A study on carbon nanotube titanium dioxide hybrids: experiment and calculation

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Abstract
Carbon nanotubes (CNTs) were coated TiO2 nanoparticles via sol–gel process using titanium tetra-isoproxide Ti[OCH(CH3)2]4 (TTIP). The structure of TiO2/CNT hybrid samples was determined by x-ray diffractometer D5005 (Siemen) with CuKα radiation. Their morphology and sizes were investigated with FE-SEM and HR-TEM, which shows that nanoparticles were coated on CNTs. The UV–vis absorption results indicate interaction between TiO2 and CNTs, the composite material can absorb at higher wavelength and the absorption even covers the whole range of visible region. By investigating different addition ratios of CNT on the photocatalytic activity of TiO2/CNTs, we find that the higher ratio in TiO2/CNT will decrease the photocatalytic activity. We have calculated the electronic structure of the anatase TiO2 and single-wall carbon nanotube (SWCNT) by first-principles stimulation. We investigate the property in hybrid structure: molecular and small clusters of TiO2 adsorbed on SWCNT support using density functional calculation. The energy and charge distribution calculations show that SWCNT can make TiO2 clusters become more stable in the hybrid system.

Keywords: TiO2, CNTs, composite, photocatalytic, DFT

Mathematics Subject Classification: 4.02, 5.07, 5.14

1. Introduction
Titanium dioxide (TiO2) is one of the most important transition metal oxides with many applications. TiO2 has been considered as a promising material for use in photocatalysis, including water and air purifications, self-cleaning surfaces, dynamic random access memories, dye-sensitized solar cells, photocatalysts for environmental remediation and water splitting, coating materials to obtain superhydrophilic surfaces, and optical devices [1–3]. In recent years, there has been considerable progress in the production of novel materials by combining TiO2 with other materials to form hybrid structures. It is an important and challenging issue to develop a new TiO2 photocatalytic system with enhanced activities under both UV and visible light irradiation compared with bare TiO2, improving the utilization efficiency of the solar energy [4–6]. Carbon nanotubes (CNTs) have been used to improve the mechanical and optoelectronic performance of TiO2 thin film. It has been reported that the CNTs not only provided a large surface area support for the catalyst, but also stabilize the charge separation by trapping the electrons transferred from semiconductor, thereby hindering charge recombination [7–9]. In particular, the excellent electronic properties of a CNT provide continuous electronic states in the conduction band (CB) for donating the transferring electrons from the nth van Hove singularity to the semiconductor. Their outstanding charge transfer abilities can favour the excited electron in the conduction band of nanocrystal semiconductor to migrate into the CNTs, thereby decreasing the ability of the recombination of the electron–hole pairs [10], and increase photocatalytic activity under visible light.
nanoparticles are about 8 nm in size (images (figure 1) illustrated the morphology of the TiO2/CNT hybrids remain open.

In this study we report synthesis of TiO2/CNTs composite by simple grinding method and study improving their photocatalytic activity under visible light. The photocatalytic activities of samples were assessed by photodegradation of methylene blue (MB). We have investigated the geometry and electronic structure of small TiO2 clusters adsorbed on single-wall carbon nanotubes (SWCNTs) support using first-principles density functional calculations. We discuss the interfacial electronic structures and electron transfer of CNT interfaced with TiO2 clusters.

2. Experimental

The preparation of TiO2/CNTs is presented by the following process. The synthesis of TiO2 nanocrystals is accomplished with the drop-wise addition of Ti[OCH(CH3)2]4 dissolved in isopropyl alcohol to doubly distilled water. By adjusting the pH of the solution, TiO2 nanocrystals can be synthesized. Then the white TiO2 precursor was mixed with CNTs with ratio $m_{TiO2}/m_{CNT}$ of 1:1; 3:1; 80:1; 500:1 and 1000:1. The mixture was ground for 6 h in an agate mortar and dried at 100 °C in vacuum for 4 h.

The photocatalytic activity of the prepared samples was evaluated by measuring the decomposition of MB under visible-light irradiation. The light source used was a 150 W high pressure xenon lamp with a cut-off filter of 400 nm. For a typical photodecomposition experiment, 25 mg of photocatalyst is mixed with 50 ml of MB solution. Before turning on the light, the suspension containing MB and photocatalyst was magnetically stirred in dark with continuous stirring until there was no change in the absorbance of the solution, this is to make sure that physical adsorption will not play a role in reducing the MB concentration.

The structure of TiO2 samples were determined by x-ray diffractometer D5005 (Siemens) with CuKa radiation. Their morphology and sizes were investigated with FE-SEM. Optical absorption spectra were measured by V-670 spectrophotometer.

3. Results and discussions

3.1. Morphology and characters of TiO2/CNT hybrids

Transmission electron microscope (TEM and HR-TEM) images (figure 1) illustrated the morphology of the TiO2/CNT hybrid materials. HR-TEM images show that the TiO2 nanoparticles are about 8 nm in size (figure 1(a)), CNTs with diameter of 50 nm (figure 1(b)), the TiO2 nanoparticles are attached on the sidewall of CNTs (figures 1(c) and (d)).

As is well known, pristine CNTs are hydrophobic and thus require functionalization with hydrophilic groups that provide an attractive interaction with the titanium sol. In this work we used HNO3 as a linking agent in the process to coat CNTs with TiO2. The different ratios $m_{TiO2}/m_{CNT}$ of 1:1; 3:1; 10:1; 30:1; 80:1; 500:1 and 1000:1 were studied to find the optimum ratio for best photocatalyst in the samples.

It was also observed that some clusters of TiO2 particles were found. This conductive network of CNTs would facilitate the electron transfer between the adsorbed MB molecules and the catalyst substrate [11]. This would be beneficial for the photocatalytic reaction because the photocatalytic reaction is carried out on the surfaces of the TiO2/CNTs composites catalysts and the CNTs network. So the TiO2/CNTs composites should show excellent photocatalytic activity.

Figure 2 shows the XRD spectra of the prepared nanoparticle TiO2 (curve a), TiO2/CNT nanocomposites with different $m_{TiO2}/m_{CNT}$ ratios (curves b, c, d, e). Anatase sample is obtained (curve a). The width of the peak broadens indicating the nanoparticle size. The particle size of about 8 nm calculated by Scherrer’s equation is in good agreement with the above TEM results. The diffraction peaks for all TiO2/CNT samples match well with the anatase TiO2. For the samples with small ratio CNT/TiO2, it can be found that the addition ratio of carbon material in the TiO2/CNT nanocomposites have no obvious influence on the characteristic XRD peaks of TiO2; no typical diffraction peaks of CNT are observed in the nanocomposites, which can be ascribed to the following reasons. Firstly, the weight addition ratios of CNT in the nanocomposites are relatively low. In the sample there are the nanoparticles TiO2 thickly coated on the wall of CNT (figures 1(c) and (d)). Secondly, the main characteristic peak of CNT (002 peak at 26.2°) is probably shadowed by the (101) peak at 25.3° of anatase TiO2 [12, 13]. However, as the weight addition ratios of TiO2:CNT reach 3:1, there are some slight differences in the XRD patterns: the TiO2 anatase XRD peak (101) is slightly moved toward 2θ increasing side (it is noticeable only in the sample for the high ratio TiO2:CNT = 3:1, see curve e), which can be explained by the incorporation of the CNT-(002) peak at 26.2°. UV–vis diffuse reflectance spectra of TiO2, CNTs and TiO2/CNTs composite are shown in figure 3. The composite material can absorb from 400 nm to 800 nm and the absorption even covers the whole range of visible region, which is caused by the addition of CNTs. Furthermore, a noticeable red shift to higher wavelength is observed in the absorption edge of TiO2/CNTs nanocomposites, which can be attributed to electronic interaction between CNT and TiO2 [14]. So the TiO2/CNTs composites should have excellent visible photocatalytic activity.

We have studied the photocatalytic properties of the TiO2/CNTs composites. Photocatalytic efficiency of samples was evaluated by intensity peak at 665 nm in absorption spectra of MB solution (see figure 4(a)). The percent degradation of MB solution was calculated using the equation

$$D = \frac{A - A_0}{A_0} \times 100\%,$$

where $D$ is the percent degradation, $A_0$ and $A$ are the maximum absorbances at 665 nm in absorption spectra of initial and constant MB solution, respectively.
Absorbance spectral changes of MB solution in the presence of TiO_2/CNTs composite are shown in figure 4(a).

From the presented results in figure 4(b), it can be seen that a photocatalytic process of MB with fast degradation efficiency was observed with TiO_2/CNTs composite, the best result is obtained in the sample with the TiO_2/CNTs ratio of 3:1. It is considered that the decreases of MB concentration in the aqueous solution can occur in two physical phenomena such as adsorption by CNTs and photocatalytic decomposition by TiO_2, and here it was mainly photocatalytic decomposition. This indicates that the decrease of MB can be concluded to be from combined effects of the photocatalytic decomposition by TiO_2 and assistance from CNT network.

It is quite reasonable to describe the combination effect to a CNT acting as electron sensitizer and donator in the...
composite photocatalysts. There are two possible means of charge transfer between CNT and TiO2, which can improve the photocatalysts, as is shown in figure 5. Hole and electron are generated in TiO2, then electron is transferred to CNT, hence e⁻–h recombination rate reduced (figure 5(a)) or hole and electron are generated in CNT, then electron is transferred to TiO2 (figure 5(b)).

3.2. Calculation study on TiO2/CNTs system

In order to understand the above CNT role in the enhanced photocatalyst of TiO2/CNT, we perform density functional theory (DFT) calculations to investigate the problem about characterizing the interfacial electronic structures and electron transfer of CNT interfaced with TiO2 clusters.

Calculations of total energy and electronic structure were carried out using the Dmol3 package within the framework of DFT. The Perdew-Burke–Ernzerhof (PBE) [15, 16] parametrization of the generalized gradient approximation (GGA) [17] was adopted for the exchange-correlation potential.

For all atoms, electron–core interactions are described by ultrasoft pseudopotentials [18]. A cutoff energy of 380 eV and a regular Monkhorst–Pack grid of 2×2×4 k-points were adopted for the Brillouin zone sample. The implementation of the DFT-Dmol3 method includes total energy and atomic force calculations, which allow structure optimization. The optimized structures for the set unit cell volume (V) and the lattice constant were decided when the total energy and the force on each atom were minimized. All results in the study were obtained under this condition set.

We considered the semiconducting CNT models, because the semiconducting CNT/TiO2 hybrids have high visible light
The CNT (10,0) tubes are used to represent typical ~1 nm semiconducting CNTs [20]. To construct the periodic interface, we choose the CNT length of 17.04 Å in its axial direction. The supercell is \((a,b,c) = (30.00, 30.00, 17.04) \text{ Å}\), which is enough to minimize interactions between surfaces of adjacent slabs.

We built the \((\text{TiO}_2)_n\) clusters \((n = 1, 2, 3)\), as shown in table 1. Among different configurations of \((\text{TiO}_2)_2\) and \((\text{TiO}_2)_3\) clusters we find that the A configurations have a least total energy \((-0.4 \text{ eV})\). These most stable configurations of \((\text{TiO}_2)_2\) and \((\text{TiO}_2)_3\) clusters were chosen to be adsorbed on the surface of CNT (figure 5).

An adsorption energy \((\Delta E_{\text{ads}})\) is a key quantity in predicting adhesive property of an adsorption system. To examine which adsorption model is the most energetically stable, we calculated the adsorption energy, which is defined as the reversible energy required to separate an adsorption system \((E_{\text{ads.sys}})\) into a CNT \((E_{\text{CNT}})\) and adsorbed TiO\(_2\) clusters \((E_{\text{Cluster}})\). \(\Delta E_{\text{ads}}\) can be expressed by subtracting the sum of total energy of optimized TiO\(_2\) clusters \((E_{\text{Cluster}})\) and CNT \((E_{\text{CNT}})\) from total energy of adsorption system \((E_{\text{ads}})\):

\[
\Delta E_{\text{ads}} = E_{\text{ads.sys}} - (E_{\text{CNT}} + E_{\text{Cluster}}).
\]

In general, a negative \(\Delta E_{\text{ads}}\) indicates that the molecule adsorption is exothermic and thus the adsorption system is energetically stable [14]. For the purpose of comparison, all energies are calculated using the supercell of identical size.

Table 2 lists the adsorption energies for the three adsorption models, as shown in figure 6. One can see that all \(\Delta E_{\text{ads}}\) have negative values, suggesting that the adsorption process can take place naturally. Among the three models, the \(n = 3\) model (the one with the clusters from three TiO\(_2\) molecules) has the lowest exothermic \(\Delta E_{\text{ads}} (~0.876 \text{ eV})\), indicating that the number of TiO\(_2\) molecules in the cluster increases the stability of the TiO\(_2\)/CNT system. The small adsorption energies suggest that the \((\text{TiO}_2)_n\) clusters are

![Figure 6. Relaxed models of the clusters \((\text{TiO}_2)_n\)-CNT\((n = 1, 2, 3)\).](image)

![Figure 7. DOS of CNT and TiO\(_2\)/CNT.](image)

![Figure 8. Structure of the \((\text{TiO}_2)_3\) clusters adsorbed on (10.0) SWCNT (a) and charge density difference in the \((\text{TiO}_2)_3\) clusters adsorbed on (10.0) SWCNT (b) at 0.038 (a.u) isosurface value.](image)
flexible and coalesce into larger clusters on the SWCNTs. We investigated the relaxed structures of (TiO$_2$)$_3$ clusters adsorbed on (10.0) SWCNT. The energy band calculation shows that the band gaps of (TiO$_2$)$_3$ clusters and CNT (10,0) are 1.63 and 0.74 eV, respectively. This result is in agreement with other reports [21, 22]. Density of state (DOS) analysis (figure 7) shows that mid-gap states are observed, which can be related to the localization character of new hybrid orbitals in the (TiO$_2$)$_3$/CNT hybrid system. DOS analysis shows that CNT absorbs long wavelength light, and TiO$_2$ clusters adsorb short wavelength light.

In order to further investigate the electronic properties and bonding character of (TiO$_2$)$_3$–CNT system, we studied the electronic charge density, difference charge density and charge distribution. The difference between the charge density of the (TiO$_2$)$_3$–CNT and sum of the charge densities of the isolated (TiO$_2$)$_3$ cluster and of isolated SWCNT (10,0), $\Delta \rho$ can be expressed by the following equation [21]

$$\Delta \rho = \rho_{(TiO_2)_3-CNT} - \left( \rho_{CNT} + \rho_{(TiO_2)_3} \right),$$

where $\rho_{(TiO_2)_3-CNT}$ is charge density of the (TiO$_2$)$_3$–CNT, $\rho_{(TiO_2)_3}$ and $\rho_{CNT}$ are the charge density of (TiO$_2$)$_3$ cluster and CNT, respectively.

Figure 8(a) shows the charge density difference in the (TiO$_2$)$_3$ clusters adsorbed on (10.0) SWCNT. One can see that the electron cloud on the CNT wall mainly distributes on C–C bonds and the changes of the electron densities occur mainly at the interface region between the (TiO$_2$)$_3$ clusters and the CNT. This trend is confirmed by the result of DOS analysis which suggests the localization character of the (TiO$_2$)$_3$/CNT hybrid system.

4. Conclusion

TiO$_2$/CNTs composite photocatalysts were prepared using a modified sol–gel method. The composite material can absorb at higher wavelength and the absorption even covers the whole range of visible region. The photocatalytic degradation of MB was observed over TiO$_2$/CNTs composite catalysts, which exhibit higher photocatalytic activity in comparison with neat TiO$_2$.

Density functional theory (DFT) calculations were successfully performed to investigate the (TiO$_2$)$_n$ ($n = 1, 2, 3$) clusters/CNT hybrid system. Adsorption energy calculation suggests that the (TiO$_2$)$_n$ clusters are flexible and coalescence into larger clusters on the SWCNTs. Density of state and difference charge density analyses show the localization character of new hybrid orbitals in the (TiO$_2$)$_3$/CNT hybrid system. This result suggested that the origin of the enhancement of photocatalytic efficiency of the composite is as follows: the presence of CNTs decreases the ability of the recombination of the electron–hole pairs and increases photocatalytic activity under visible light.

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