.8 eV corresponds to CeC and the three peaks at 285.8, 287.5 and 289.4 eV corresponds to CN , CeN and CeO bonds

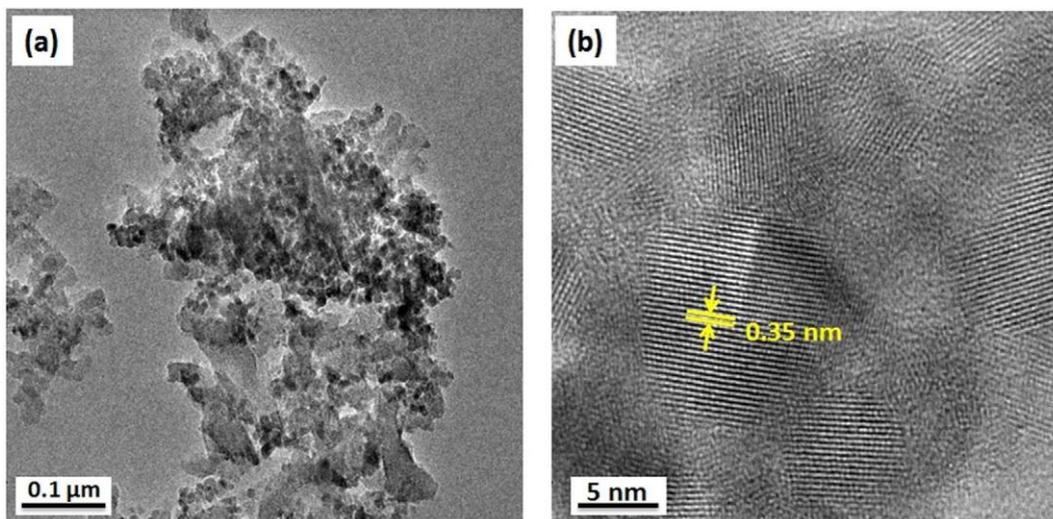


Fig. 5. Transmission electron micrograph illustrating (a) uniform distribution of the TiO_xN_y -derived materials and (b) Lattice fringes unveiling a spacing of 0.35 nm consigned to (1 0 1) plane of the anatase phase in the TiO_xN_y -derived materials.

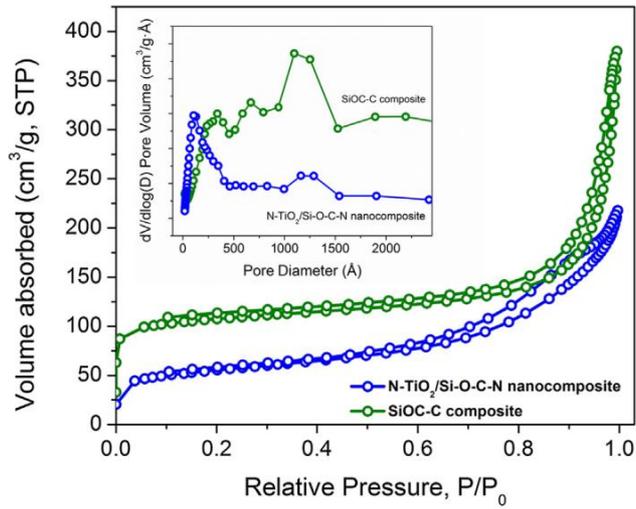


Fig. 6. N₂ adsorption-desorption isotherm indicating the presence of mesopores in SiOC-C composite and N-TiO₂/Si-O-C-N nanocomposite and the inset image shows the BJH pore size distribution curve.

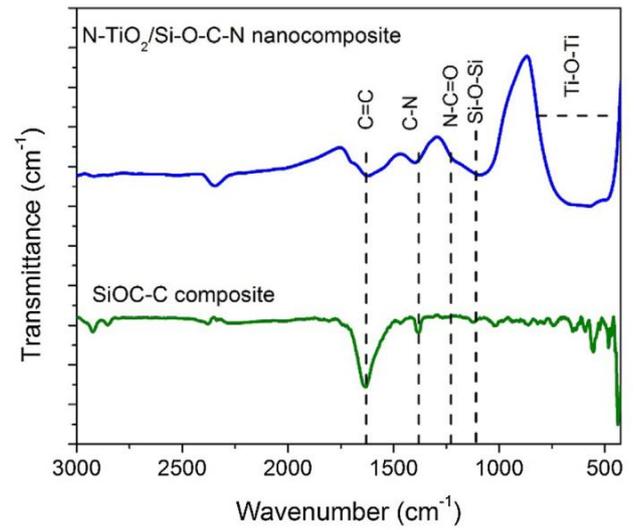


Fig. 8. FTIR spectrum showing the bonding characteristics of the SiOC-C composite and N-TiO₂/Si-O-C-N nanocomposite.

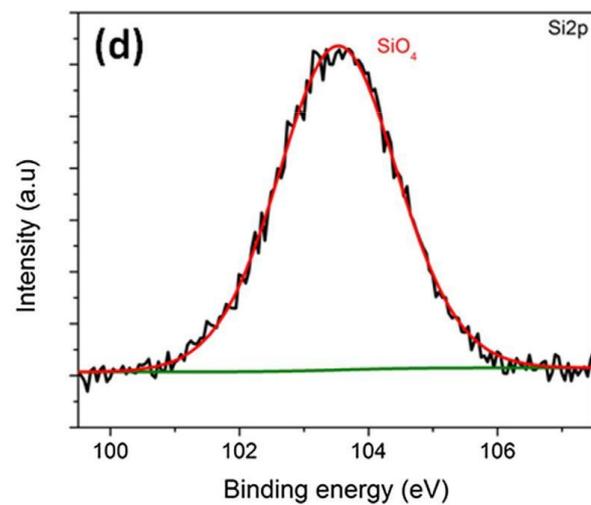
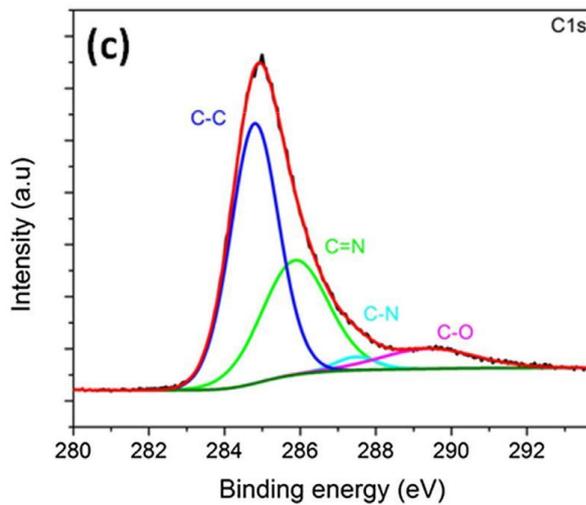
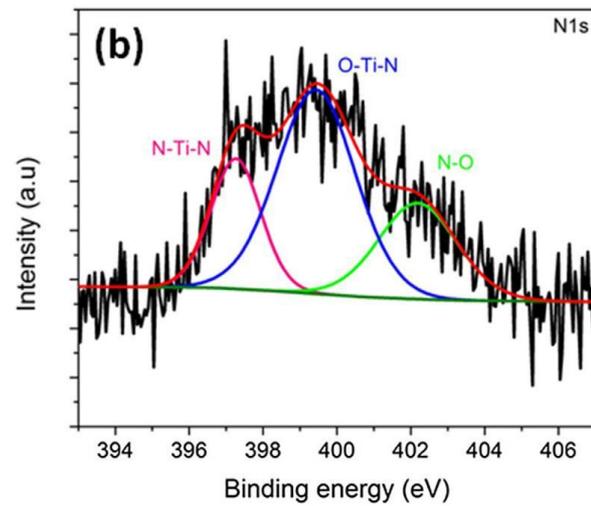
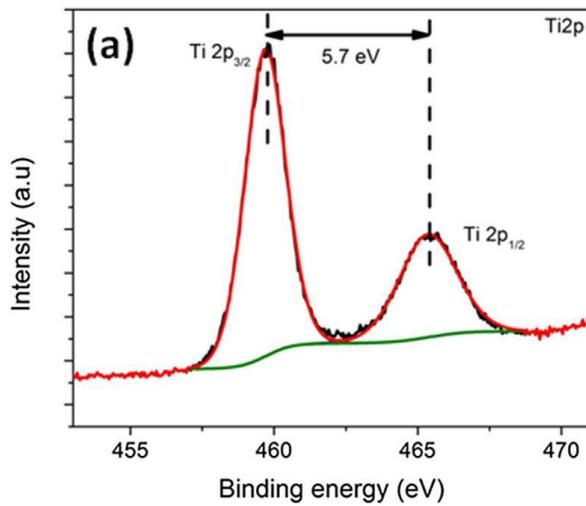


Fig. 7. XPS spectra (a) Ti2p (b) N1s (c) C1s and (d) Si2p of the nanocomposite.

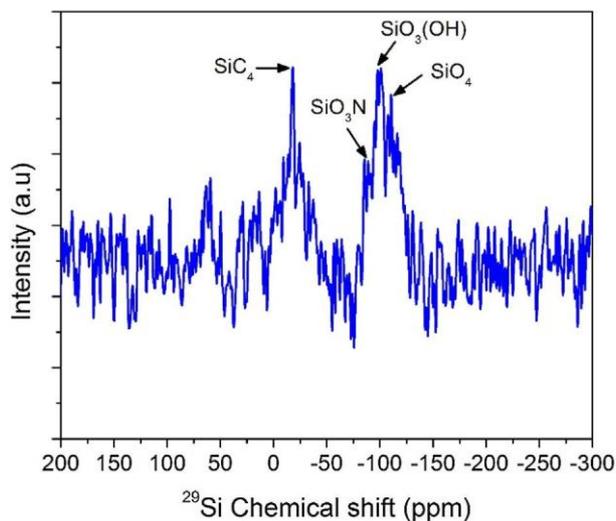


Fig. 9. ^{29}Si MAS NMR spectra of N-TiO₂/Si-O-C-N nanocomposite implying the incorporation of N atoms in the Si-based network.

respectively [34,35]. This in turn suggests that the amorphous matrix to be composed of CeNeO bonds.

XPS clearly highlights the presence of a TiO_xN_y most probably supported by a Si₂O₂C matrix. FTIR of the SiOCeC composite and mesoporous nanocomposite were also performed to understand the chemical bonding and is exemplified in Fig. 8. The FTIR spectrum of SiOCeC composite shows a peak at 1630 cm⁻¹ corresponding to C=C bond [23], indicating the presence of mesoporous carbon. In the case of mesoporous nanocomposite, the broad peak at around 1000–1100 cm⁻¹ and 600–800 cm⁻¹ corresponds to the presence of Si₂O₂C bonds and Ti₂O₂C stretching modes respectively [36]. The peak at around 1420 cm⁻¹ corresponds to the C=N bond [34]. This further confirms the incorporation of nitrogen into the amorphous matrix. Apart from this, the peak at 1210 cm⁻¹ corresponding to N=C=O was also observed [37]. Hence, it is understood that pyrolyzing in ammonia atmosphere not only leads to the doping of nitrogen into TiO₂ lattice but also modifies the amorphous matrix.

The local environment around silicon atoms was further investigated by analyzing the NMR spectrum shown in Fig. 9. The peaks present at -100 ppm and -109 ppm could be attributed to SiO₃(OH) and SiO₄ units, respectively. The shoulder peak at -90 ppm could be assigned to SiO₃N units, where Si atoms share bonds with oxygen and nitrogen atoms [38,39]. The occurrence of SiO₃N peak implies the fact that the pyrolysis of the molecular precursor under ammonia atmosphere has led to the incorporation of nitrogen atoms in the Si-based network. The signal at -18 ppm corresponds to SiC₄. In general, besides the presence of SiC₄ and SiO₄ signals, the silicon oxycarbide based ceramics exhibits additional resonance peaks at SiO₃C (-70 ppm), SiO₂C₂ (-35 ppm) and SiOC₃ (6 ppm) [40]. The absence of these mixed bonds implies that the ammonolyzed sample has undergone phase separation at higher temperatures resulting in the formation of multi-phasic system and free carbon. The XRD and Raman spectra (Figs. 2 and 3) also substantiate the aforementioned fact.

Fig. 10a shows the absorption spectra of MB solution of 0.06 mM kept in dark for 12 h. It is clearly observed that due to the ultra-high adsorption capacity exhibited by the nanocomposite, most of the MB molecules gets adsorbed on to the material system which results in complete decolorization of the solution. Hence, in order to comprehend the kinetics of photocatalytic degradation in visible light, the concentration of MB solution was doubled to 0.12 mM. The absorption spectrum of MB solution (0.12 mM) before and after exposure of visible light is exemplified in Fig. 10b. As seen from the spectrum, the concentration of the MB solution gradually decreases with increase in

irradiation time indicating the reaction of catalyst with the solution in the presence of light. The photocatalytic activity of the nanocomposite in visible light could be ascribed to the doping of nitrogen in the TiO₂ lattice.

In order to determine the photodegradation constant, Langmuir – Hinshelwood kinetic model was used which determines the photo-catalytic activity independent of the amount of MB concentration left in the solution [41]. The experimental data was fitted using first order kinetic equation, $\ln(C/C_0) = -kt$ where C is the concentration of the MB at time t, C₀ is the initial concentration and k is the photo-degradation constant. The plot of $\ln C/C_0$ vs time follows a first order reaction in which $\ln C/C_0$ linearly decreases with time as depicted in Fig. 10c. The photocatalytic degradation constant, $k(\times 10^{-3} \text{ min}^{-1})$ was calculated to be 8.3. The UV–vis diffuse reflectance spectrum of the N-TiO₂/SiOCN nanocomposite exhibited a very strong absorption in the visible to near infra-red region as shown in Fig. 10d. However, no specific band edge was observed in the UV-DRS spectrum. This could be due to the presence of amorphous Si-O-C-N matrix present in the nanocomposite, since the Bloch theorem is no longer applicable in amorphous materials due to the lack of lattice periodicity, leaving the crystalline hk momentum unidentified [42].

The BET surface area of the N-TiO₂/SiOCN nanocomposite was found to be 130 m²/g after the adsorption/catalysis experiments (Fig. 11) in contrast to 186 m²/g for the nanocomposite before the experiments. This further proves the fact that pores play a major role in the adsorption process.

In order to investigate the active species involved in dye degradation, reaction species trapping experiments were carried out (Fig. 12). The isopropanol (0.02 M), benzoquinone (0.001 M) and triethanolamine (0.01 M) were used as sacrificial agents for scavenging hydroxyl radicals ([•]OH), superoxide anion radicals (⁻O₂[•]) and photogenerated holes (h⁺) respectively. Fig. 12 shows the degradation efficiency of methylene blue with and without the presence of scavengers. It could be clearly understood that the methylene blue without the presence of catalyst showed highest degradation efficiency. The introduction of isopropanol drastically reduced the degradation efficiency, implying that [•]OH plays a significant role towards the degradation of methylene blue dye. A decrease in degradation efficiency was also observed with the addition of triethanolamine, indicating that h⁺ also has a minor role to play in the degradation process. However, the catalyst in the presence of benzoquinone had the least effect on the degradation efficiency, manifesting that ⁻O₂[•] has minimal role to play in the catalytic degradation process.

The plausible mechanism for the visible light photocatalytic activity of N-TiO₂/Si-O-C-N nanocomposite is shown in Fig. 13a. The crystalline form of anatase transfers the electron from the valence band to the conduction band up on irradiation of an UV light, thereby favoring the photocatalytic reaction. However, since the band gap of TiO₂ being high, the electrons fails to excite in the visible light regime. The incorporation of nitrogen in the TiO₂ lattice, substantiated by the XPS analysis, is believed to alter the electronic band structure of TiO₂. The doping of nitrogen atoms results in the creation of an additional N2p band above the O2p band, which results in the reduction of band gap. Thus, instead of electron being excited from the O2p band (in pure TiO₂), diffusion of charge carriers occurs from the N2p band to Ti3d conduction band. The resulting electrons in the conduction band reduce with the oxygen molecules to produce superoxide ions, O₂⁻. Concomitantly, the holes in the valence band react with the water molecules to produce the hydroxyl radical, OH[•]. The aforementioned superoxide anions and the hydroxyl radical are believed to be responsible for the degradation of MB molecules. The heterojunction formation between amorphous Si-O-C-N and crystalline N-TiO₂ is expected to reduce the recombination rate as evident from HR-TEM micrograph (Fig. 13b). The heterojunction formation between the crystalline N-TiO₂ and amorphous Si-O-C-N matrix results in the migration of photo-generated electrons from the conduction band of amorphous Si-O-C-N

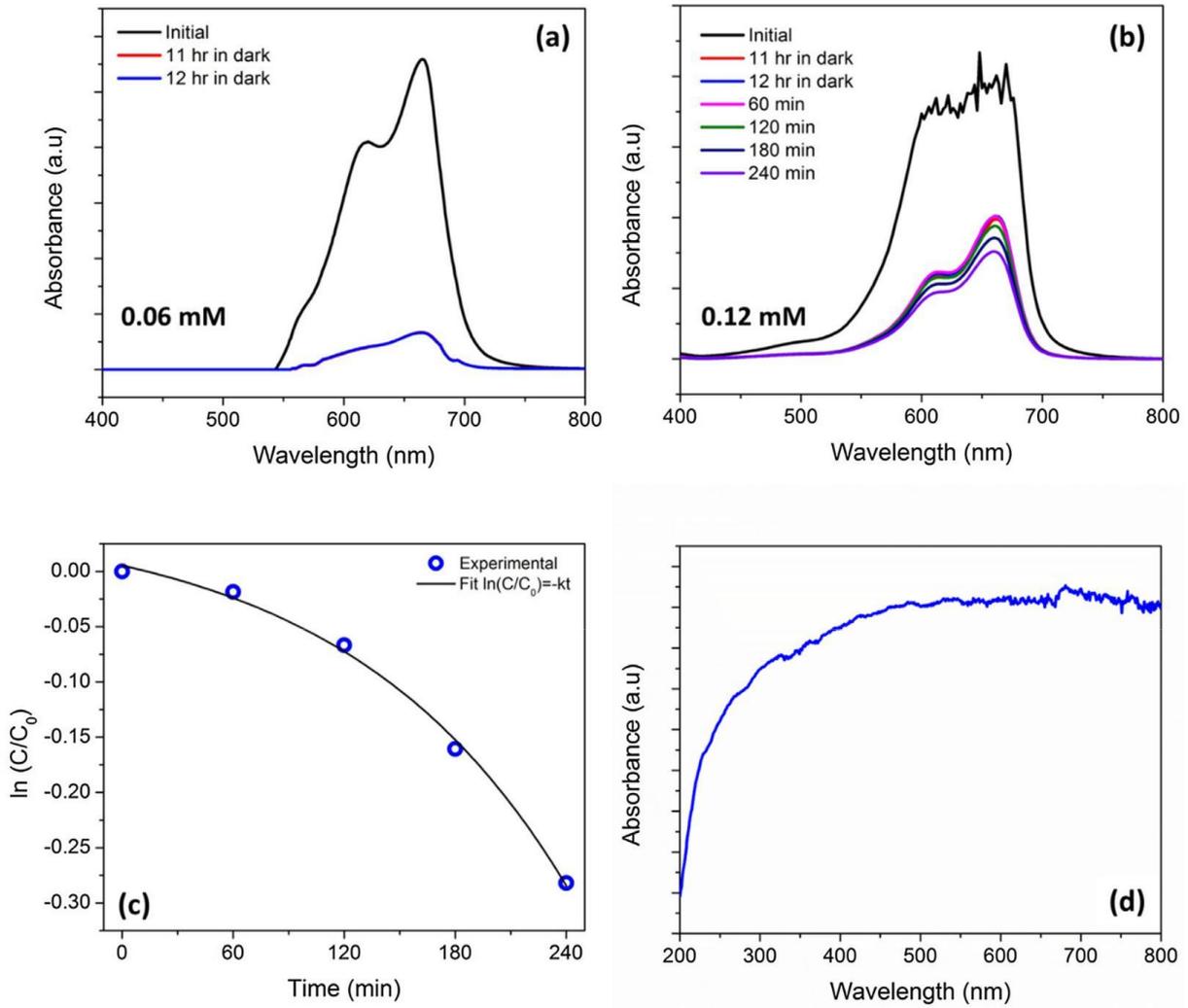


Fig. 10. UV-vis absorption spectra of (a) 0.06 mM of MB with 50 mg of the catalyst kept in dark for 12 h (b) 0.12 mM of MB with 50 mg of the catalyst exposed to visible light after keeping it in dark for 12 h (c) photocatalytic activity of the mesoporous nanocomposite and (d) UV-visible absorption spectrum of the mesoporous nanocomposite.

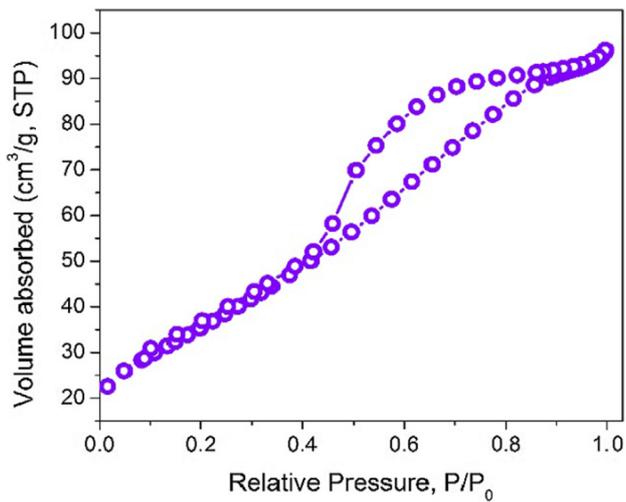


Fig. 11. N_2 adsorption-desorption isotherm of the nanocomposite after the adsorption/catalysis.

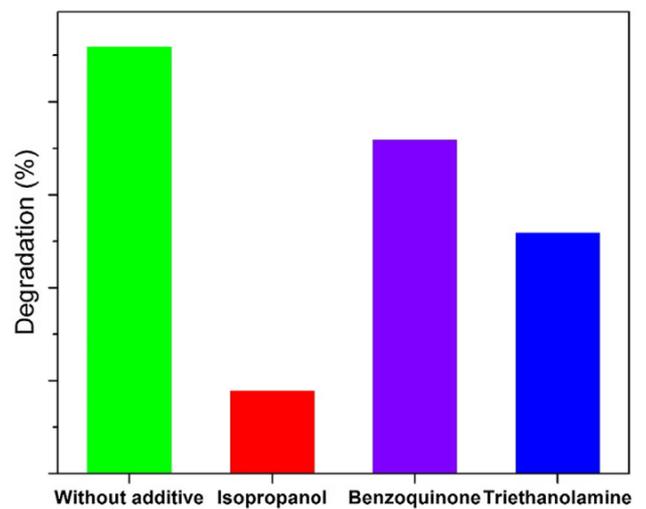


Fig. 12. Catalytic degradation efficiency of methylene blue solution with and without the presence of scavengers.

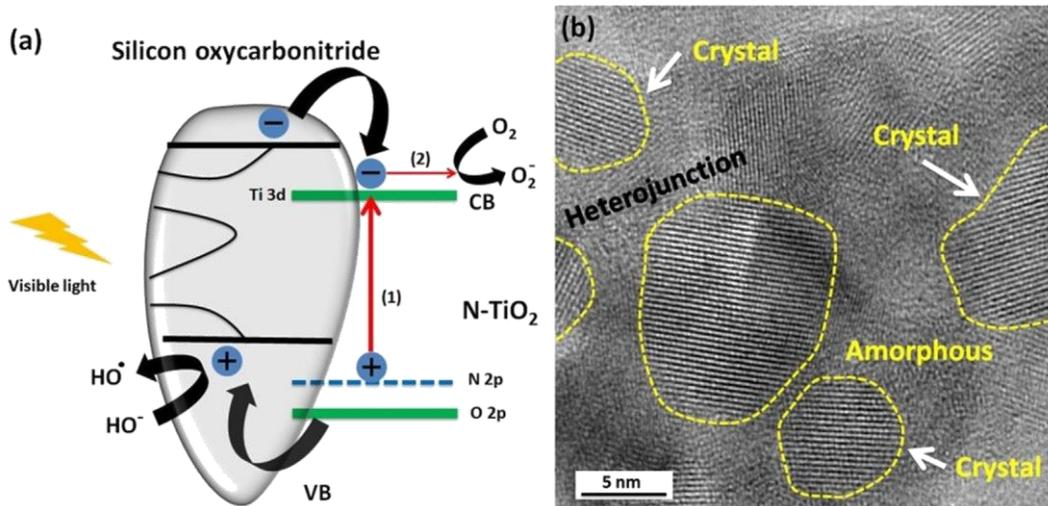
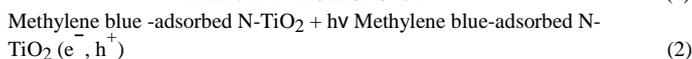
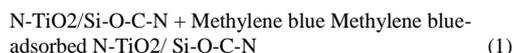


Fig. 13. (a) Schematic representing the visible light photocatalytic activity of the nanocomposite and (b) TEM micrograph exemplifying the heterojunction formation.

to the conduction band of N-TiO₂. Similarly, the photogenerated holes will migrate from the valence band of N-TiO₂ to the valence band of amorphous Si-O-C-N.

The reactions occurring during dye degradation could be general-ized as follows:

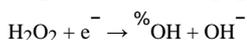
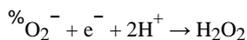
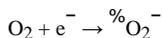
The methylene blue molecules gets adsorbed on to the surface which turns out to be the first step (Eq. (1)) in the catalytic process. Up on exposure to visible light, the charges are excited (Eq. (2)) to form [•]O₂⁻ and [•]OH radicals.



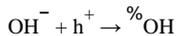
However, as the reaction trapping experiments suggests, the [•]OH

radicals are the major contributing species when compared to [•]O₂⁻, indicating that [•]O₂⁻ are unstable in aqueous solution resulting in immediate conversion to [•]OH radicals. The plausible degradation mechanism is explained in the below mentioned reactions.

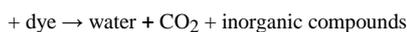
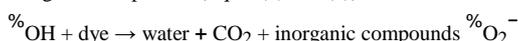
The [•]O₂⁻ radicals are formed when photogenerated electrons reacts with the oxygen molecules as shown in Eq. (3) H₂O₂ are formed when [•]O₂⁻ radicals gets disproportionated or reduced by an electron (Eq. (4)) and the formed H₂O₂ subsequently reacts with electrons to form [•]OH radicals as expressed in Eq. (5).



The h⁺ also reacts with the water molecules resulting in the formation of [•]OH radicals Eqs. (6) and (7).



Finally, the [•]OH and [•]O₂⁻ reacts with the dye methylene blue molecules decomposing into water, carbon dioxide (CO₂) and other inorganic compounds (Eqns. (8) and (9)).



4. Conclusions

A hard template assisted precursor derived approach was adopted to synthesize mesoporous, in-situ crystallized nitrogen doped TiO₂ in an amorphous Si-O-C-N matrix. The pyrolysis of pre-ceramic polymer in Ar/NH₃ atmosphere resulted in complete polymer to ceramic transformation leading to the formation of uniformly distributed nitrogen doped TiO₂ in an amorphous Si-O-C-N matrix. Pyrolysis in a reactive ammonia atmosphere has led to the inclusion of nitrogen atoms in the

TiO₂ lattice as well as in the amorphous matrix. The ammonia assisted pyrolysis treatment has also aided in the reduction of CMK-3 template,

resulting in a high surface area (186 m²/g) mesoporous nanocomposite.

The mesoporous nanocomposite exhibited high adsorption capacity and visible light photocatalytic activity towards degradation of methylene blue. The doping of nitrogen in to the TiO₂ lattice is expected to

reduce the band gap, thereby harnessing light in the visible light wavelength regime. The hydroxyl radicals and the superoxide anions formed are believed to degrade the organic molecules. The re-

combination rate is expected to be lowered due to the formation of

heterojunctions between the amorphous and crystalline phases.

References

- [1] A. Fujishima, K. Honda, Electrochemical photolysis of water at a semiconductor electrode, *Nature* 238 (1972) 37–38.
- [2] M. Anpo, M. Takeuchi, The design and development of highly reactive titanium oxide photocatalysts operating under visible light irradiation, *J. Catal.* 216 (2003) 505–516.
- [3] J. Tang, J.R. Durrant, D.R. Klug, Mechanism of photocatalytic water splitting in TiO₂. Reaction of water with photoholes, importance of charge carrier dynamics, and evidence for four-hole chemistry, *J. Am. Chem. Soc.* 130 (2008) 13885–13891.
- [4] S. Pavasupree, S. Ngamsinlapasathian, M. Nakajima, Y. Suzuki, S. Yoshikawa, Synthesis, characterization, photocatalytic activity and dye-sensitized solar cell performance of nanorods/nanoparticles TiO₂ with mesoporous structure, *J. Photochem. Photobiol. A Chem.* 184 (2006) 163–169.
- [5] A. Houas, H. Lachheb, M. Ksibi, E. Elaloui, C. Guillard, J.-M. Herrmann, Photocatalytic degradation pathway of methylene blue in water, *Appl. Catal. B Environ.* 31 (2001) 145–157.
- [6] J. Zhang, P. Zhou, J. Liu, J. Yu, New understanding of the difference of photo-catalytic activity among anatase, rutile and brookite TiO₂, *Phys. Chem. Chem. Phys.* 16 (2014) 20382–20386.
- [7] N. Luo, Z. Jiang, H. Shi, F. Cao, T. Xiao, P.P. Edwards, Photo-catalytic conversion of oxygenated hydrocarbons to hydrogen over heteroatom-doped TiO₂ catalysts, *Int. J. Hydrogen Energy.* 34 (2009) 125–129.
- [8] J.H. Xu, J. Li, W.L. Dai, Y. Cao, H. Li, K. Fan, Simple fabrication of twist-like helix N, S-codoped titania photocatalyst with visible-light response, *Appl. Catal. B Environ.* 79 (2008) 72–80.
- [9] J.C. Yu, J. Yu, W. Ho, Z. Jiang, L. Zhang, Effects of F- doping on the photocatalytic activity and microstructures of nanocrystalline TiO₂ powders, *Chem. Mater.* 14 (2002) 3808–3816.
- [10] X. Chen, C. Burda, The electronic origin of the visible-light absorption properties of C-, N- and S-doped TiO₂ nanomaterials, *J. Am. Chem. Soc.* 130 (2008) 5018–5019.
- [11] R. Asahi, T. Morikawa, T. Ohwaki, K. Aoki, Y. Taga, Visible-light photocatalysis in nitrogen-doped titanium oxides, *Science* 293 (2001) 269–271.
- [12] Q. Li, Y.W. Li, P. Wu, R. Xie, J.K. Shang, Palladium oxide nanoparticles on nitrogen-doped titanium oxide: accelerated photocatalytic disinfection and post-illumination catalytic “memory”, *Adv. Mater.* 20 (2008) 3717–3723.
- [13] S. Yin, Y. Aita, M. Komatsu, J. Wang, Q. Tang, T. Sato, Synthesis of excellent visible-light responsive TiO_{2-x}N_y photocatalyst by a homogeneous precipitation-sol-vothermal process, *J. Mater. Chem.* 15 (2005) 674–682.
- [14] S. Yin, Y. Aita, M. Komatsu, T. Sato, Visible-light-induced photocatalytic activity of TiO_{2-x}N_y prepared by solvothermal process in urea–alcohol system, *J. Eur. Ceram. Soc.* 26 (2006) 2735–2742.
- [15] S. Yin, K. Ihara, Y. Aita, M. Komatsu, T. Sato, Visible-light induced photocatalytic activity of TiO_{2-x}A_y (A = N, S) prepared by precipitation route, *J. Photochem. Photobiol. A Chem.* 179 (2006) 105–114.
- [16] H.-H. Tseng, W.W. Lee, M.-C. Wei, B.-S. Huang, M.-C. Hsieh, P.-Y. Cheng, Synthesis of TiO₂/SBA-15 photocatalyst for the azo dye decolorization through the polyol method, *Chem. Eng. J.* 210 (2012) 529–538.
- [17] E. Ionescu, H.-J. Kleebe, R. Riedel, H. Xu, J.A.P. Cha, P.C.L. Wong, G. Wen, X. Zhang, X. Jing, F. Wang, B.Z. Tang, U.A. Jayasooriya, D. Hourlier, H.-J. Kleebe, G.D. Soraru, S. Enzo, F. Babonneau, Silicon-containing polymer-derived ceramic nanocomposites (PDC-NCs): preparative approaches and properties, *Chem. Soc. Rev.* 41 (2012) 5032.
- [18] M. Zaheer, T. Schmalz, G. Motz, R. Kempe, Polymer derived non-oxide ceramics modified with late transition metals, *Chem. Soc. Rev. Chem. Soc. Rev.* 41 (2012) 5102–5116.
- [19] S. Bernard, P. Miele, Ordered mesoporous polymer-derived ceramics and their processing into hierarchically porous boron nitride and silicoboron carbonitride monoliths, *New J. Chem.* 38 (2014) 1923.
- [20] E. Ionescu, H.J. Kleebe, R. Riedel, Silicon-containing polymer-derived ceramic nanocomposites (PDC-NCs): Preparative approaches and properties, *Chem. Soc. Rev.* 41 (2012) 5032–5052.
- [21] P. Colombo, G. Mera, R. Riedel, G.D. Soraru, Polymer-derived ceramics: 40 years of research and innovation in advanced ceramics, *J. Am. Ceram. Soc.* 93 (2010) 1805–1837.
- [22] R. Riedel, G. Mera, R. Hauser, A. Klönczynski, Silicon-based polymer-derived ceramics: synthesis properties and applications—a review dedicated to Prof. Dr. Fritz Aldinger on the occasion of his 65th birthday, *J. Ceram. Soc. Jpn.* 114 (1330) (2006) 425–444.
- [23] L. Meng, X. Zhang, Y. Tang, K. Su, J. Kong, Hierarchically porous silicon-carbon-nitrogen hybrid materials towards highly efficient and selective adsorption of organic dyes, *Sci. Rep.* 5 (2015) 7910.
- [24] Y. Shi, Y. Wan, Y. Zhai, R. Liu, Y. Meng, B. Tu, D. Zhao, Ordered mesoporous SiOC and SiCN ceramics from atmosphere-assisted in situ transformation, *Chem. Mater.* 19 (2007) 1761–1771.
- [25] H. Bréquel, J. Parmentier, S. Walter, R. Badheka, G. Trimmel, S. Masse, J. Latournerie, P. Dempsey, C. Turquat, A. Desmartin-Chomel, L. Le Neindre-Prum, U.A. Jayasooriya, D. Hourlier, H.J. Kleebe, G.D. Soraru, S. Enzo, F. Babonneau, Systematic structural characterization of the high-temperature behavior of nearly stoichiometric silicon oxycarbide glasses, *Chem. Mater.* 16 (2004) 2585–2598.
- [26] H. Fukui, K. Eguchi, H. Ohsuka, T. Hino, K. Kanamura, Structures and lithium storage performance of Si-O-C composite materials depending on pyrolysis temperatures, *J. Power Sources* 243 (2013) 152–158.
- [27] N. Subramanian, B. Viswanathan, Nitrogen- and oxygen-containing activated carbons from sucrose for electrochemical supercapacitor applications, *RSC Adv.* 5 (2015) 63000–63011.
- [28] M.C. Bechelany, V. Proust, A. Lale, P. Miele, S. Malo, C. Gervais, S. Bernard, Nanocomposites through the chemistry of single-source precursors: understanding the role of chemistry behind the design of monolith-type nanostructured titanium nitride/silicon nitride, *Chem. – Eur. J.* 23 (2017) 832–845.
- [29] M.C. Bechelany, V. Proust, C. Gervais, R. Ghisleni, S. Bernard, P. Miele, In situ controlled growth of titanium nitride in amorphous silicon nitride: a general route toward bulk nitride nanocomposites with very high hardness, *Adv. Mater.* 26 (2014) 6548–6553.
- [30] C. Di Valentin, E. Finazzi, G. Pacchioni, A. Selloni, S. Livraghi, M.C. Paganini, E. Giamello, N-doped TiO₂: theory and experiment, *Chem. Phys.* 339 (2007) 44–56.
- [31] D. Kusano, M. Emori, H. Sakama, Influence of electronic structure on visible light photocatalytic activity of nitrogen-doped TiO₂, *RSC Adv.* 7 (2017) 1887–1898.
- [32] H. Chen, A. Nambu, W. Wen, J. Graciani, Z. Zhong, J.C. Hanson, E. Fujita, J.A. Rodriguez, Reaction of NH₃ with titania: N-doping of the oxide and TiN formation, *J. Phys. Chem. C* 111 (2007) 1366–1372.
- [33] M.A. Abass, A.A. Syed, C. Gervais, G. Singh, Synthesis and electrochemical performance of a polymer-derived silicon oxycarbide/boron nitride nanotube composite, *RSC Adv.* 7 (2017) 21576–21584.
- [34] L. Yan, G. Chen, S. Tan, M. Zhou, G. Zou, S. Deng, S. Smirnov, H. Luo, Titanium oxynitride nanoparticles anchored on carbon nanotubes as energy storage materials, *ACS Appl. Mater. Interfaces* 7 (2015) 24212–24217.
- [35] D.-H. Wang, L. Jia, X.-L. Wu, L.-Q. Lu, A.-W. Xu, One-step hydrothermal synthesis of N-doped TiO₂/C nanocomposites with high visible light photocatalytic activity, *Nanoscale* 4 (2012) 576–584.
- [36] W. Wang, Y. Liu, J. Qu, Y. Chen, Z. Shao, Nitrogen-doped TiO₂ microspheres with hierarchical micro/nanostructures and rich dual-phase junctions for enhanced photocatalytic activity, *RSC Adv.* 6 (2016) 40923–40931.
- [37] R. Wang, Q. Wu, Y. Lu, H. Liu, Y. Xia, J. Liu, D. Yang, Z. Huo, X. Yao, Preparation of nitrogen-doped TiO₂/graphene nanohybrids and application as counter electrode for dye-sensitized solar cells, *ACS Appl. Mater. Interfaces.* 6 (2014) 2118–2124.
- [38] S. Kohn, W. Hoffbauer, M. Jansen, R. Franke, S. Bender, Evidence for the formation of SiON glasses, *J. Non. Cryst. Solids* 224 (1998) 232–243.
- [39] F. Hayashi, K.I. Ishizu, M. Iwamoto, Fast and almost complete nitridation of mesoporous silica MCM-41 with ammonia in a plug-flow reactor, *J. Am. Ceram. Soc.* 93 (2010) 104–110.
- [40] R. Kalfat, F. Babonneau, N. Gharbi, H. Zarrouk, 29Si MAS NMR investigation of the pyrolysis process of cross-linked polysiloxanes prepared from poly-methylhydrosiloxane, *J. Mater. Chem.* 6 (1996) 1673–1678.
- [41] Y. Ao, J. Xu, D. Fu, C. Yuan, A simple route for the preparation of anatase titania-coated magnetic porous carbons with enhanced photocatalytic activity, *Carbon N. Y.* 46 (2008) 596–603.
- [42] S. Adachi, *Optical Properties of Crystalline and Amorphous Semiconductors: Materials and Fundamental Principles*, Kluwer Academic Publishers, Boston, 1999.