

Effect of swift heavy ion irradiation on CNT- TiO₂ composite for medical applications

P. KUMARESAN*, P. AMBALAVANAN

P. G. Department of Physics, Thiru. A. Govindasamy Government Arts College, Tindivanam-604 002, Tamil Nadu, India

Photocatalytic hydrogen production using suspended photo catalysts were studied. TiO₂ anatase in a powder form was used as photo catalyst. Our investigation aims to wards the creation of improved photo catalysts to be used in the production of hydrogen from water or aqueous solutions of organic compounds. TiO₂ anatase in a powder form was used originally as photo catalyst. It was found that the photocatalytic activity depends significantly on catalyst type and its modification such as loading with various transition metal oxides. Carbon nanotube-anatase titanium dioxide (CNT-TiO₂) composite systems are currently being considered for many applications including their potential use to address environmental problems.

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1. Introduction

TiO₂ powders have been commonly used as white pigments from ancient times (1). They are inexpensive, chemically stable and harmless, and have no absorption in the visible region. Therefore, they have a white color. However, the chemical stability of TiO₂ holds only in the dark. Instead, it is active under UV light irradiation (2), inducing some chemical reactions. Such activity under sunlight was known from the flaking of paints and the degradation of fabrics incorporating TiO₂. Scientific studies on such photo activity of TiO₂ have been reported since the early part of the 20th century (3). For example, there was a report on the photo bleaching of dyes by TiO₂ both in vacuo and in oxygen in 1938 (4). It was reported that UV absorption produces active oxygen species on the TiO₂ surface, causing the photo bleaching of dyes. It was also known that TiO₂ itself does not change through the photoreaction, although the “photo catalyst” terminology was not used for TiO₂ in the report, but called a photo sensitizer (5).

TiO₂ has always been one of the best candidate materials due to its photo catalytic properties (6), its relative nontoxicity, and long-term thermodynamic stability(7). Several groups managed to enhance the photocatalytic properties and optimized titania’s use to degrade various organic and inorganic pollutants (7). Two TiO₂ polymorphs are typically being used-anatase and rutile, with the anatase phase exhibiting a significantly higher photo catalytic activity than the rutile phase (8). Although the reasons are not yet fully understood, it is speculated that the higher charge-carrier mobility, which is 89 times faster than in rutile, causes their superior photo catalytic properties.

The enhancement is attributed to the special electronic states of the two crystal structures, which allow for a

semiconductor–semiconductor junction (9). The details of such mechanisms will be explained later. The mixture of two types of semiconductor particles, semiconductor particles with metal particles, and recently carbon particles with anatase, showed photo catalytic enhancements in many cases to be described later (10). This concept can then be extended to defined carbon structures with tailored electronic properties (11).

2. Structural and elemental analysis

Novel kind of carbon nanotubes/titanium dioxide (CNTs/TiO₂) composite photocatalyst was prepared by a modified sol-gel method in which the nanoscaled TiO₂ particles were uniformly deposited on the CNTs modified with poly(vinyl pyrrolidone) (PVP). The XRD technique was used to determine the crystallographic structure of the organic constituent of the composite. The components profile of carbon and TiO₂ for the composite catalysts determined by XRD was shown in Fig. 1(a).

In case of sample MCT [Fig. 1(b)] synthesized without HCl treatment procedure, the XRD patterns reveal that only anatase phase can be identified for CNT/TiO₂ composite. But, the sample HMCT [Fig. 1(c)] synthesized with HCl treatment was observed the mixed phase of anatase and rutile. In the former studies for the TiO₂ the XRD results were shown that the anatase phase has disappeared with the increasing temperature process and the rutile phase has occurred at relatively high temperature (12). In this study, it was worthy of notice that the characteristic peaks of CNT can hardly been identified from all the patterns of composite catalysts. It is considered that the peak widths broaden slightly and gradually with a decrease with peak intensity of CNT for the composite catalysts (13).

The absence of CNT aggregated in the composite catalysts proves a homogeneous dispersion of CNT in TiO₂ matrix (14), which was also supported by the disappearance of CNT characteristic peaks in their XRD patterns. In case of another study, however, the XRD lines for the anatase type structure of CNT- TiO₂ derived from CNT and TiO₂ at 673 K were observed the sharpened peaks and the separation of these diffraction peaks becomes clear. The XRD patterns of TiO₂/CNT composite showed the very similar results for the formation of anatase crystallites at low temperatures. The increase in the pyrolysis temperature, however, the patterns were shown the results in mixtures of anatase and rutile structures (15).

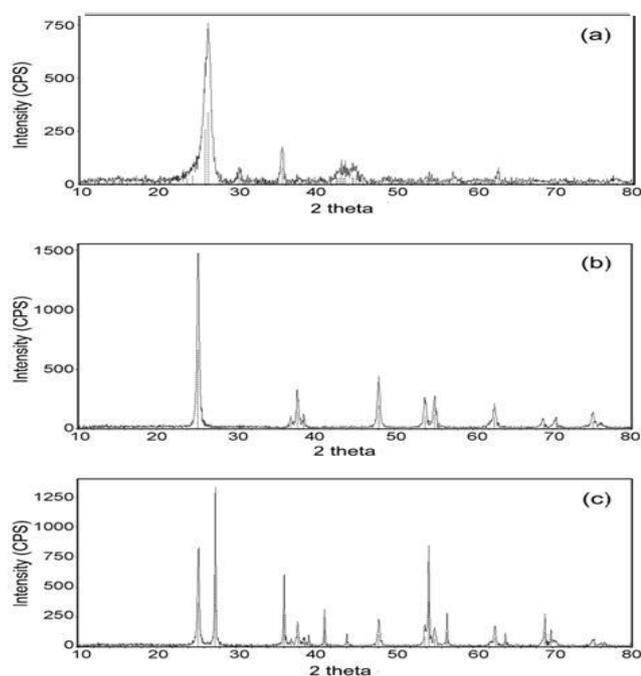


Fig. 1. XRD patterns of CNT/TiO₂ composites; (a) Pristine MWCNT, (b) MCT composite catalyst and (c) HMCT composite catalyst.

This means that the increase in the heat treated temperature is include phasing transition from pure anatase phase to mixture phase of anatase and rutile or to rutile phase. In this study for the CNT/ TiO₂ composite, the TiO₂ structure shown was the anatase phase for the sample MCT. It was observed that the major peaks are diffractions from (101), (004), (200) and (204) planes of anatase. In case of sample HMCT, the main crystalline phase had presented the rutile plans of (101), (103), (112), (105), (211), (204), (116) and (220) with anatase plans, indicating the TiO₂ prepared.

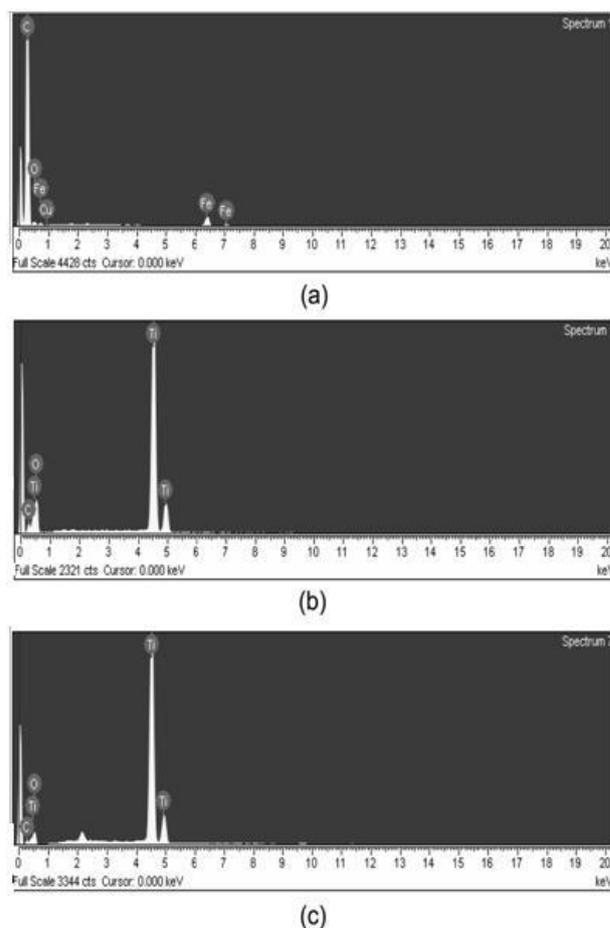


Fig. 2. EDAX elemental microanalysis for the CNT/TiO₂ composites; (a) Pristine TiO₂, (b) MCT composite catalyst and (c) HMCT composite catalyst.

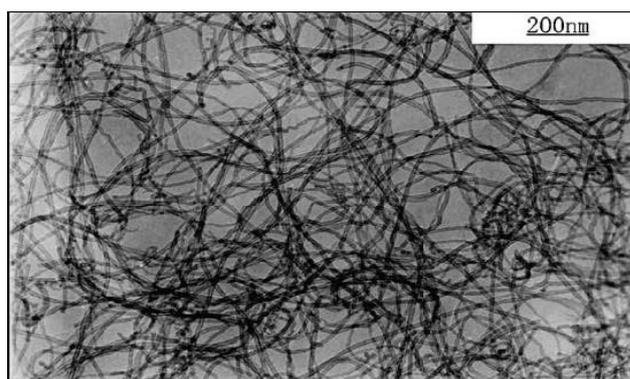


Fig. 3. SEM image of CNT-TiO₂ Composite.

3. CNTs and TiO₂ photocatalysis

Aside from introducing various surface irregularities to provide trap states for electrons, another more effective method of increasing recombination times for electron-hole pairs is to form a semiconductor-metal junction called a Schottky barrier, where there is a space-charge

separation region (16). At the interface of the two materials, electrons flow from one material to the other to align the Fermi energy levels (17). In the case of a metal with a higher work function than the n-type semiconductor, such as TiO_2 , electrons will flow from the semiconductor into the metal to adjust the Fermi energy levels. This formation of a Schottky barrier results in the metal having an excess negative charge and the semiconductor an excess positive charge. In between is a depletion layer that maintains charge separation (18). Traditionally, this method of extending recombination times was established with platinum and other noble metal interfaces.

CNTs have a variety of electronic properties. Similar to the metals above, they may also exhibit metallic conductivity as one of the many possible electronic structures. CNTs have a large electron-storage capacity, and therefore may accept photon-excited electrons in mixtures or nanocomposites with titania, thus retarding or hindering the recombination. CNTs may also enhance the TiO_2 photocatalytic efficiency by acting as a photosensitizer. Anatase TiO_2 requires UV light in order to excite an electron with enough energy to overcome the band-gap.

4. Mechanisms of photocatalysis enhancement in CNT- TiO_2 composites

Two mechanisms are being discussed to explain the enhancement of the photocatalytic properties of CNT- TiO_2 composites. The first is a modified mechanism proposed by Hoffmann et al. Here, a high-energy photon excites an electron from the valence band to the conduction band of anatase TiO_2 . Photo generated electrons formed in the space-charge regions are transferred into the CNTs, and holes remain on the TiO_2 to take part in redox reactions. A schematic of this mechanism is shown in Fig. 1a. The second mechanism was proposed by Wang et al., whereby the CNTs act as sensitizers and transfer electrons to the TiO_2 . The photo generated electron is injected into the conduction band of the TiO_2 , allowing for the formation of superoxide radicals by adsorbed molecular oxygen. Once this occurs, the positively charged nanotubes remove an electron from the valence band of the TiO_2 leaving a hole. The now positively charged TiO_2 can then react with adsorbed water to form hydroxyl radicals. The proposed mechanism is provided in Fig. 1b. However; the CNT- TiO_2 nanocomposite system proves to be more complex. Pyrgiotakis et al. reported two distinct contributions from the CNT- TiO_2 composite.

The second is the electronic configuration of the CNTs. Arc-discharge grown and CVD-grown CNTs were coated with TiO_2 via sol-gel processes. Although both nano composites were structurally similar, the photocatalytic dye degradation rate for the arc-discharge CNTs was ten-fold higher than for the CVD-grown CNT nanocomposite. The difference in activity is therefore attributed to the electronic nature of the CNTs. Raman

spectroscopy indicated that arc-discharge-synthesized CNTs must have a higher electrical conductivity and fewer defects. This is also supported by scanning electron microscopy (SEM) image of the nanocomposite (Fig. 3) Arc-discharge-synthesized CNTs were found to retain their straight walls without major defects in

5. Photocatalytic activity

CNT- TiO_2 nanocomposites are novel, and there are only few publications on their photocatalytic activity to date. Additionally, the comparison of photocatalytic activities from lab to lab is very challenging, due to a variety of methodologies for testing. The most common method of assessing the activity of a nanocomposite photocatalyst is by measuring the time dependence of the concentration loss of an organic compound under irradiation. This can be done with a dye or, alternatively, with potential pollutants, such as phenol. Recently, there have also been reports of degrading toxic gases such NO_2 . The degradation usually follows the Langmuir-Hinshelwood reaction kinetics, which predicts an exponential decay of concentration as a function of time.

Many exciting new technologies can be realized through the use of CNT- TiO_2 composites, extending the already extensive range of applications of photocatalytic TiO_2 . The most recognized application that the photocatalyst system may be incorporated into is for treatment of various biological, organic, or inorganic hazardous pollutants in both water and air streams. Furthermore, the composite may be utilized in the passive decontamination of surfaces. With regard to biological pollutants, bacterial endospores contain three distinct layers of thick protein coatings surrounding the nucleus, which prevent decontamination by harsh chemicals, thermal treatments, and/or irradiation. This is the first report that photocatalysts can effectively destroy spores. The effect of irradiation on pure and dyes doped CNT- TiO_2 composite was investigated. Ion irradiation and the inevitable damage it creates has long been a topic of great interest in the field of nanomaterials. The samples were irradiated with 50 MeV Li^{3+} ions by using a 15 UD Pelletron Accelerator. The dose of charge accumulated in the sample was measured and 1×10^{11} ions cm^{-2} fluences are used in the experiment.

However, the processing has not yet matured and quality-control issues need to be addressed. High-yield synthesis techniques, such as combustion chemical-vapor deposition or chemical-vapor deposition using metal catalysts still exhibit issues such as nonuniform or uneven product properties, leading to less than optimal enhancement of photocatalytic activity. Furthermore, residual catalyst materials tend to remain in the products, and post-production treatments may be necessary to further purify the nanotubes.

Other synthesis techniques that result in higher purities, such as CVD technique, have low yield and are therefore unfeasible for industrial implementation. Research and discovery opportunities exist for the CNT-

TiO₂ composite systems. Being able to tailor and synthesize high quantities of uniform composite and further research into catalytic activity and its standardization is necessary. Especially, a more thorough understanding, perhaps by the use of EPR measurements, of the actual mechanisms of how CNT enhance the photocatalytic properties of TiO₂-based systems needs to be undertaken. Nevertheless, CNT-TiO₂ composites are expected to be developed as a robust means to address various environmental and self-cleaning issues.

6. Conclusion

CNT-based TiO₂ composites were fabricated successfully by means of hydrolysis, and CNT was partly coated with TiO₂. There were some polar oxygenated groups such as C–O, C=O and O–C=O which might stimulate formation of the composites, and enhance the interfacial combination of TiO₂ with carbon nanotubes. The formation of TiO₂ and its compounding with CNT happened almost simultaneously in this process. The method is a convenient route to fabricate CNT-based TiO₂ composites with different ratios, which could be used as new functional fillers with more effects than the one component fillers. The addition of TiO₂ was supposed to increase the space among CNT and improve the dispersion of CNT in matrix. In addition to that, due to the semiconducting properties of TiO₂, the CNT–TiO₂ composites may also be applied in photo catalytic degradation of aromatic pollutants in aqueous medium under irradiation. Additionally, analytical testing methods and devices will be developed, and biological and environmental aspects of photocatalysis will be investigated. In addition, irradiation of higher doses of Li⁺ ion damages the lattice effectively and the crystalline quality of the irradiated region. Based on a number of pertinent control experiments it is possible to conclude that the overall nanoscale drug system is more selective and effective than the free drug and it should result in reduced general toxicity and hence reduced side effects in patients and also allows a lower amount of the drug to be applied.

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*Corresponding author: logeshkumaresan@yahoo.com