Photodegradation of Humic Substances on MWCNT/Nanotubular-TiO_2 Composites

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We report on the first use of MWCNT/nanotubular-TiO_2 (multiwalled carbon nanotube, MWCNT; TiO_2-derived nanotube, nanotubular-TiO_2) composites as catalysts for photodegradation of aquatic humic substances (HSs). The MWCNT was demonstrated to be capable of enhancing the activity of the photocatalyst. The best degradation efficiency was obtained by using MWCNT/nanotubular-TiO_2 composites having 20% MWCNTs as the photocatalyst.

Elimination of humic substances (HSs) from contaminated water is significant in aquatic system for a number of reasons. First, HSs impart a visible (yellow/brown) color[1,2] to water; this can cause aesthetic contamination even at very low concentrations. Second, HSs are capable of forming complexes with heavy metal ions[3] and/or pollutant organic species[4] (such as pesticides); this can enhanse the absolute solubility and/or the lifetime of these pollutants in water. Moreover, HSs are suspected to be the essential precursors of mutagenic halogenated compounds formed in water after the chlorination.[5,6]

A number of promising techniques have been established for elimination of HSs from the contaminated water. Physical treatment, such as the conventional coagulation/filtration, adsorption and reverse osmosis method offers simpler approaches to the aquatic HSs.[7,8] Chemical and biological elimination methods, on the other hands, also find wide range of applications.[9,10]

Photoelimination, for example, the use of photocatalysts for degrading aquatic HSs, as a typically chemical treatment, is of great interest. However, in case of using titanium dioxide (TiO_2) as the photocatalysts, sufficient amounts of oxygen must be supplied to the reaction system by continuously bubbling the HS/TiO_2 suspension with CO_2-free oxygen.[11]

In this study, we have established a new type of photocatalyst with which aquatic humic substances (HSs) can be degraded without need for oxygen supply. Multiwalled carbon nanotubes (MWCNTs) were coupled with TiO_2-derived nanotubes (nanotubular-TiO_2) to form MWCNT/nanotubular-TiO_2 composite photocatalysts. To our best knowledge, this is the first report dealing with the use of MWCNT/nanotubular-TiO_2 composite photocatalysts for photoelimination of aquatic HSs.

The nanotubular-TiO_2 was prepared using the TiO_2 nanoparticles as the precursory materials. The TiO_2 nanoparticles were obtained by a sol–gel method[12,13] using titanium tetrabutoxide $Ti[O(CH_2)_3CH_3]_4$ as the precursors. The resultant TiO_2 nanoparticles (0.6 g), a certain amount ($MWCNT/TiO_2 = 5$, 10, 20, and 30 wt %) of highly dispersed MWCNTs (those were obtained by the zwitterionic surfactant dispersion method[14]) were introduced into a Teflon-lined stainless steel autoclave containing 10 M NaOH. This mixture was then heated in an oven at 125 °C for 24 h, similarly to previous reports.[15,16] After being cooled down to room temperature, they were filtrated (Millipore 0.45 µm membrane filter); washed with 0.1 M aqueous HCl solution and then deionized water until its pH value reached to about 7. The products were dried at 105 °C for 6 h and then were calcined at 350 °C for 8 h in ambient atmosphere.

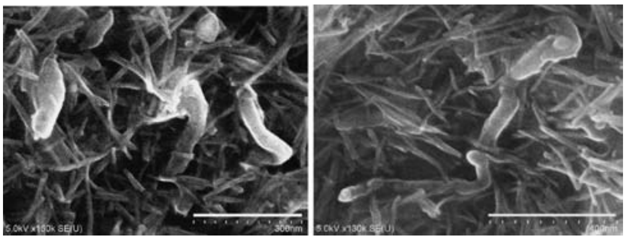

Figure 1. Typical scanning electron microscope (SEM, Hitachi S4800) images of the resultant MWCNT/nanotublar-TiO_2 composites. Bar full size: 300 nm. MWCNTs = 20%.

Scanning electron microcopy (SEM) observations (Figure 1) have demonstrated that the resultant products were consisted of TiO_2-derived nanotubes (nanotubular-TiO_2) together with the highly dispersed MWCNTs. Nanotublar-TiO_2, in general, were built up mainly by amorphous components and hence having poor photocatalysis activities. The MWCNT/nanotubular-TiO_2 composites were further calcined at 350 °C in air, in order to convert nanotubular-TiO_2 into anatase (and hence the higher photocatalysis activities). The successful conversion of the nanotubular-TiO_2 into anatase was demonstrated by XRD analysis of the calcined MWCNT/nanotubular-TiO_2 composites (data not shown). Note that MWNTs disappeared at the calcination temperature higher than 495 °C.

Model aquatic HS solutions (30 mg/L humic acid; pH was adjusted at 4.0 with ammonia and nitric acid solution) were photolyzed in 0.1% suspensions of the resultant MWCNT/nanotubular-TiO_2 composite catalysts using a mercury lamp. Before the mercury lamp was being switched on, the model aquatic HS/MWCNT/nanotubular-TiO_2 solutions were sonicated for 5 min, magnetically stirred in a dark condition for 30 min, in order to achieve the adsorption–desorption equilibrium. This concentration value (C_0) was used as the beginning concentration after the dark adsorption.[17] During the photodegradation, approximately 3 mL samples were withdrawn regularly from the photoreactor (every 30 min or 1 h for each sampling). These samples were filtrated with 0.45 µm Millpore membrane filters and measured using a UV–vis spectrophotometer at 436 and 400 nm (indicating color removal), and 365, 280, and 254 nm (representing TOC normalized aromatic moieties). As can be seen from the typical photodegradation experimental data (Figure 2), the MWCNT/nanotubular-TiO_2 composites provided a better pho-

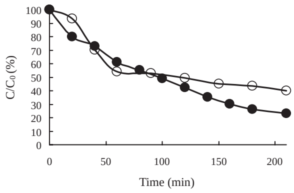

Figure 2. Photodegradation of aquatic humic substances (HSs) with MWCNT/nanotublar-TiO_2 composites (●) and the sole nanotublar-TiO_2 (○) as the photocatalysts. MWCNT = 20%; $\lambda = 254$ nm.

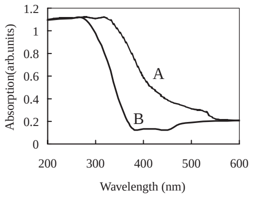

Figure 3. UV–vis absorption spectra of the sole nanotublar-TiO_2 (A) and the MWCNT/nanotublar-TiO_2 composites (B, MWCNT = 20%).

todegradation coefficient than that of the sole nanotubular-TiO_2 for degradation of the aquatic humic substance (HS). Furthermore, for the MWCNT/nanotubular-TiO_2 composites, a significant change (decrease) in concentrations of the aquatic HSs was observed over all the photolyzing process. However, for the nanotubular-TiO_2 alone, it took about an hour to reduce the concentrations of the aquatic HSs by half; after that period of the photolyzation, significant changes of the HS concentrations were not observed.

The synergetic effect of MWCNTs on the photodegradation of the aquatic HSs was found in an order of $20 > 30 > 10 > 5\%$ of the carbon nanotubes in the MWCNT/nanotubular-TiO_2 composites. Namely, the MWCNT/nanotubular-TiO_2 composites with a weight ratio of 20% MWCNTs provided the best synergetic effect on the photodegradation of the aquatic HS.

The diffuse reflectance UV–vis spectra of the MWCNT/nanotubular-TiO_2 composites (Figure 3) gave new insights into the photodegradation mechanism of the MWCNT/nanotubular-TiO_2 composite catalysts. The nanotubular-TiO_2 has showed the characteristic spectrum of anatase with its fundamental absorption edge rising at 400 nm. The MWCNT/nanotubular-TiO_2 composites, on the other hand, have shifted to shorter wavelength. In other words, combining MWCNT with the nanotubular-TiO_2 has resulted a blue shift. It is noticeable that the MWCNT/nanotubular-TiO_2 composites of 20% MWCNTs provided a largest change of the UV–vis spectrum, followed by 30, 10, and then 5%.

MWCNTs are capable of absorbing the irradiation (photons); this results in production of photoinduced electrons over the carbon nanotubes. The photoinduced electrons transferred from MWCNTs into conduction band of the nanotubular-TiO_2. Superoxide radicals (very reactive) formed over the nanotubular-TiO_2 surfaces by transferring the photoinduced electrons into the adsorbed oxygen. Highly reactive hydroxyl radicals might be also formed; in case of formation of positively charged holes by electron migration from the nanotubular-TiO_2 valence band to the carbon nanotubes.[18–20] These resultant radicals are responsible considerably for the degradation of the aquatic humic substances.

Finally, note here that the thermal stability of the MWCNT/nanotubular-TiO_2 composites were investigated using the thermogravimetric method. TG curve indicated mass loss up to 510 °C of a total 21% for the composites containing 20% MWCNTs.

In conclusion, a new type of photocatalysts was established by combination of the TiO_2-derived nanotubes and the highly-dispersed MWCNTs. The nanotubular shapes of TiO_2 provide the desirable morphologies for attaching the photocatalyst onto the sidewalls of the carbon nanotubes. Identification of the main products by analysis of the photolyzed solutions using LC-MS is under investigation.

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