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Fabrication of Ordered Arrays of CNT/TiO₂ Nanotubes and Their Photocatalytic Properties
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In this work, fabrication and characterization of ordered arrays of CNT/TiO₂ nanotubes imbedded in porous anodic aluminum oxide (AAO) membranes were reported. The coaxial core-shell structures were exploited for the photocatalytic degradation of organic pollutant, such as methyl orange. The presence of the CNT greatly enhanced the efficiency of photocatalytic activity compared with the bare TiO₂ nanotubes. The key achievement of this work is to fabricate ordered arrays of CNT/TiO₂ composite nanotubes with coaxial core-shell structures by using a simple, convenient, and environmentally friendly process. Further application of this CNT/TiO₂ hybrid material in many fields could be hopefully expected.

In recent years, there has been increasing interest in TiO₂ because of its biological and chemical inertness, excellent stability and non-toxicity. Although the catalysts in the form of nanoparticles show a good activity due to the large surface-to-volume ratios, separation of these powdered photocatalysts from suspended solution could be very difficult for the purpose of recycle usage. Another limitation encountered with TiO₂ is that due to its wide band gap of ~3.2 eV, it only absorbs light with wavelengths of ~387 nm and below, which significantly diminishes the utilization of solar energy. In addition, most applications of TiO₂ nanotubes suffer from the easy recombination of photogenerated electron-hole pairs.

Compared with nanoparticles or bulk materials, the photocatalysts in the form of nanotube arrays own many advantages including facilitation of recycle usage and higher photocatalytic activity derived from long-distance electron transport and larger specific surface area. As for the limitation of light absorption and easy recombination of the photogenerated electron-hole pairs TiO₂ suffers from, the idea coupling TiO₂ with CNT has been popular. For CNTs, owing to their large surface-to-volume ratio, good mechanical behavior and excellent properties of transporting or shuttling electrons, they have been extensively combined with TiO₂ to overcome TiO₂’s limitations. Up to now, various approaches including hydrothermal process, sol-gel method, and electrochemical coating method have been exploited in the synthesis of CNT/TiO₂ composites and the composites CNT/TiO₂ have been investigated in many fields, such as photo-catalysis, solar cell, lithium storage, and so on.

The conventional techniques preparing CNT/TiO₂ composites usually have some disadvantages. For example, the CNTs need to be treated with strong acids to introduce active function groups on their surface; some organic stabilizers are introduced in order to prevent nanoparticles from agglomerating. In addition, most of these methods only concern about loading TiO₂ particles on the outer wall of randomly dispersed CNTs. To our knowledge, there is only one paper about loading TiO₂ in the inner wall of CNT and it is reported that a high photoactivity under visible-light irradiation could be obtained for the structure TiO₂ confinement inside CNT.

Here, we report a simple and effective route to prepare well-ordered CNT/TiO₂ nanotube arrays with the assistance of AAO membranes as templates. AAO membrane contains lots of ordered nanochannels, which makes it a suitable template for the fabrication of one-dimensional nano-structures. As for the CNT/TiO₂ composites, some other approaches to fabricate TiO₂ nanotubes require the use of a metallic Ti substrate to support the TiO₂ nanotube array, but the process to remove the Ti substrate and barrier layer is complex and involves the use of hydrogen fluoride which may be harmful for the environment. In this work, CNT/TiO₂ composite core-shell coaxial nanotube arrays were fabricated by chemical vapor deposition (CVD) and hydrolytic reaction using AAO membranes as the templates and our work has following highlights:

1. Compared to the forms of nanoparticles or other bulk materials, the product in the form of nanotube arrays is easier to be recycled, avoiding secondary pollution.

2. A new structure was obtained in our work. TiO₂ nanotubes are assembled on the innerwall of ordered CNT arrays while many studies are mainly focusing on loading TiO₂ on the outer wall of randomly dispersed CNT.

3. The method to fabricate CNT/TiO₂ core-shell coaxial nanotube arrays is environmentally friendly with no strong acids or alkali during the process.

In a typical process, the carbon nanotubes were firstly deposited on the entire surface of the AAO membrane by using a chemical vapor deposition (CVD) method, and then TiO₂ was deposited on the inner surface of the AAO/CNT via hydrolysis of titanium isopropoxide. Further experimental details are provided in the ESI. The morphologies of the prepared samples were examined by SEM and TEM tests. For CNTs, the hollow feature could be seen from the tips of the nanotubes in Fig. S1(a). The obtained CNTs kept a good orientation and parallel with each other. The outside diameter of these nanotubes was equivalent to the pore...
diameter (200-300 nm) of the AAO template, and the length of these nanotubes was equal to the thickness of the employed AAO membrane (~50 µm) (the inset of Fig. S1a). Fig. S1b showed the TiO$_2$ nanotubes were arranged roughly parallel to one another, and were highly uniform in diameter, which indicated that the ordered TiO$_2$ nanotubes could be successfully constructed in nanochannels of AAO using hydrolysis of titanium isopropoxide with the help of sonication operation. For CNT/TiO$_2$, the feature of the core/shell structure was clear in the broken section from Fig. S1c (indicated by circles). It could be seen that some TiO$_2$ nanoparticles appeared in the broken part for the composite nanotubes. Here the energy dispersive spectroscopy (EDS) data corresponding to the samples were also shown in the right parts of Fig. S1. The peaks of Ti, O, and C could be clearly seen, indicating that the TiO$_2$ nanotubes, CNTs and CNT/TiO$_2$ composite nanotubes could be obtained in our work. The element of Na could be introduced by the operation of dissolving the AAO template using NaOH solution. The Si signal originated from the silicon wafer, which was used as the substrate to hold the samples. The additional reflection of Pt in the EDS spectra were due to Pt coating convenient for the SEM measurements.

Further evidence for the core/shell structure could be found from the transmission electron microscopy (TEM) image shown in Fig. 1. Fig. 1a and Fig. 1b were the TEM images of the carbon nanotube and TiO$_2$ nanotube, respectively, showing that the wall thickness of CNT and TiO$_2$ nanotube was both about 10 nm. In addition, a typical TEM image of CNT/TiO$_2$ composite nanotube was shown in Fig. 1c. The distinct interface between the outer layer of CNT and the inner layer of TiO$_2$ suggested the structure of core-shell coaxial nanotube heterojunctions were obtained by our method. The structures of the prepared nanotubes were determined by selected area electron diffraction (SAED) studies. It clearly showed that CNT/TiO$_2$ composite nanotube was composed of anatase-type TiO$_2$ structure with four diffraction rings corresponding to the (101), (004), (200), and (211) planes and graphitic multiwalled CNT structure with typical (100) and (004) planes (inset of Fig. 1c) \[3,19\]. Based on the analysis of SEM and TEM, it could be concluded that the average outer diameter of the prepared nanotubes was 200-300 nm and the length was up to 50 µm, which perfectly corresponded to the size of the AAO template. HRTEM may offer further insight into the morphology and microstructure of CNT/TiO$_2$ composites, as shown in Fig. 1d. The lattice fringes with spacing of 0.35 nm were in good agreement with the characteristic of anatase TiO$_2$.

XPS technique was further used to investigate the chemical composition of the samples. Fig. 2a was the whole scanning spectrum of the sample TiO$_2$ and CNT/TiO$_2$, including C, Ti and O. Fig. 2b showed the high-resolution spectra of the C1s. For CNT/TiO$_2$, the peak at 286.4 eV attributed to Ti-O-C bond \[20\]. The other peaks for CNT/TiO$_2$ (284.6 eV, 290.2 eV) and for TiO$_2$ (284.8 eV, 288.7 eV) were assigned to C-C bond and COO bond \[21\]. The existence of these polar groups may indicate that the surface of the CNT was oxidized to some extent, which may be helpful for the absorption of the precursor molecules and/or the nucleation of the TiO$_2$ on the surface of CNTs \[22\]. The two peaks for TiO$_2$ at about 458.6 eV and 464.2 eV and for CNT/TiO$_2$ at 458.8 eV and 464.5 eV in Fig. 2c could be assigned to the levels of Ti$^{4+}$ 2p$_{3/2}$ and Ti$^{4+}$ 2p$_{1/2}$, respectively \[23\]. The additional two peaks

**Fig. 1.** TEM and SAED analyses of (a) CNTs, (b) TiO$_2$ nanotubes (c) CNT/TiO$_2$ nanotubes. (d) High-resolution TEM image of CNT/TiO$_2$ nanotubes.
for CNT/TiO$_2$ composite at 457.7 eV and 463.1 eV corresponded to Ti$^{3+}$ 2p$_{1/2}$ and Ti$^{4+}$ 2p$_{3/2}$, respectively, suggesting the presence of the Ti$^{3+}$ species. Ti$^{3+}$ could be regarded as a surface defects on the surface of TiO$_2$ (Ti$^{4+}$). It was reported that the increased Ti$^{3+}$ could not only increase oxygen adsorption and, then photooxidation but also inhibit the photogenerated electrons-holes recombination. Therefore, the existence of the Ti$^{3+}$ species in the CNT/TiO$_2$ composite may be responsible for its enhanced photocatalytic property. As shown in Fig. 2d, the peak of O 1s located at 532.5 eV for CNT/TiO$_2$ could be identified, corresponding to H$_2$O molecules chemisorbed on the sample surface. The peak at 530.4 eV for CNT/TiO$_2$ and 530.0 eV for TiO$_2$ could be assigned to the binding energy of Ti-O. The peak at 531.7 eV for TiO$_2$ corresponded to Ti-OH.

N$_2$ adsorption-desorption isotherms of the samples CNT, TiO$_2$ and CNT/TiO$_2$ core-shell coaxial structures were also measured (Fig. S2). It was shown that all the samples exhibited type-IV isotherms. The BET surface areas of the prepared catalysts were excited much higher surface areas than the bare TiO$_2$ nanotube catalyst. A large specific surface area could benefit the absorption of the target pollutant, which was crucial during the photocatalytic activities. For CNT/TiO$_2$ composite nanotubes, because of the higher surface area, it may own better photocatalytic activity than that of bare TiO$_2$ nanotubes.

The light absorption of the samples TiO$_2$ nanotubes, CNTs, and CNT/TiO$_2$ composite nanotubes were characterized using UV-Vis diffuse reflectance spectra (Fig. S3). The absorption threshold of TiO$_2$ was about 387 nm, corresponding to the band gap of anatase (∼3.2 eV). While CNT absorption covered the whole range of the measured UV-vis region. For CNT/TiO$_2$, it could be seen that the introduction of the carbon into TiO$_2$ led to an increasement of light absorption in the visible spectral region, which was consistent with the reported paper.

For the samples, the comparison about the photocatalytic activities was shown in Fig. 3. The kinetics of the degradation reaction were fitted to a pseudo-first-order rate using the equation

$$\ln(C_0/C) = kt,$$

where $k$ was the apparent rate constant and $t$ was the irradiation time. The following $k$ data for TiO$_2$ nanotube, TiO$_2$ nanotubes imbedded in an AAO template, CNTs and TiO$_2$/CNTs composite nanotubes was 0.0080, 0.0035 and 0.0143 min$^{-1}$, respectively (see Table 2 in ESI†). It was clear that the CNT/TiO$_2$ composite Nanotube arrays owned better photocatalytic activity than that of TiO$_2$ nanotubes and CNTs.

As a photocatalyst, the activity is greatly affected by many factors, such as crystal structure, catalyst’s surface, size distribution, band gap and so on. In our work, one reason for the higher photocatalytic activity of the CNT/TiO$_2$ coaxial core-shell nanostucture may be the higher carrier mobility and less recombination of photogenerated electrons and holes resulting from the coupling of CNTs. When the CNT/TiO$_2$ photocatalyst was illuminated under UV light, electrons in TiO$_2$ were excited from valence band (VB) into conduction band (CB), leaving highly oxidative holes in VB and forming negative sites in CB. Some photogenerated electrons could recombine with holes, which led to the decrease of photocatalytic efficiency. Some were quickly conveyed to the CNTs because of the strong interactive force between two materials CNT and TiO$_2$ and the large electron storage capacity of CNT. Because the photogenerated electrons quickly moved to the CNT while holes were left behind in TiO$_2$, separation of the e$^-$/h$^+$ pairs could be created and the recombination of e$^-$/h$^+$ could be reduced. Thus, the integration of nanotubular TiO$_2$ and CNT in a proper fashion could combine advantages of them and the enhanced photocatalytic performance could be obtained for CNT/TiO$_2$ composite nanotubes in comparison with the bare TiO$_2$ bulk materials or nanoparticles.

In addition, due to the large specific surface area of CNT/TiO$_2$, it may have enhanced adsorption capacity and exhibit superior photocatalytic performance compared with that of bare TiO$_2$. Adsorption is a key process in the photocatalytic destruction of pollutants. The last but not the least, Ti$^{3+}$ could be regarded as a surface defects on the surface of TiO$_2$ (Ti$^{4+}$). The existence of the Ti$^{3+}$ species in the CNT/TiO$_2$ composite may be helpful for the photocatalytic activity.

Based on several factors above, CNT/TiO$_2$ owned enhanced photocatalytic activity compared with that of bare TiO$_2$. A large specific surface area could benefit the absorption of the target pollutant, which was crucial during the photocatalytic activities. For CNT/TiO$_2$ composite nanotubes, because of the higher surface area, they may own better photocatalytic activity than the bare TiO$_2$ nanotubes.
photocatalytic properties compared with bare TiO$_2$ nanotube arrays.

**Conclusions**

In conclusion, a new method for preparing ordered coaxial core-shell CNT/TiO$_2$ nanotube arrays with heterojunction structures by using AAO template was proposed. The length of the coaxial CNT/TiO$_2$ core-shell nanotubes was 50 µm, which was the same as the thickness of the AAO membranes. The heterojunction nanotubes were much longer than those obtained from methods using dispersed CNTs. The wall thickness of the coaxial CNT/TiO$_2$ core-shell nanotubes was uniform. The fabrication process is simple, convenient, and is suitable for application over large areas of the AAO membranes to produce large size and well-ordered core-shell heterojunction arrays.

The CNT/TiO$_2$ core-shell nanotube arrays exhibited higher photocatalytic activity in comparison to the bare TiO$_2$ nanotubes:

1. Compared with bare TiO$_2$ nanotubes, CNT/TiO$_2$ composite nanotubes exhibited enhanced sunlight absorption in the visible region.
2. CNT/TiO$_2$ composite nanotube arrays owned larger specific surface area than that of bare TiO$_2$ arrays.
3. After coupling with CNTs, Ti$^{3+}$ was confirmed to be existed in the CNT/TiO$_2$ composite core-shell coaxial nanotubes, which may be responsible for its superior photocatalytic performance.

Furthermore, the noble metals, which could act as electron traps, such as Pt, Au, or other active materials, have been considered to enhance the catalytic activity of the CNT/TiO$_2$ photocatalyst and the relative investigation will soon be presented in future report.

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**Notes and references**

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