Original Article

**TiO<sub>2</sub> nanoparticles immobilized on carbon nanotubes for enhanced visible-light photo-induced activity**

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**A B S T R A C T**

CNT-TiO<sub>2</sub> nanocomposites were prepared through (i) simple mixing of as prepared CNTs and TiO<sub>2</sub> nanoparticles (NPs), (ii) simple mixing of as prepared CNTs and TiO<sub>2</sub> NPs followed by heat treatment and (iii) simple mixing of as prepared CNTs and TiO<sub>2</sub> NPs followed by UV illumination. The synthesis of CNTs and TiO<sub>2</sub> NPs were performed individually by arc discharge in water and sol-gel methods, respectively and characterized by X-ray diffraction (XRD), ultra violet and visible spectroscopy (UV–vis), Fourier transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The visible-light photocatalytic performance of CNT–TiO<sub>2</sub> nanocomposites was successfully demonstrated for the degradation of Rhodamine B (Rh. B) as a model dye at room temperature. It is found that CNT–TiO<sub>2</sub> nanocomposites extended the light absorption spectrum toward the visible region and considerably improved the photocatalytic efficiency under visible-light irradiation. The visible-light photocatalytic activities of CNT–TiO<sub>2</sub> nanocomposites in which CNTs are produced by arc discharge in deionized (DI) water at 40, 60 and 80 A arc currents and combined through three different protocols are also investigated. It was found that samples prepared at 80 A arc current and 5 s arc duration followed by UV illumination revealed best photocatalytic activity compared with the same samples prepared under simple mixing and simple mixing followed by heat treatment. The enhancement in the photocatalytic property of CNT–TiO<sub>2</sub> nanocomposites prepared at 80 A arc current followed by UV illumination may be ascribed to the quality of CNTs produced at this current, as was reported before.

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1. Introduction

Titanium dioxide has been widely used as an efficient photocatalytic material in decomposing toxic organic molecules to H₂O, CO₂ and other harmless molecules [1,2]. This property also has been applied in inactivation of bacteria and harmful components from water and air, as well as in self-cleaning or self-sterilizing surfaces for places such as medical centers [3–6]. But, the problem is that the band edge of TiO₂ photocatalyst lies in the UV region which covers about 4% of the solar spectrum [7]. Consequently conventional TiO₂ photocatalysts are inactive under visible-light irradiation and as a result with limited practical applications [8]. In this regard, researchers have been interested in the modification of electronic and optical properties of this semiconductor for its efficient use in environmental purification under visible-light irradiation [9,10].

Strategies of making TiO₂ visible-light-active photocatalyst usually classified into three main categories: doping TiO₂ with transition metal ions such as V, Cr, Mn, Fe, Ag, Co, Ni, C; doping nitrogen into TiO₂ and coupling of TiO₂ with a small band-gap semiconductor which extends light absorption into the visible region. Although lots of reports are available on nitrogen and silver doped TiO₂ as two common ways for making visible-light-active photocatalyst but, carbon doped TiO₂ was also as an appropriate alternative among researchers in past years [11,12].

Li and co-workers prepared CNT–TiO₂ nanocomposites using sol–gel method. They have shown that TiO₂ film thickness on the surface of CNTs is the key factor controlling electron transfer and photocatalytic activity in CNT/TiO₂ hybrid nanostructures. It is found that thinner TiO₂ layer enhances photodegradation of methylene blue and higher CNT content in the composites correlates with higher photocurrents and electronic conductivity of the nanocomposites catalyst film increases [13]. Bouazza et al., also synthesized CNT–TiO₂ nanostructures through sol–gel method for the photocatalytic oxidation of propene. They have found CNT–TiO₂ nanocomposites with 70% of TiO₂ and 30% of CNT, shows the highest photocatalytic activity for the oxidation of propene [14].

While most of the reported works for synthesis of visible-light-active TiO₂ were based on sol–gel, hydrothermal or conventional chemical methods [15–23], in this work we introduce a new approach to prepare visible-light-driven TiO₂ photocatalyst using through three different coupling alternatives: (i) simple mixing of as prepared CNTs and TiO₂ nanoparticles (NPs), (ii) simple mixing of as prepared CNTs and TiO₂ NPs followed by heat treatment and (iii) simple mixing of as prepared CNTs and TiO₂ NPs followed by UV illumination.

There are some well defined techniques for synthesis of CNTs, the most common ways of which are chemical vapor deposition (CVD), laser ablation (LA) and electrical arc discharge [24–26]. Among these methods, electrical arc discharge in liquid for production of CNTs attracted much attention because of simplicity of apparatus building, low impurity introduction, no need for complicated vacuum equipment, high-throughput, and cost-effective procedure to generate a high yield of CNTs. The simplicity of this method also allows scaling up for mass production of CNTs [27].

In this study, CNTs and TiO₂ NPs individually were prepared by arc discharge in water and sol–gel methods and then combined through three different coupling alternatives to form CNT–TiO₂ nanocomposites. We have specifically studied the effect of each coupling method on photocatalytic performance of CNT–TiO₂ nanocomposites under visible-light illumination.

2. Experimental details

2.1. Synthesis of TiO₂ NPs

For synthesis of TiO₂ NPs 1 mL TiCl₄ (Merck, 99%) was slowly added dropwise into 10 mL ETOH (Merck, 99.8%) under vigorous stirring at room temperature. A large amount of HCl gas was exhausted and a transparent yellowish solution was formed. The as prepared solution was dried at 100 °C for 24 h leading to a white amorphous gel. The extracted powder was then annealed at 450 °C for 1 h leading to white crystalline TiO₂ nanopowder.

2.2. Synthesis of CNTs

The arc discharge method in DI water was used for synthesis of CNTs. The arc discharge set up includes a high current DC power supply and a reactor including anode, cathode and a micrometer which moves the anode toward the cathode, as we have reported in details in our previous works as a novel technique for synthesis of various nanostructures [27]. In a typical discharge process a 40–80 A current was applied between two graphitic electrodes in DI water. The voltage was dropped to about 10–20 V during the arc formation while the current was fixed to a desired amount. Both the anode and cathode were wire shaped, 2 mm in diameter and 99.9% purity (from Sigma–Aldrich). Initially, we bring the two electrodes into touch leading to a small contact cross section and thus to a high current density. Then we separate them from each other and as a result graphite is ablated from the anode and then condensed in solution and CNTs in addition to some carbonaceous nanostructures are formed.

2.3. Purification of CNTs

For purification of CNTs and removing unwanted products such as amorphous carbon, carbon particles and other carbonaceous structures three distinct processes were performed. First, the as prepared solution was dried at 100 °C for 24 h to get a black powder. The powder was then dispersed in ethanol medium and sonicated (using a 30 kHz power for 30 min) for 1 h followed by drying at 60 °C for 12 h and annealing at 500 °C for 1 h. Then, the obtained powder dispersed in 10 mL HCl (Merck, 99%) and sonicated for another 30 min. Finally, all samples centrifuged and washed with DI water followed by drying at 100 °C for 12 h and annealing at 500 °C for 1 h as the last step of purification process.
2.4. Synthesis of CNT–TiO₂ nanocomposites

Three different strategies including simple mixing, UV illumination and heat treatment were performed for coupling of TiO₂ NPs and CNTs. In simple mixing method 0.1g of TiO₂ powder and 0.02g purified CNTs were dispersed and mixed in 100mL DI water under slow stirring rate at room temperature for 15 min. In UV illumination method the suspension prepared by simple mixing method exposed to UV illumination with 254nm wavelength for 2h while stirring slowly at room temperature. In the heat treatment method the suspension prepared by simple mixing method dried at 100°C for 24h and then annealed at 500°C for 1h. This value is the temperature that causes oxidation of amorphous carbon while does not change significantly the anatase crystalline phase of TiO₂ NPs.

2.5. Characterization

Analysis of the crystalline structures was performed by XRD diffractometer (X’pert Philips) equipped with a Philips high intensity ceramic sealed tube (3kW) X-ray source and wavelength of Cu Ka (λ ~ 1.5405 Å) radiation in 2θ range from 10° to 90° by 0.005° s⁻¹ steps. UV–vis spectroscopy of the samples was taken out by a double beam Optizen POP spectrophotometer (Mecasys Company, Korea) from 200 nm to 1100 nm wavelengths. A Pyris 1 TGA thermogravimetric analyzer was used for the analysis of the composition of CNTs. 1mg of the sample was heated from 50°C to 1000°C with a heating rate of 10°C min⁻¹ under ambient air. FT-IR analysis was performed by a Thermo Nicolet spectrometer equipped with a MCT detector (4 cm⁻¹ resolution) and a 100mW Nd:YAG laser with wavelength of 1064 nm. The spectral resolution was 0.5 cm⁻¹, spot size was 10 mm and precision of wavelength was 0.01 cm⁻¹. SEM analysis was taken out by a SEM instrument (Philips XL30) at 5–20 keV accelerating energy. Before taking images all samples were coated with a 10 nm gold layer using a physical vapor deposition system from Bal-Tec company (Switzerland). TEM analysis was performed by a LEO 912 AB instrument at 150–200 keV accelerating energy by deposition of nanoparticles onto the copper grid at room temperature. DI water was supplied from a Millipore water purification system (Direct-Q-3) with 18.2 MΩ cm (0.055 µS) resistance.

2.6. Photocatalytic activity measurement

Photocatalytic activity of the CNT–TiO₂ nanocomposites was measured by photodegradation of Rh. B as a model dye with the initial concentration and volume of 10⁻⁵ M and 30 mL respectively at the presence of 30 mL CNT–TiO₂ solution. First the mixed Rh. B and CNT–TiO₂ solution was stirred in dark for 30 min to equilibrate the absorption/desorption between dye molecules and TiO₂ photocatalyst. Then it was irradiated at room temperature by a 90W halogen lamp. The degradation rate was measured by UV–Vis spectrophotometer at the maximum absorption wavelength of Rh. B.

3. Results and discussion

3.1. XRD analysis of the products

XRD analysis was taken out to find the crystalline phase and structure of the products. The results for pure TiO₂ and CNT–TiO₂ samples are depicted in Fig. 1. XRD results of TiO₂ NPs shows formation of anatase phase peaks at 2θ = 25.3, 37.7, 47.8, 54, 62.7 and 75.2 degree with no impurity which is in agreement with 21-1272 standard card from JCPDS [22]. Crystallographic data obtained from XRD demonstrates co-existence of both TiO₂ and CNT in samples prepared by simple mixing and also samples followed by heat treatment or UV illumination. Due to the similar patterns, XRD analysis of
the simple mixed CNT–TiO₂ sample is only demonstrated in Fig. 1b as representative. The peak appeared at 2θ = 26.95° is related to formation of (002) planes of CNTs in which the intensity of TiO₂ peaks somehow decline by mixing CNT with TiO₂ NPs [10]. This is while the main anatase phase peak is still visible at 2θ = 25.3° which is related to (101) crystalline planes of anatase TiO₂. This calcination temperature was selected both to have a crystallized anatase TiO₂ and avoid from remarkable loss of CNTs from the CNT–TiO₂ structures at higher temperatures (see for example thermal gravimetric analysis (TGA) in Fig. 1c). TGA of pristine CNT showed a negligible mass loss at 500 °C but, above this temperature a progressively increasing rate of mass loss was observed up to the combustion point of 700 °C. Presence of CNTs in TEM images after calcination at 500 °C confirm intactness of the CNTs in this temperature. In fact, between 500 and 700 °C a significant weight loss was observed due to the decomposition of CNTs, as reported by Li and co-workers [13].

Fig. 2 – FT-IR spectra of CNT–TiO₂ nanocomposites in which CNTs are prepared at 40 A and (a) simple mixed, (b) simple mixed followed by heat treatment, (c) simple mixed followed by UV illumination, CNTs are prepared at 60 A and (d) simple mixed, (e) simple mixed followed by heat treatment, (f) simple mixed followed by UV illumination, CNTs are prepared at 80 A and (g) simple mixed, (h) simple mixed followed by heat treatment and (i) simple mixed followed by UV illumination.

3.2. FT-IR spectroscopy

Fig. 2 demonstrates FT-IR spectra of CNT–TiO₂ nanocomposites in which CNTs prepared at 40, 60 and 80 A arc currents using arc discharge method and combined through the three mentioned alternatives. The bands at 2847 and 2910 cm⁻¹ are assigned to the symmetric and anti-symmetric C–H band related to CH₂ and CH₃ stretching vibrations, respectively. The sharp band of COOH group at 1720 cm⁻¹ and 1460 cm⁻¹ is related to the anti-symmetric C–H mode of CH₃ bending vibrations due to the presence of CNTs [28,29]. The peaks at 560 cm⁻¹ and 1090 cm⁻¹ are also attributed to the bending vibrations of Ti–O–Ti and Ti–O–C bonds [30]. In fact, modification of band gap energy of TiO₂ and extension of light absorption into the visible region is due to the presence of
Ti–O–C bonds which causes reduction of band gap energy for photogenerating of electrons and holes. The IR absorption at 3400 cm\(^{-1}\) also arises from the superposition of the OH mode of interacting hydroxyl groups and symmetric and anti-symmetric OH modes of molecular water coordinated to Ti\(^{4+}\) cations [28,31].

3.3. Microscopic studies

The shape and size distribution of produced nanostructures were characterized by both SEM and TEM analyses. Fig. 3a–c shows SEM images of bare TiO\(_2\) NPs prepared via sol–gel, pure CNTs prepared by arc discharge at 80 A arc current and the CNT–TiO\(_2\) nanocomposites prepared by simple mixing methods, respectively. The results reveal that nearly spherical TiO\(_2\) NPs with an appropriate size distribution are formed during the sol–gel process. Furthermore, Fig. 3b clearly reveals formation of high quality CNTs by arc discharge method after purification process. Moreover, it was found that TiO\(_2\) NPs are well decorated on CNTs surface through simple mixing method. These results show that it is possible to easily decorate CNTs with TiO\(_2\) NPs by simple mixing.

As clarified by SEM analysis CNTs with average diameter of ~50 nm were obtained in purified samples. TEM analysis provides more insight into the specific details of nanostructures due to the higher resolution. Fig. 4a–c demonstrates TEM images of bare TiO\(_2\) NPs prepared via sol–gel, pure CNTs prepared by arc discharge at 80 A arc current and the CNT–TiO\(_2\) nanocomposites prepared by simple mixing method, respectively. TEM images of the CNT–TiO\(_2\) samples show the existence of well spread TiO\(_2\) NPs, with almost narrow size distribution, along the tube walls of the samples (see Fig. 4d). In all three different coupling approaches, TiO\(_2\) NPs were well decorated on the surface of CNTs and there was not any remarkable difference in the corresponding TEM images and therefore one of them is presented.

These results confirm that in all three coupling alternatives TiO\(_2\) NPs attach to the CNT surface and form CNT–TiO\(_2\) nanocomposites. But as we reported in details in our previous work the type of bonding is physisorption and TiO\(_2\) NPs may detach from the CNT surface through some severe mechanical process such as sonication [10]. This implies that TiO\(_2\) NPs may attach to the CNTs surface through van der Waals interactions.

3.4. Photocatalytic activity measurements

Fig. 5 illustrates the final kinetic curves of changes in Rh. B concentration under visible-light illumination for the CNT–TiO\(_2\) nanocomposites through three different coupling alternatives. As is clear from the results the reaction rate changes are linear, which indicates that the photocatalytic reactions on CNT–TiO\(_2\) surface can be expressed by the Langmuir–Hinshelwood model. The reaction rate after the adsorption equilibrium can be expressed as

\[-\ln \left( \frac{C}{C_0} \right) = Kt\]

where \(C\) and \(C_0\) are the reactant concentration at time \(t=t\) and \(t=0\), respectively, \(K\) and \(t\) are the apparent reaction rate constant and time, respectively. In comparison with the
samples prepared by the same currents and different methods, UV illumination method had more influence on photocatalytic activity. Also by comparing Fig. 5a–c we observe that in each coupling method, 80 A sample has had the most influence on photocatalytic activity. So 80 A sample prepared via UV illumination method showed the highest photocatalytic yield among purified samples.

Fig. 6 demonstrates changes of Rh. B concentration under visible-light illumination for the samples with the best photocatalytic performance, pure TiO₂, blank Rh. B as a control and a commercial TiO₂ photocatalyst (Degussa P25) for comparison. As is clear from the results the sample prepared at 80 A arc current and 5 s arc duration has had the most photocatalytic activity among all samples. A summary of the reaction rate constants of CNT–TiO₂ nanocomposites prepared through the mentioned coupling methods is presented in Table 1. Also, a similar photocatalytic behavior and reaction rate constants of all mentioned samples were observed under UV light illumination and since the main objective of this study was the photocatalytic performance under visible-light irradiation, those data are not shown here.

### 4. Conclusion

CNT–TiO₂ nanocomposites were prepared using three different coupling protocols. XRD analysis revealed the formation of both CNT and TiO₂ phases and co-existence of them in composites. Furthermore, microscopic studies confirmed that the prepared TiO₂ NPs deposited onto the CNTs surface in all three different coupling alternatives. Photocatalytic performance of the CNT–TiO₂ nanostructures for decolorization of
Rh. B under visible-light irradiation showed that CNT incorporated into TiO$_2$ matrix, improved the photocatalytic efficiency under visible-light irradiation. It was found that samples prepared at 80 A under UV illumination method have had the best photocatalytic activity compared with simple mixed and heat treated CNT and TiO$_2$ samples. In fact introducing CNT into TiO$_2$ matrix facilitates longer charge separation by trapping photogenerated electrons and thus higher photocatalytic activity under visible-light irradiation.

**Conflicts of interest**

The authors declare no conflicts of interest.

**Acknowledgment**

This work was supported by Iran National Science Foundation (INSF).

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