

## Hydrothermal preparation of ZnO:CNT and TiO<sub>2</sub>:CNT composites and their photocatalytic applications

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Received: 8 November 2006 / Accepted: 11 July 2007 / Published online: 21 February 2008  
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**Abstract** ZnO:CNT and TiO<sub>2</sub>:CNT composites were fabricated under mild hydrothermal conditions ( $T = 150\text{--}240\text{ }^{\circ}\text{C}$ ) with an autogenous pressure. The as prepared composites were characterized using X-ray diffraction, Scanning electron microscopy and FTIR spectroscopy. Photocatalytic applications of the composites were investigated using indigo carmine dye. The effect of the catalyst content, pH of the medium, source and intensity of illumination on the photo-degradation of the indigo carmine dye was studied and the efficiency of the composites were investigated based on different parameters like percent transmittance (%T), percent decomposition, and chemical oxygen demand of the dye solution to obtain optimum treatment conditions. The results obtained exhibit higher photocatalytic activity when compared to the reagent grade ZnO, TiO<sub>2</sub> and hydrothermally prepared ZnO:AC and TiO<sub>2</sub>:AC composites.

### Introduction

Carbon nanotubes (CNTs) have generated a great deal of interest since their discovery [1] due to their unique physical [2], mechanical [3–5], electrical [6, 7] and thermal properties [8, 9]. The interest in using CNTs as catalytic support materials arises due to their large surface area; high aspect ratio and their ability to disperse catalytically active metal particles which play a significant role in catalytic applications. Most of the photocatalytic studies are employed using traditional TiO<sub>2</sub> and ZnO photocatalyst [10–13]. The design and development of highly efficient photocatalytic composites have attracted the interest owing to their potential applications for the degradation of toxic organic dyes and industrial effluents. Composites prepared using different semiconducting metal oxides and carbon materials are currently the active photocatalytic materials for the degradation of dyes and industrial effluents. CNTs have been successfully used as catalyst supporting materials with properties superior to that of other regular catalyst-supports like activated carbon, soot or graphite [14]. CNTs were recently found to be able to adsorb some toxic gases such as dioxins [15], fluoride [16], lead [17], alcohols [18] and other toxins better than materials used currently as filters like activated carbon or other polyaromatic materials.

Different techniques have been employed to coat carbon supports for specific applications. The first TiO<sub>2</sub> coating by hydrolysis of TiCl<sub>4</sub> was realized on active carbon fibers [19] in order to obtain absorptive materials for NH<sub>3</sub>. TiO<sub>2</sub> has been deposited by sol–gel method on carbon fibers in order to increase the thermal stability [20]. Activated carbon spheres coated with TiO<sub>2</sub> by hydrothermal treatment demonstrated very good performance in photocatalytic degradation of methylene blue [21]. Preparation of CNT–TiO<sub>2</sub> composites by sol–gel, hydrolysis and hydrothermal

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method has also been reported [22, 23]. On the other hand ZnO coated carbon nanotubes using the filtered cathodic vacuum arc technique and growth of ZnO nanowires on modified well-aligned CNT arrays by hydrothermal process is also reported [24, 25]. The present work is based on the previous work carried out on ZnO:AC [26] and TiO<sub>2</sub>:AC [27] by our group. Photocatalytic properties of the hydrothermally prepared CNT composites have been studied and reported for indigo carmine dye.

## Experimental

### Preparation of ZnO:CNT composites

Multiwalled carbon nanotube (MWCNT) used in the present work was provided by Beijing Key Lab of Green Chemical Engineering, Tsinghua University, Beijing, PR China. Zinc hydroxide gel was prepared by hydrolyzing commercially available zinc nitrate hexahydrate (LR LOBA Chemicals, India). The prepared zinc hydroxide gel was mixed with MWCNTs in a definite ratio and ultrasonicated for 5 min. The solution was transferred into a Teflon liner and 3 mL of formic acid was added as mineralizer. The experimental run was carried out in Teflon (PTFE) lined autoclaves made of SS 316, at 150 °C and 240 °C for 40 h in a hot air oven. At the end of the experiment, the system was quenched by cooling with compressed air. The run product was washed repeatedly with double distilled water and dried at 50 °C in a dust proof environment. The same procedure was followed when reagent grade ZnO was used as a precursor, but in case of ZnCl<sub>2</sub>, 1 M NaOH was used as a mineralizer.

### Preparation of TiO<sub>2</sub>:CNT composites

Commercially available titanium isopropoxide (LR Across Organics, Belgium) of 4 mL was mixed with as received MWCNTs of 0.005 gm. The solution was ultrasonicated for 5 min to get uniform dispersion and it was transformed to a Teflon liner along with 3 mL H<sub>2</sub>SO<sub>4</sub> (1 M) as mineralizer. The autoclave assembly was kept in a hot air oven maintained at 150 °C for 40 h. In case of reagent grade TiO<sub>2</sub> as starting charge, 1 M HCl and 1 M HNO<sub>3</sub> were used as mineralizers under the same experimental conditions. The run product obtained was washed thoroughly with double distilled water and dried at 50 °C in a dust proof environment.

### Characterization

XRD patterns of the composite powders were obtained using powder X-ray diffractometer (XRD, M/s Bruker

AXS, 40 kV, Germany). The nature of the crystalline phases present in the prepared composites was checked using the database of the JCPDS, PCPDF WIN version 2.01. The SEM photographs of the prepared CNT composites were taken using TSL MSC-2200 instrument (Tex SEM Laboratories Inc., USA). The FTIR spectra of the composites were recorded using FTIR spectrophotometer (JASCO-460 PLUS, Japan).

### Photocatalytic studies

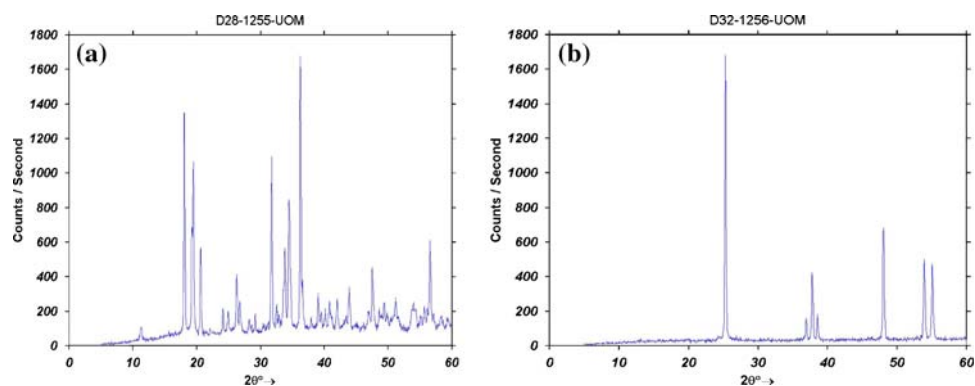
In the photocatalytic treatment of Indigo carmine dye, a known concentration of  $1 \times 10^{-5}$  M dye solution (50 mL) was taken in a 500 mL clean beaker. A known amount of catalyst (TiO<sub>2</sub>:CNT, ZnO:CNT) was added into this dye solution. It is to be noted that no external supply of oxygen was employed. Then the beaker was exposed to sunlight and UV light independently. The intensity of UV and sunlight was estimated by photolysis of uranyl oxalate [28]. It was found that UV light had an intensity of  $2.3775 \times 10^{15}$  quanta per second and sunlight had an intensity of  $6.722 \times 10^{16}$  quanta per second. Dye sample of about 2–3 mL was taken out at a regular time interval from the test solution, it was centrifuged for 5 min at 950–1,000 rpm and then used in the measurement of %T at 540 nm using UV/VIS spectrophotometer (Model: Minispec SL 171, Elico, India), light source used for illumination in the photocatalytic degradation experiment was UV tube (8 W, Sankyo, Denki, Japan). Chemical oxygen demand (COD) was estimated before and after the treatment (using K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> oxidation method) for the photocatalytic experiment in the present work.

## Results and discussion

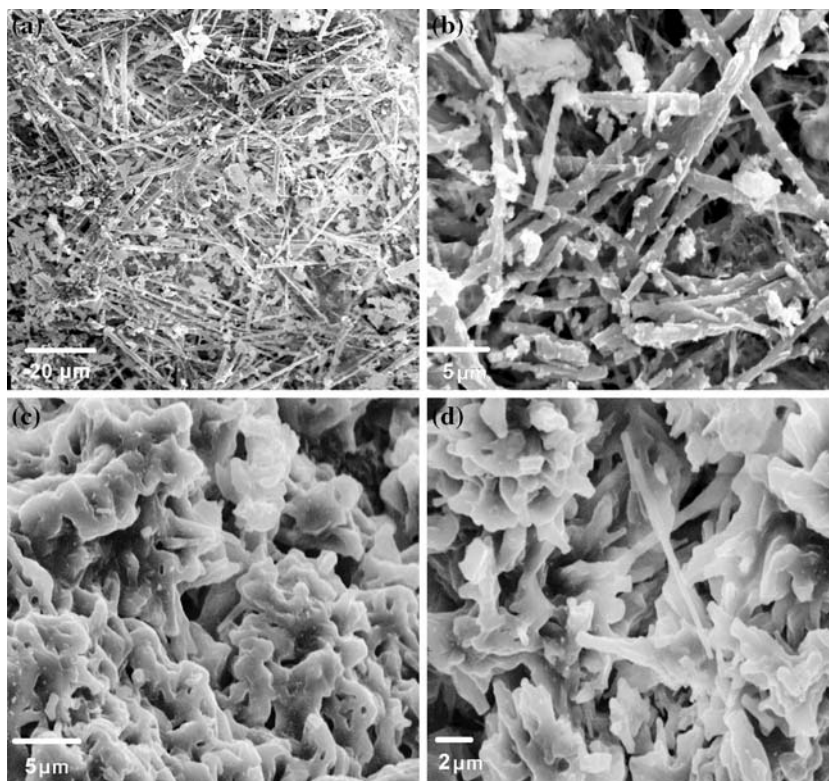
### Characterization of ZnO:CNT and TiO<sub>2</sub>:CNT composites

The X-ray powder diffraction patterns of ZnO:CNT and TiO<sub>2</sub>:CNT composites are shown in Fig. 1. The crystalline phases of TiO<sub>2</sub> (anatase) and ZnO was accomplished by comparison with JCPDS files 832,243 and 870,075 respectively (PCPDF WIN version 2.01). SEM images taken at different magnification give an overview of the prepared composites. The representative SEM micrographs are shown in Fig. 2. CNTs act as substrates for the growth of ZnO and TiO<sub>2</sub> crystallites. The formation of ZnO and TiO<sub>2</sub> and their compounding with the CNTs has happened simultaneously in the hydrothermal process. FTIR spectra of the commercial CNT, reagent grade ZnO, TiO<sub>2</sub> and prepared photocatalytic composites are shown in Fig. 3A and B, respectively. The bonding between Ti–O is clearly represented in the region of

**Fig. 1** X-ray diffraction patterns of hydrothermally prepared ZnO:CNT (a) and TiO<sub>2</sub>:CNT composites (b)



**Fig. 2** SEM images of ZnO:CNT (a, b) and TiO<sub>2</sub>:CNT composites (c, d)



470–500  $\text{cm}^{-1}$  (Fig. 3B) and the bands near 476 and 522  $\text{cm}^{-1}$  represent Zn–O bond (Fig. 3B). On the other hand –C=C– bond is represented at 1,570  $\text{cm}^{-1}$  in the prepared composites. Other characteristic bands are generated due to different mineralizers used in the preparation of composites. FTIR studies indicate successful hydrothermal preparation of ZnO:CNT and TiO<sub>2</sub>:CNT composites.

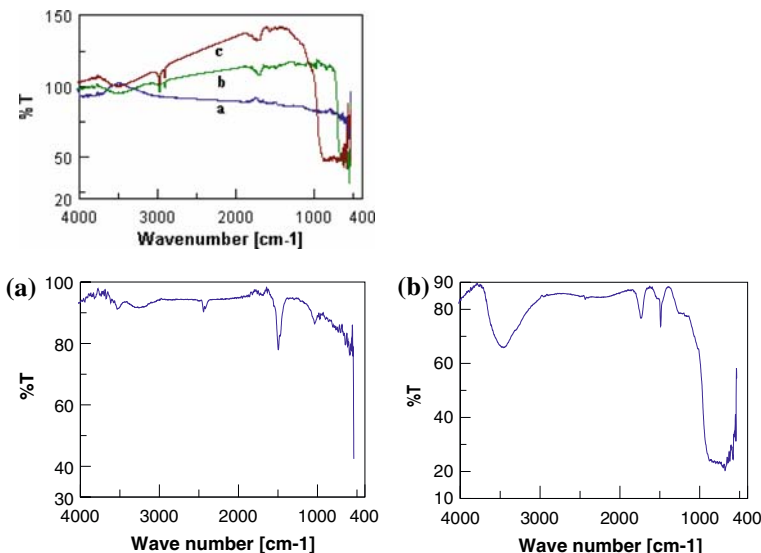
#### Photocatalytic activity of TiO<sub>2</sub>:CNT and ZnO:CNT composites

The photocatalytic experiments were carried out in order to test the activity of TiO<sub>2</sub>:CNT and ZnO:CNT composites in the degradation of indigo carmine dye and to compare its efficiency with reagent grade TiO<sub>2</sub> and ZnO. It was found

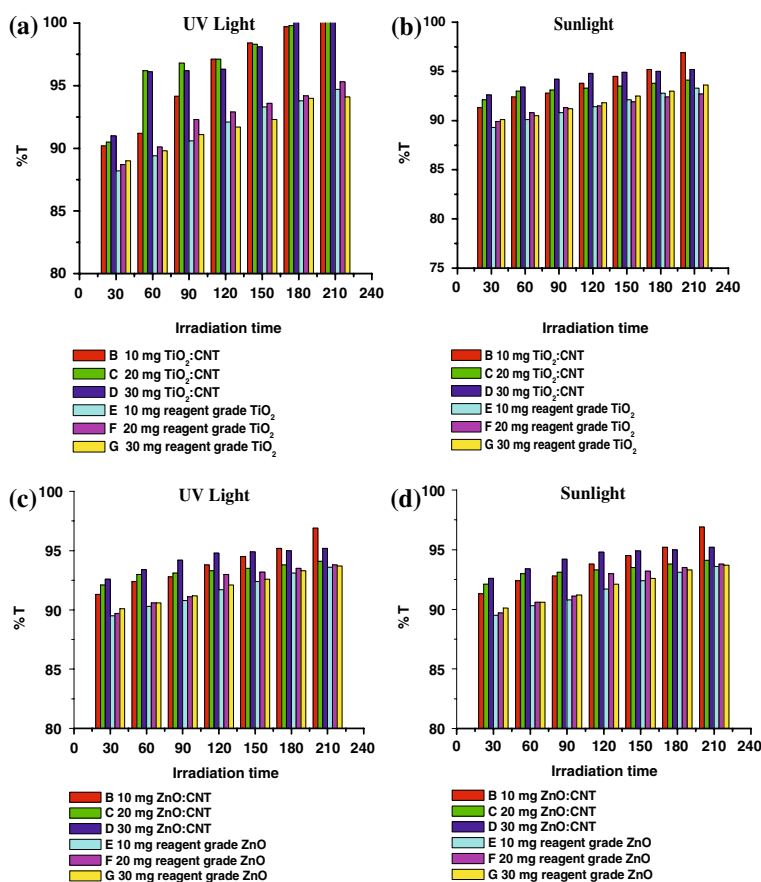
that the hydrothermally prepared TiO<sub>2</sub>:CNT and ZnO:CNT show very high photocatalytic efficiency when compared with the untreated reagent grade TiO<sub>2</sub> and ZnO. The Fig. 4 gives the percent transmission (%T) vs. irradiation time for TiO<sub>2</sub>:CNT, ZnO:CNT, TiO<sub>2</sub> and ZnO with varying amount of catalyst (10–30 mg). The increase in the %T reveals the efficiency of the composite. Both sunlight and UV light were used as the source of illumination in the present photocatalytic degradation experiments.

The efficiency of the composites used in the photocatalytic reaction depends on various parameters like nature and concentration of the organic substrate, concentration and type of semiconductor, nature of the light source and its intensity, pH of the medium, etc [29–32]. In order to ensure a constant illumination and intensity, UV light was considered as the source of light.

**Fig. 3** (A) FTIR spectra of commercial CNT (a), reagent grade ZnO (b) and TiO<sub>2</sub> (c). (B) FTIR spectra of hydrothermally prepared TiO<sub>2</sub>:CNT (a) and ZnO:CNT composites (b)



**Fig. 4** Comparative study of TiO<sub>2</sub>:CNT (a, b) and ZnO:CNT (c, d) with reagent grade TiO<sub>2</sub> and ZnO on %T of indigo carmine dye solution



*Effect of pH on the photodegradation of indigo carmine dye*

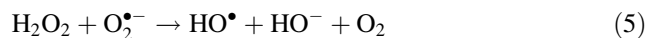
The efficiency of the photocatalytic process strongly depends upon the pH of the dye solution [33] which was adjusted using varying concentration of HNO<sub>3</sub> or NaOH. The result of the study has been presented in Fig. 5. The

maximum efficiency was observed either at extreme acidic or basic condition. This is in agreement with most of the previous studies [32, 33].

The change in pH of the solution varies with the dissociation of the dye molecule and also the surface properties of the composite used. The initial adsorption of the dye molecules onto the composite greatly depends on

the solution pH [34]. Increase in the degradation efficiency under the alkaline condition could be attributed to the increase in hydroxyl ions, which induce more hydroxyl radical formation. In acidic condition the perhydroxyl radical can form hydrogen peroxide, which in turn gives rise to the hydroxyl radical.

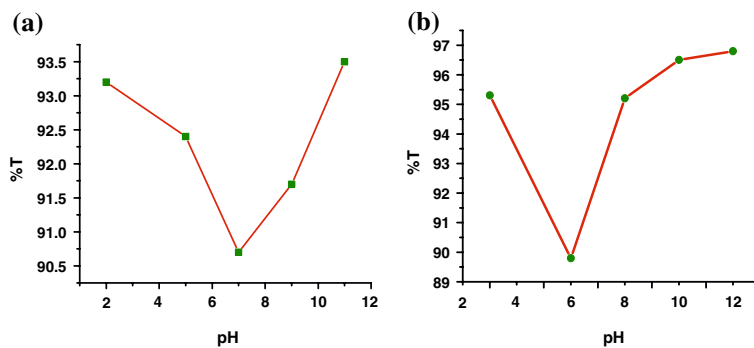
The Eqs. 1–7 indicate the possible radical formation reactions both at acidic and basic pH conditions.



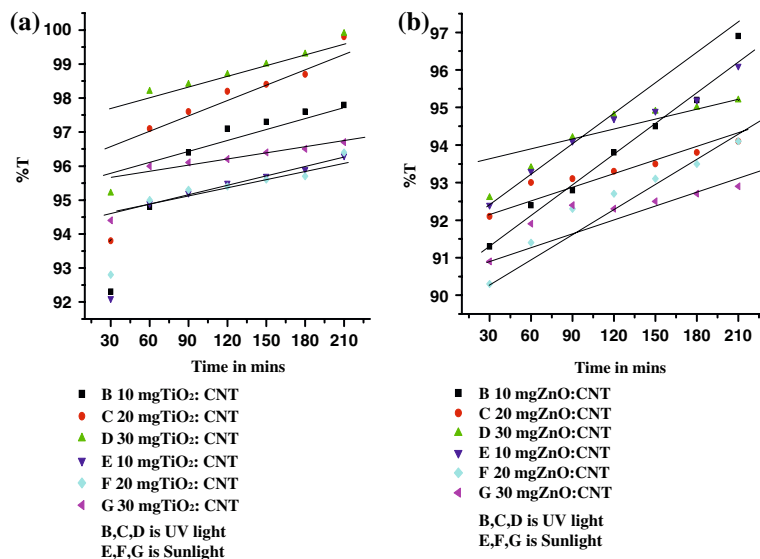
#### Effect of catalyst content

In order to determine the optimal amount of the photocatalyst, a series of experiments with a varying amount of TiO<sub>2</sub>:CNT composites have been conducted. The amount of the catalyst was varied between 10–30 mg/50 mL of the aqueous dye solution. The results of these experiments are shown in Fig. 6. The degree of decolourization of the dye solution increases with increasing amount of catalyst, and the highest efficiency was attained at 30 mg/50 mL in case

**Fig. 5** Effect of pH on %T of the indigo carmine dye using TiO<sub>2</sub>:CNT (a) and ZnO:CNT composites (b)



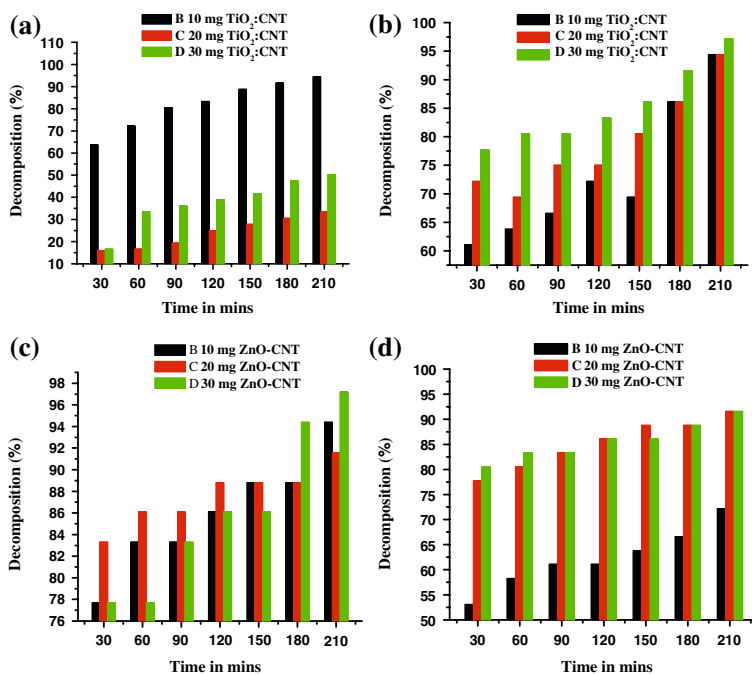
**Fig. 6** Effect of TiO<sub>2</sub>:CNT (a) and ZnO:CNT composites (b) on %T of the indigo carmine dye



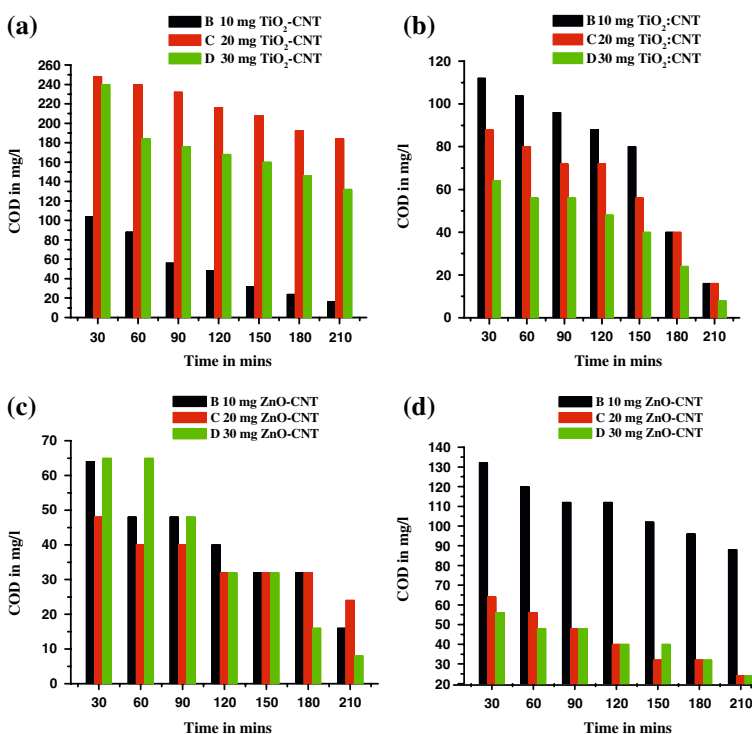
of TiO<sub>2</sub>:CNT both in sunlight as well as in UV light, and 10 mg/50 mL in case of ZnO:CNT and then decreases with an increase in the weight of the composite. An increase in the efficiency is due to the increase in number of active sites in TiO<sub>2</sub>:CNT and ZnO:CNT composites available for the reaction, which in turn increases the rate of radical formation.

The reduction in the decomposition efficiency may be due to the reduction in the penetration of light with surplus amount of TiO<sub>2</sub>:CNT and ZnO:CNT. The surplus addition of the composite makes the solution more turbid which in turn reduces the light penetration reaching the composite surface. Further addition of surplus amount of composite will also results in the deactivation of activated molecules

**Fig. 7** Decomposition of indigo carmine dye using TiO<sub>2</sub>:CNT under UV light and sunlight (a, b) and decomposition of indigo carmine dye using ZnO:CNT under UV and sunlight respectively (c, d)



**Fig. 8** Reduction in COD of the indigo carmine dye using TiO<sub>2</sub>:CNT under UV and sunlight (a, b) and reduction in COD of the indigo carmine dye using ZnO:CNT at different time intervals under UV and sunlight (c, d)





by collision with ground state molecules and photodegradation efficiency drops down.

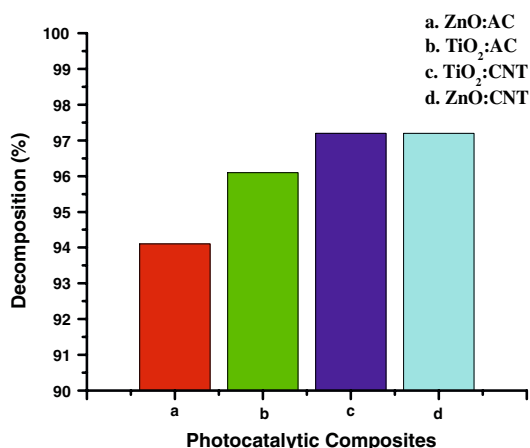
#### Photocatalytic degradation of indigo carmine dye solution

Photocatalytic degradation efficiency on the indigo carmine dye was carried out using both  $\text{TiO}_2$ :CNT and  $\text{ZnO}$ :CNT composites under both sunlight and UV light. Figure 7 shows the decomposition rate of the dye molecules with respect to the weight of the composite used. Figure 8 shows the reduction in COD of the dye solution, which confirms the destruction of the organic molecules present in the dye solution.

The comparative study was made to know the decomposition rate efficiency of  $\text{TiO}_2$ :CNT and  $\text{ZnO}$ :CNT composites. The results obtained by  $\text{TiO}_2$ :CNT and  $\text{ZnO}$ :CNT were found to be higher when compared with the results of  $\text{ZnO}$ :AC and  $\text{TiO}_2$ :AC composites (Fig. 9).

#### Conclusion

Based on the above observations we conclude that  $\text{TiO}_2$ :CNT and  $\text{ZnO}$ :CNT composites were successfully fabricated using hydrothermal technique under mild *PT* conditions. CNTs act as substrates for the growth of  $\text{ZnO}$  and  $\text{TiO}_2$  crystallites. The crystallization of  $\text{ZnO}$  and  $\text{TiO}_2$  and their compounding with the CNTs happened simultaneously in this process, which is convenient to fabricate CNT based composites with different ratios since CNTs are stable up to 600 °C and pressure of 100 MPa under hydrothermal conditions [35]. The composites prepared were found to be very effective in the degradation of indigo carmine dye. The efficiency of the composites was studied



**Fig. 9** Decomposition of indigo carmine dye using different photocatalytic composites

based on different parameters like %T, decomposition (%), and COD of the dye solution to obtain optimum treatment conditions. The increase in the photodegradation efficiency is due to large surface area and high aspect ratio of CNTs and change in the morphology of  $\text{ZnO}$  and  $\text{TiO}_2$  due to higher degree of crystallinity obtained by hydrothermal method. It is expected that large scale production of CNTs in recent years will decrease CNT cost almost equal to that of activated carbon, which opens an interesting field in tackling environmental issues like degradation of toxic dyes and industrial effluents at nanometer scale. Further work is in progress for different dyes and industrial effluents.

**Acknowledgements** The authors wish to thank Dr. S. Ananda, DOS in Chemistry, for fruitful discussions and Dr. G. V. Narasimha Rao, ARC International, Hyderabad, for X-ray patterns. This work is supported by Department of Science and Technology, New Delhi, India.

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