Benefits of tubular morphologies on electron transfer properties in CNT/TiNT nanohybrid photocatalyst for enhanced H₂ production

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In order to study the influence of one dimensional tubular structures for effective electron and hole transportation onto the surface of a photocatalyst leading to efficient solar photocatalytic hydrogen production, functionalized carbon nanotube (FCNT)/TiO₂ nanotube nanohybrids were prepared. TiO₂ nanotubes (TiNTs) were prepared by hydrothermal method. A series of novel functionalized carbon nanotube/TiO₂ nanotube nanohybrids (CTT) were prepared for different wt% (1–20) of FCNTs by wet impregnation method to extend absorption in the visible region and also to retard the electron–hole pair recombination and thereby to enhance the H₂ production capability under solar light irradiation. The functionalized carbon nanotube/TiO₂ nanotube nanohybrids (CTT) were characterized with XRD, TEM, DRS-UV-Vis, Raman spectroscopy and XPS for crystal structure, morphology, optical properties and chemical composition. Addition of FCNTs to the TiNTs in CTT nanohybrids extended the absorption to the visible region. Relative electron–hole recombination times were measured with photoluminescence spectra. The highest H₂ generation of 29 904 μmol g⁻¹ was observed after 4 h under optimal conditions due to better separation of electron–hole pairs and electron conducting properties.

Introduction

Since the discovery of carbon nanotubes by Ijima,¹ they have been of great interest to researchers for their 1D tubular structure, good conductivity, high surface area and unique optical properties.¹⁻⁵ Due to these interesting properties, they have been used as co-catalyst and also as sensitizer in photocatalytic applications such as photodegradation of organic dyes, removing pollutants from air and water, and hydrogen generation from water splitting etc.³ Photocatalysts that generate hydrogen through water splitting by utilizing solar energy, contribute to environmentally friendly programs due to their properties such as zero emissions. Among the photocatalysts, TiO₂ is a promising candidate because of its relatively low cost, non-toxicity, stability and suitable band edge positions for redox reactions.

Among several nanocrystalline structures of TiO₂ photocatalysts, TiO₂ nanotubes (TiNT) have more optimal properties for photocatalytic H₂ production due to their one dimensional nanostucture. Previous studies have shown that combination of TiNT with other nanomaterials have increased photocatalytic activity.¹⁻³ Several studies⁴ have been carried out to utilize CNTs in improving the photocatalytic H₂ production efficiency of TiO₂ nanoparticles in view of their unique optical and electron transport properties. Silva et al.⁵ studied the photocatalytic H₂ production of MWCNT/TiO₂ photocatalyst from aqueous methanol and saccharide solutions. Recently Tarigh et al.⁶ reported a simple, effective and recoverable photocatalyst MWCNT/TiO₂ for enhanced photocatalytic activity. There is still a significant potential for improvement in the photocatalytic activity of all the above photocatalysts by reducing the electron–hole recombination through one dimensional nanostucture.⁷ This motivated us to study effect of one dimensional nanostucture of both CNTs and TiNTs on the photocatalytic H₂ production under solar irradiation.

Also, less attention has been paid to synthesis of CNT/TiNT nanohybrid and its photocatalytic activity. Doong et al.⁸ studied degradation efficiency of CNT/TiNT composite and found that it is a promising nano-adsorbent for coupled removal of organic as well as heavy metal ions in solution. However, to the best of our knowledge research work on CNT/TiNT (TiO₂ nanotubes) nanohybrid for hydrogen generation under natural solar light by water splitting, is scarce.

In the present work we study the preparation method for CNT/TiNT nanohybrid and its hydrogen generation efficiency under natural solar light irradiation by water splitting.
Experimental methods

Materials

All the chemicals used for the present work are of analytical grade and the details of the chemicals and catalysts used are given below. Commercial titanium dioxide TiO₂ P-25 catalyst (anatase 80%, rutile 20%, surface area = 50 m² g⁻¹ and particle size 27 nm) was received from Degussa Corporation, Germany. Commercial TiO₂ (particle size ≈ 150 nm, surface area = 5.1 m² g⁻¹, LAB) used for nanotube synthesis was purchased from Merck, India. Sodium hydroxide pellets (99%), hydrochloric acid (35%), HNO₃ (33%), H₂SO₄ (38%) and glycerol (98%) were received from Merck, India. De-ionized water (100%, battery grade) used for synthesis, impregnation process and photocatalytic experiments was procured from LIMRA, Kadapa, India.

Synthesis of TiNTs

TiO₂ nanotubes (TiNTs) were prepared by alkaline hydrothermal method. Briefly, functionalization of CNTs was carried out to remove amorphous carbon, metal catalyst and also to introduce acid functional groups to the carbon nanostructures, by ultrasonating them in 3 : 1 volume ratio mixture of H₂SO₄/HNO₃ at 40 °C for 2 h, followed by washing with plenty of water till reaches pH ≈ 7 and drying at 80 °C overnight.

Synthesis of FCNTs

Carbon nanotubes were synthesized by arc discharge method in open air. Functionalization of CNTs has been described in detail in an earlier report. Briefly functionalization of CNTs was carried out to remove amorphous carbon, metal catalyst and also to introduce acid functional groups to the carbon nanostructures, by ultrasonating them in 3 : 1 volume ratio mixture of H₂SO₄/HNO₃ at 40 °C for 2 h, followed by washing with plenty of water till reaches pH ≈ 7 and drying at 80 °C overnight.

Synthesis of FCNTs/TiNTs nanohybrid

TiO₂ nanotubes/FCNT nanohybrid photocatalysts were prepared through wet impregnation method. Functionalized CNTs (FCNTs) and hydrothermally synthesized TiNTs were taken as starting materials. In a typical impregnation procedure, required amount (1–20 wt%) of FCNTs (Table 1) was dispersed in ethanol aqueous solution in beaker-1, ultrasonicated and magnetically stirred for 1 h. Simultaneously, in beaker-2, TiNT was dispersed in ethanolic aqueous solution. Then contents in beaker-1 was transferred into beaker-2 and resulting mixture was ultrasonicated for 1 h. The TiNT/FCNT mixture containing ethanolic aqueous solvent, was subjected to heating and magnetic stirring till the solution is completely evaporated. Nanohybrid mixture was kept for drying in oven at 80 °C overnight and calcination in tubular furnace in air at 450 °C for 2 h, with a heating rate of 5 °C min⁻¹.

Characterization

Transmission Electron Microscopy (TEM) images were recorded on a PHILIPS instrument (120 kV). The powder catalyst samples for TEM observations were directly deposited onto carbon coated Cu-grids. The XRD patterns were recorded on Siemens D-5000 X-ray diffractometer (2θ = 20–90°). Thermo gravimetric analysis (TGA) was performed on a universal instrument using TGA Q 500 analyzer with a heating rate of 10 °C min⁻¹ under nitrogen flow. Diffuse Reflectance UV-Visible spectra were recorded on a GBC UV-Visible Cintra 10e spectrometer, in the wavelength range 200–500 nm. X-ray photoelectron spectra (XPS) were recorded on a KRATOS AXIC 165 equipped with Mg Kα radiation. Confocal Raman spectra of all the samples were recorded using Raman spectrometer (RENISHAW) operating with an excitation wavelength of 532 nm and a power 1 mW. Photoluminescence (PL) spectra were recorded using Spectrofluorometer, (FLUORA MAX 4P) excitation wavelength at 320 nm.

Photocatalytic H₂ production activity

Photocatalytic hydrogen evolution reactions were carried out in a 150 mL quartz reactor sealed using an air-tight rubber septum to keep the experimental set up leak-proof and enable gas sampling. Typically, 5 mg of catalyst was suspended in 50 mL of a 5 vol% glycerol aqueous solution. Prior to solar experiments, the catalyst suspension was stirred in dark for 30 min followed by degassing and purging with nitrogen (high pure) gas to eliminate oxygen from the reaction system. Catalytic activities were performed under continuous magnetic stirring and solar light was used to excite the photocatalyst for red-ox reaction on the catalyst surface. The amount of H₂ and O₂ produced was measured by offline gas chromatography. Control experiments were carried out under similar experimental conditions in the absence of photocatalyst or sun light, neither H₂ nor O₂ gas was detected.

Results and discussion

X-ray diffraction

Fig. 1 presents the XRD patterns of TiNT, CTT-1, CTT-2, CTT-10, CTT-20 and FCNT photocatalysts. FCNT showed a broad peak located between 20° and 30° which is assigned to the (002) plane of the carbon structure. The diffraction peaks of TiO₂ were identified with reference to JCPDS database. The photocatalysts TiNT, CTT-1 and CTT-2 displayed diffraction peaks at 2θ = 25.3°, 37.8°, 48.0°, 53.8°, 54.9° and 62.5° which are the peaks of

Table 1 Photocatalysts used

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<th>Photocatalyst</th>
<th>Nomenclature</th>
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<tr>
<td>Functionalized carbon nanotubes</td>
<td>FCNT</td>
</tr>
<tr>
<td>TiO₂ nanotube</td>
<td>TiNT</td>
</tr>
<tr>
<td>1 wt% FCNT loaded TiNT</td>
<td>CTT-1</td>
</tr>
<tr>
<td>2 wt% FCNT loaded TiNT</td>
<td>CTT-2</td>
</tr>
<tr>
<td>10 wt% FCNT loaded TiNT</td>
<td>CTT-10</td>
</tr>
<tr>
<td>20 wt% FCNT loaded TiNT</td>
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(101), (004), (200), (105), (211) and (204) respectively for anatase phase (JCPDS 21-1272). Also, with increase in FCNT content, a new peak at 26.2° is observed clearly for CTT-20 corresponding to the carbon (100) in FCNT. Carbon (100) peak is not observed in CTT-2 and slightly in CTT-10, due to the presence of lower amount of FCNT. Kim et al., studied TiO2 nanoparticle loaded on graphene/carbon nanocomposites photocatalysts and XRD pattern displayed characteristic peaks of anatase-rutile phases in addition to carbon nanostructures. We have also observed characteristic XRD peaks of both TiO2 anatase-rutile and carbon in FCNTs/TiO2 nanoparticles nanohybrid material. The results reveal that addition of FCNTs to TiO2 nanotubes suppressed both grain growth and phase transformation. This is mainly attributed to fine dispersion of TiO2 nanotubes on FCNTs surface.

**TEM**

TEM image Fig. 2 shows the as-prepared CTT-2 nanohybrid. Fig. 2(a) shows that bundles of TiO2 nanotubes of lengths 100–500 nm are dispersed on the FCNTs whose diameters are in the range of 30–50 nm. As both FCNTs and TiNTs are tubular structure, in order distinguish one from the other, rectangle marked region is magnified as shown in Fig. 2(b). Further, HRTEM image Fig. 2(c) showing the lattice spacing of TiNT is subjected to profile of live FFT image Fig. 2(d) to measure the observed interplanar spacing. Measured lattice spacing from live FFT is 0.352 nm which is approximate to that of (101) anatase TiO2. This is further confirmed by the SAED pattern shown in the inset of Fig. 2(c).

**UV-Visible DRS**

Optical properties of the prepared nanohybrids CTT-1, 2, 10, 20 & TiNT were studied by analyzing UV-Visible Diffuse Reflectance spectrum (Fig. 3(a)). It is seen that CTT-1, 2, 10 & 20 showed enhanced absorption towards visible region than TiNT. Approximate absorption edges of CTT-1, 2, 10 & 20 are in the order 395, 424, 413 and 449 nm while that of TiNT is 389 nm. A clear red shift of the absorption lengths can be attributed to presence of FCNTs in the nanohybrid. It is observed that CTT-2 showed higher absorption and absorption edge than CTT-10 and CTT-20. This increased absorption in visible region could also be due to π → π* of CNT and n → π* between n-orbit of oxygen species of TiNT.

Kubelka–Munk plot (Fig. 3(b)) shows that the band gap values of CTT nanohybrids are reduced to 2.98 eV from a value

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**Fig. 1** XRD patterns of TiNT, CTT-1, CTT-2, CTT-10, CTT-20 and FCNTs.

**Fig. 2** TEM and HRTEM images of TiO2 nanotube/FCNT nanohybrid (a), (b) showing the morphological structure (c), (d) showing the interplanar spacing and live FFT image respectively.

**Fig. 3** (a) UV-Vis DRS and (b) transformed Kubelka–Munk functions (ahv)^2 vs. photon energy (hν, eV) of CTT-1, 2, 10, 20 & TiNT photocatalysts.
3.2 eV of TiNT. This decrease in band gap energies is due to synergetic effect of presence of FCNTs attached to the surface of TiNT rather than occupying lattice sites in the nanohybrid.\textsuperscript{6c}

**XPS analysis**

XPS analysis was performed on prepared CTT-2 and the wide scan spectrum (Fig. 4(a)) contains Ti 2p, O 1s and C 1s of TiO\(_2\). High resolution XPS of Ti 2p shows (Fig. 4(b)) intense peaks at 459.70 eV and 460.2 eV corresponding to \(2p_{3/2}\) and second highest peak at 465.9 eV corresponding to \(2p_{1/2}\), indicating the presence of Ti\(^{4+}\) in the nanohybrid. Also, these binding energies are slightly shifted from the corresponding original binding energies at 458.7 eV and 464.5 eV in TiO\(_2\). Such results were reported earlier indicating the strong interaction between TiO\(_2\) nanoparticles and CNTs.\textsuperscript{7,8} O 1s region is composed of two peaks (Fig. 4(c)). Peaks at BE 530.5 eV and 532.7 eV correspond to bulk oxygen in Ti–O–Ti and surface oxygen from the hydroxyl group Ti–OH.

XPS of CTT-2 curve has peaks at 283.4 eV, 286.2 eV and 288.5 eV corresponding to the C–O, C=O and –COO (Fig. 4(d)). Binding energy peaks around 286 eV and 288 eV were attributed to C–O and C=O bonds. This indicates the formation of carbonated structures and probable Ti–O–C bonding.\textsuperscript{9} The interaction of TiNT with FCNTs was further studied using Raman analysis.

**Raman analysis**

Raman spectrum of CTT-2 is shown in the Fig. 5(a). Characteristic bands at 1326 cm\(^{-1}\) and 1579 cm\(^{-1}\) in CTT-2 corresponds to D and G bands of CNTs respectively. The relative intensity ratio of D band to G band (\(I_D/I_G\)), known as index of graphitization, is found to be 1.1 for CTT-2 nanohybrid while that of CNTs is 0.7.

This indicates that functionalization in acid mixture and calcination temperature during nanohybrid formation did not significantly alter the CNT structure in the nanohybrid. Dai \textit{et al.} also reported an \(I_D/I_G\) ratio of 0.78 for MWNT–TiO\(_2\), comparable to that of the pure MWNTs (0.70), indicating that the graphitic structure of MWNTs in the nanocomposites did not change much after functionalization in nitric acid or during the hydrothermal treatment.\textsuperscript{10} The new peak observed at 1616 cm\(^{-1}\) (Fig. 5(b)) is due to the interaction between FCNTs and TiNTs. This is in agreement with reported results.\textsuperscript{2c}

**BET surface area**

The surface area of the TP, TiNT and CTT nanohybrid photocatalysts are as shown in the Table 2. An increase in the surface area of the catalyst with increase in ratio of FCNTs to TiNT, is observed. Generally addition of FCNTs reduces the agglomeration of TiO\(_2\).\textsuperscript{6c} This property of FCNTs ensures the higher surface area of the nanohybrid with increase in FCNTs addition. The decrease in photocatalytic activity of the CTT-10, CTT-20 is due to high surface area where CNTs become recombination centers for the generated electron–hole pairs and is confirmed by the PL spectra.

**Photoluminescence spectra**

Fig. 6 displays the PL spectra of TiNT, CTT-1, -2, -10 & 20 in the wavelength range of 350–550 nm. TiNT showed broad spectrum centred around 375 nm, whereas the nanohybrid catalysts showed decrease in peak intensity in the following order CTT-1 < CTT-2 < CTT-10 < CTT-20. The CTT-20 catalyst displayed blue shift in PL intensity which is attributed to the decrease in TiO\(_2\).
component in nanohybrid catalyst. These results suggest that drastic reduction of charge carrier recombination with associated reduction of PL-intensity. Both CTT-1 and CTT-2 have lower peak intensity and hence showed higher rate of H₂ production (vide supra). Kim et al., compared the PL intensity of TiO₂/graphene carbon nanocomposites with TiO₂ itself, and they explained that strong interaction between excited electrons on TiO₂ particles and graphene diminished the peak intensity of nanocomposites, this phenomenon was attributed to decrease in charge carrier recombination.

Praveen Kumar et al., observed decrease in PL peak intensity with Cu₂O sensitized TiO₂ nanorods with nanocavities. They concluded that decrease in peak intensity is due to lower recombination rate of charge carriers localized in nanocavities of TiO₂ nanorods. These results are in agreement with earlier reports.¹⁰⁹,¹⁰⁰

Photocatalytic H₂ production activity

The photocatalytic performance of the FCNT/TiO₂ nanotube was evaluated by H₂ evolution in the presence of 5 vol% glycerol aqueous solution, which is the sacrificial reagent, under natural solar irradiation. Fig. 7 shows the H₂ production activity of TiNT, CTT-1, 2, 10 & 20 photocatalysts with increase in solar irradiation time. Linear increase in the H₂ production activity of all the photocatalysts is observed with increase in time. H₂ production activity is enhanced with the addition of FCNT to TiNT. Also, H₂ production activity of CTT-1 and CTT-2 showed enhanced and almost similar activity. This enhancement may be attributed to higher surface area of FCNT and better bonding of FCNT and TiNT. H₂ production activity of CTT-10 showed lower solar photocatalytic H₂ production than unmodified TiNT due to losses in light absorption and electron–hole recombination. Among CTT nanohybrids CTT-2 showed highest H₂ production of 7476 μmol h⁻¹ g⁻¹.

CTT nanohybrid also shows increase in H₂ production activity due to FCNT acting as both co-catalyst and sensitizer. However (TiO₂ nanotubes/FCNTs) CTT samples showed higher activity compared to other TiO₂/MWCNTs photocatalyst reported in literature mainly due to the following reasons. Formation of Ti–O–C at the interface of TiO₂ and FCNTs favours the effective charge transfer between them. Also, the 1D tubular structures of TiO₂ nanotubes, in addition to the FCNTs, which allowed uni-directional flow of electrons, hence reducing electron–hole recombination.

Photocatalytic stability

Fig. 8 depicts amount of the H₂ production tested for 4 h in 4 cycles of study. These results reveal that almost identical amount of the H₂ generation was recorded in the all the four experiments. The minor decrease in the total H₂ generation was observed in 3rd and 4th cycles which can be attributed to the poor surface interaction of reaction intermediates formed during oxidation of glycerol in solution. These intermediates could have been adsorbed onto the surface of the photocatalyst which influenced the light penetration to the surface and resulted decrease in the rate of the H₂ production. The stability of TiNTs under recycling conditions was reported elsewhere.

Table 2  BET surface area of TiNT and CTT photocatalysts

<table>
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<th>S. No.</th>
<th>Nanohybrid</th>
<th>SBET (m² g⁻¹)</th>
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<tr>
<td>1</td>
<td>CTT-1</td>
<td>121.8</td>
</tr>
<tr>
<td>2</td>
<td>CTT-2</td>
<td>120.5</td>
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<tr>
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<td>TiNT</td>
<td>70.2</td>
</tr>
<tr>
<td>6</td>
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<td>50</td>
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Fig. 5  (a) Raman spectra of CTT-2 catalyst and (b) its expanded view from 1500 to 1640 cm⁻¹.
the enhanced rate of H\textsubscript{2} production under solar and visible light irradiation.\textsuperscript{10c,d}

Structure activity correlation

Based on the characterization results of the data it is evident that impregnation of FCNTs with TiNT's resulted in well dispersed catalysts and indicates strong interaction of FCNTs with TiNT. Electrons and holes get generated as the nanohybrid is exposed to sunlight in the conduction and valence bands respectively. Improvement in the visible light absorption and decreased band gap energy values of the nanohybrid could be due to the creation of intermediate energy levels of doped FCNTs. The possible photoexcitation and charge transfer processes are as shown in the Fig. 9. Lu et al., deduced that band gap is probably reduced as a result of doping state creation near to the E\textsubscript{F}.\textsuperscript{10e} The electrons accumulated on the conduction band of TiNT could be transferred to H\textsuperscript{+} to produce H\textsubscript{2} while holes in the valence band of TiNT are consumed by the sacrificial agent glycerol which subsequently gets mineralized leading to suppression of recombination of photogenerated charge carriers and enhancement of H\textsubscript{2} production.

Conclusions

In conclusion this work resulted in synthesis of a series of novel functionalized carbon nanotube/TiO\textsubscript{2} nanotube nanohybrid materials by wet impregnation method to extend absorption to the visible region and also to retard the electron–hole pair recombination and thereby to enhance the H\textsubscript{2} production capability under solar light irradiation. The percentage addition of FCNTs to TiNTs influences the photocatalytic activity of CTT composite. Highest photocatalytic H\textsubscript{2} production was observed for CTT-2 photocatalysts mainly due to extension of absorption edge to the visible region and also by retardation of electron–hole recombination as compared to other photocatalysts.

Acknowledgements

Financial support from University Grants Commission (UGC), New Delhi, India (F. No. 43-405/2014), is gratefully acknowledged.

References


