Short Communication

Atomic layer deposition of hybrid metal oxides on carbon nanotube membranes for photodegradation of dyes

Jianhua Feng\textsuperscript{a,b}, Sen Xiong\textsuperscript{a,*}, Yong Wang\textsuperscript{b,*}

\textsuperscript{a} State Key Laboratory of Materials-Oriented Chemical Engineering, Jiangsu National Synergetic Innovation Center for Advanced Materials, College of Chemical Engineering, Nanjing Tech University, Nanjing 211816, China
\textsuperscript{b} College of Material and Chemical Engineering, Chuzhou University, Chuzhou 239000, China

ARTICLE INFO

Keywords:
Atomic layer deposition
Carbon nanotubes
Hybrid metal oxides
Photocatalytic degradation

ABSTRACT

Synthetic dye pollution is a worldwide problem and quick remedies are urgently needed. Photocatalysis is a promising method to solve this problem and carbon nanotubes (CNTs) are promising components in producing high-performance composite photocatalysts. Nevertheless, the strong hydrophobicity dramatically impedes its application in aqueous environments. In this study, hydrophilic CNT-hybrid metal oxides (ZnO and TiO\textsubscript{2}) membranes were prepared by atomic layer deposition (ALD). We demonstrate that ALD is an efficient and flexible method to enhance the photocatalytic activity of CNT-based membranes, especially the membranes used in wastewater treatments. The hybrid hexagonal wurtzite ZnO and anatase TiO\textsubscript{2} on CNTs after calcination could effectively enhance electron transfer and reduce photo-generated electron-holes recombination. The membranes exhibit preferable photocatalytic activity and stable reusability in dye degradation. This strategy of “ALD on CNTs” is expected to create other CNT-based membranes with additional functionalities and has bright prospect for wastewater treatments.

1. Introduction

Due to their extensive consumption, toxicity, carcinogenicity and bioaccumulation properties, particular attention should be paid on the synthetic dye pollutions in aquatic systems and quick remedies are urgently needed \cite{1,2}. Among all purification processes, photocatalysis is a promising method for dye-contaminated wastewater treatments, due to its easy-to-operation, high-efficiency and no hazardous by-products properties \cite{3,4}. However, the photocatalytic activity of the catalysts will be dropped rapidly because the photo-generated electrons and holes of the photocatalysts, which performed as active sites, recombined quickly \cite{5}. How to extend the life span of photocatalysts is a key point for more practical applications of dye photodegradation. Semiconductor photocatalysis has emerged as one of the most promising techniques because it could utilize the energy from artificial illumination to natural light \cite{6–8}. Moreover, doping semiconductor into photocatalysts is deemed as reliable solution to impede the recombination of electron-hole pairs and maintain the photocatalytic activity \cite{9–11}.

Carbon nanotubes (CNTs) are promising carbon-based materials and have potential applications in solar cells, energy storage, transparent electrodes, and photocatalysis owing to their chemical properties, superior mechanical and thermal stability \cite{12–15}. Free-standing CNT membranes with randomly interlaced CNTs and pores exhibited high specific surface areas which have been used in diversified applications \cite{16–19}. However, the intrinsic strong hydrophobicity of CNTs significantly restrains their applications in aqueous systems. Recently, CNTs incorporated with metal oxide semiconductors have shown high photocatalytic activity \cite{14,20–23}. Among the semiconductor catalysts, ZnO and TiO\textsubscript{2} have been widely used because they are abundant, environmentally friendly and have high electron mobility \cite{24–26}. Their combination with CNTs is expected to improve the migration of photon-generated electron-hole pairs, and thereby enhance the lifetime of charge carriers, and presents a desired combination \cite{27}. In these processes, the hydrophilicity of the functionalized CNTs was improved obviously, however, these CNTs commonly exist in the shape of powders and are dispersed in aqueous systems during the photodegradation process. It has been reported that CNTs may create serious security problems when exposed to water or atmosphere \cite{28–30}, thus the CNTs should be collected after using through time- and energy-consuming separation processes. If the CNTs could be used as hydrophilic blocks, they will be more suitable for wastewater treatments.

\textsuperscript{⁎} Corresponding authors at: State Key Laboratory of Materials-Oriented Chemical Engineering, Jiangsu National Synergetic Innovation Center for Advanced Materials, College of Chemical Engineering, Nanjing Tech University, Nanjing 211816, China.

E-mail addresses: xiongsen@njtech.edu.cn (S. Xiong), yongwang@njtech.edu.cn (Y. Wang).

https://doi.org/10.1016/j.coco.2018.12.007

Received 6 December 2018; Received in revised form 24 December 2018; Accepted 25 December 2018
Available online 26 December 2018

2452-2139/ © 2018 Elsevier Ltd. All rights reserved.
Atomic layer deposition (ALD), based on self-limiting reaction mechanism, is a highly controllable technique which could realize the deposition of target materials on substrate surface with superb precision, and down to atomic level through chemical adsorption and reaction between gas precursors. ALD has the capability and controllability to deposit metal oxides on various porous substrates, precisely regulating surface properties, pore sizes and separation/adsorption performances [31–34]. Both ZnO and TiO₂ are extraordinary photocatalysts, however, the photocorrosion of ZnO is inevitable, and the TiO₂ needs specific crystalline to work as a photocatalyst. To combine the advantages of ZnO and TiO₂ together, we explore the application of ALD techniques in the fabrication of ZnO and TiO₂ hybrid metal oxides modified free-standing CNT membranes for photocatalytic degradation of methylene blue (MB). Significant improvement in hydrophilicity and photocatalytic activity were achieved by ALD of metal oxides on the CNT membranes. The ALD-modified CNT membranes also exhibited stable reusability during MB degradation. This strategy of “ALD on CNT substrates” opens a new way to create other photocatalytic membranes and has potential applications in wastewater treatments.

2. Experimental section

2.1. Materials

Sheets of multi-walled CNT membranes (Suzhou Jiedi Nanotechnology Co., Ltd) with a thickness of ~8 µm were chosen for ALD in this study. Diethyl zinc (DEZ, 99.99%, Metalorganic Center, Nanjing University) and deionized (DI) water (8–20 µs/cm, Wahaha) were applied for ZnO deposition. Titanium tetrachloride (TiCl₄, 99.99%, Metalorganic Center, Nanjing University) and DI water were selected for TiO₂ deposition. High purity nitrogen (99.9%) and ultrahigh purity nitrogen (99.999%) were used as the purge gas and carrier.
gas during the ALD process, respectively. The methylene blue with purity > 99% was purchased from Tianjin Chemicals Institute. Anhydrous ethanol, hydrochloric acid and other reagents used in this work were obtained from local suppliers and used without further purification.

2.2. ALD on CNT membranes

To remove surface impurities, especially the catalysts used to grow CNTs, the pristine CNT membranes were pretreated with 20% hydrochloric acid and thoroughly washed with DI water, then dried at 100 °C and cut into pieces with diameter of 2.5 cm as substrates. Then the substrates were put into ALD reactor chamber (f-100-31, Wuxi MNT Co., Ltd) at 150 °C for 30 min in vacuum (~1 Torr) before deposition. Pieces of Si wafer were set in the chamber close to the CNT membranes as a reference to examine the thickness of deposition layers. ALD precursors were stored in stainless cylinders at room temperature, and precursors were pulsed into the ALD reactor by the carrier gas alternatively. To ensure uniform deposition on the porous membranes, the “exposure mode” was adopted in ALD process. In one typical ZnO ALD cycle, the DEZ pulse/exposure/purge/H2O pulse/exposure/purge time were 0.075 s/10 s/60 s/0.05 s/10 s/60 s; and in one TiO2 ALD cycle, the TiCl4 pulse/exposure/purge/H2O pulse/exposure/purge time were 0.03 s/5 s/15 s/0.015 s/5 s/15 s, respectively. All operations are automatically controlled via fast valves. During the ZnO ALD process, the substrates were deposited for 10, 30, 50, 70 and 90 cycles, respectively; and in the TiO2 ALD process, the cycle numbers are 50, 100, 150, 200 and 300, respectively. The hybrid metal oxides layer was deposited with several ZnO cycles and several TiO2 cycles alternatively, and the total ALD cycles were up to 60. For example, the (10ZnO + 10TiO2)3 means 10 cycles of ZnO deposition followed by 10 cycles of TiO2 deposition, then this 10ZnO + 10TiO2 step repeat for another 2 times. The TiO2 and hybrid metal oxides deposited samples were calcined in high purity Ar gas at 600 °C for 6 h with a heating rate of 1.5 °C/min in a high temperature furnace (OTF-1200×-S, Hefei Kejing Co., Ltd) for crystalline transformation.

2.3. Characterizations

Surface morphologies of the membranes were directly observed by Hitachi S-4800 field emission scanning electron microscope (FESEM) operated at 5 kV. A contact angle goniometer (Dropmeter A-100, Maist) was employed to investigate the surface wettability of pristine and modified CNT membranes at ambient temperature. Each sample was measured with 5 µL water for at least 3 times and the average water contact angle (WCA) was recorded. The X-ray diffraction (XRD)
patterns of deposited CNT membranes were performed on a Rigaku MiniFlex 600 X-ray diffractometer with a Cu Kα X-ray source and pristine CNT membranes were tested as reference. The thicknesses of ZnO, TiO2 and hybrid metal oxides deposited on Si wafers were determined by a spectroscopic ellipsometer (Compete EASEM-2000U, J. A. Woollam) with an incident angle of 70°.

2.4. Evaluation of photocatalytic activity

The photocatalytic activities of pristine and modified membranes were evaluated by using MB (with a characteristic peak at 664 nm in UV–vis spectrum) as a model pollutant under UV light irradiation. Before irradiation, the CNT membranes was immersed into the MB solution and kept in the dark for 1 h to reach adsorption-desorption equilibrium at room temperature. Then the sample was taken out and placed on the bottom of a quartz cup which contained 20 mL of 20 mg/L MB solution. The distance between the light source (wavelength was 254 nm) and the active membrane surface was 15 cm. The concentration of MB solution was measured by UV–vis spectrometer (NanoDROP 2000C, Thermo Scientific). As a comparison, the blank MB solution was irradiated under the same condition. The degradation percentage of MB can be calculated from the following Eq. (1):

\[ D(\%) = \frac{A_0 - A_t}{A_0} \times 100\% \]  

where \( D(\%) \) is the percentage of degradation, \( A_0 \) represents the absorbance of the MB solution before irradiation and \( A_t \) represents the absorbance of the dye solution are irradiated after \( t \) time. The stability and reusability of the samples were tested by reusing the same membrane in several cycles and the irradiation time was set to 100 min. Before the recycle test, the membranes were thoroughly washed with ethanol to remove the adsorbed MB and dried at 100 °C, then were reused for MB degradation.

3. Results and discussion

3.1. Morphology evolution of CNT membranes with ALD

The morphologies of the pristine, ALD-deposited and calcined CNT membranes were investigated by FESEM. It can be seen from Fig. 1a that the pristine CNT membrane consists of intertwined smooth fibers. As shown in Fig. 1b and Fig. S1a-d, the ZnO coverage on CNTs increases with the increment of ALD cycles. Some fine ZnO nanoparticulates are observed on the surface of CNTs after 10 ALD cycles (Fig. S1a), which indicates that the oxides nucleate on the inert membrane surface successfully. With further increasing ALD cycles, the adjacent nanoparticulates are gradually approaching each other, thus forming an intact layer along the CNTs. The TiO2 nanoparticulates on the CNT surface grow with increasing ALD cycles (Fig. 1c and Fig. S1e-h). Below 150 ALD cycles, TiO2 nanoparticulates are relatively tiny and separate from each other. They get interconnected into continuous and compact layers at large number of ALD cycles, e.g., 200 cycles (Fig. S1g). We have

Fig. 4. Water contact angles of (a) ZnO, (b) TiO2 deposited CNT membranes with different ALD cycles and (c) water contact angles of 60ZnO, (30ZnO + 30TiO2), (15ZnO + 15TiO2)2, (10ZnO + 10TiO2)3 and 60TiO2 ALD-deposited CNT membranes.
investigated the growth rate (growth per cycle, GPC) of ZnO and TiO$_2$ on Si wafers under the same deposition conditions. The GPC of ZnO is $\sim$1.8 Å, while the GPC of TiO$_2$ was $\sim$0.49 Å, which was much smaller than the GPC of ZnO. We also fabricated the hybrid metal oxides deposited CNT membranes at 150 °C using alternative ZnO and TiO$_2$ depositions. As shown in Fig. 1d and Fig. S1i-l, after (30ZnO + 30TiO$_2$) cycles deposition, most of the membrane surface was coated by the hybrid metal oxides, which also confirmed the success of hybrid metal oxides deposition through this ALD process.

The metal oxide loading amounts of the ZnO, TiO$_2$ and hybrid metal oxides on CNT membranes after ALD were shown in Fig. 2. The ZnO loading amount on the CNT membrane was greatly increased to 2.24 mg/cm$^2$ after 50 ALD cycles and the TiO$_2$ loading on the membrane was increased to 1.41 mg/cm$^2$ after 150 ALD cycles (Fig. 2a). With low ALD cycles, such as 10 cycles for ZnO and 50 cycles for TiO$_2$, nanoparticulates on the CNT surface are in the nucleation stage, so ZnO and TiO$_2$ loading amounts are very low (0.22 and 0.35 mg/cm$^2$ for ZnO and TiO$_2$, respectively). After the short nucleation period, the metal oxide loading amounts were continually enhanced and reached to 3.98 and 2.37 mg/cm$^2$ for 90 cycles ZnO deposited and 300 cycles TiO$_2$ deposited CNT membranes, respectively. For the hybrid metal oxides deposited CNT membranes (Fig. 2b), the 60 cycles ZnO deposited CNT membrane has a maximum loading (2.39 mg/cm$^2$) and the 60 cycles TiO$_2$ deposited CNT membrane exhibits a minimum loading amount (0.55 mg/cm$^2$). The 30ZnO + 30TiO$_2$ deposited CNT membrane loading amount is about 1.53 mg/cm$^2$, which is higher than that of (15ZnO + 15TiO$_2$)$_2$ and (10ZnO + 10TiO$_2$)$_3$ deposited CNT membranes. For the ALD deposition, the growth rate was limited to minimum level during the nucleation period. Due to the alternative pulse strategy, the metal oxides must nucleate again on the newly formed interface, thus the (15ZnO + 15TiO$_2$)$_2$ and (10ZnO + 10TiO$_2$)$_3$ groups had longer nucleation period and lower loading amounts than the 30ZnO + 30TiO$_2$ process.

3.2. Crystalline and surface properties of modified CNT membranes

As shown in Fig. 3a, the ZnO was easily crystallized after ALD process and form hexagonal wurtzite ZnO, as we demonstrated in our previous work [35]. However, the crystalline property of TiO$_2$ was quite different from the ZnO. We have demonstrated that there are no characteristic peaks of TiO$_2$ observed after 800 ALD cycles, indicating that the as-deposited TiO$_2$ layer was amorphous [31]. For the 50 ALD-deposited CNT membrane (Fig. 3b), the TiO$_2$ characteristic peaks are undetectable after calcination due to the very limited amount of the TiO$_2$ nanoparticulates. With more ALD cycles, the peaks at 2$\theta$ of 25.0°, 37.3°, 48.0°, 53.9°, 55.1°, 62.2°, and 75.0° which correspond to (101), (004), (200), (105), (211), (204), and (215) crystal plane of the anatase TiO$_2$ (JCPDS 21-1272) are reinforced obviously. The XRD patterns of hybrid metal oxides deposited CNT membranes are shown in Fig. 3c. Due to the larger GPC of ZnO, the ratio of ZnO in the hybrid metal oxides was higher than the TiO$_2$, thus the main diffraction peaks of hybrid metal oxides are similar to those of ZnO-deposited membranes. The surface wettability of CNT membranes plays a significant role in their applications in aqueous environments. Herein, WCAs of the ZnO, TiO$_2$ and hybrid metal oxides deposited CNT membranes were measured. As illustrated in Fig. 4, the WCA of the calcined pristine CNT
membrane is ~110°, implying a hydrophobic surface. After only 10 cycles of ZnO deposition (Fig. 4a), the WCA decreased to ~74°, and further decreased to ~25° with 70 cycles deposition. This result showed that the ZnO could enhance the affinity between the water and the membrane. For TiO₂ deposition, as shown in Fig. 4b, an obvious decrease of the WCA to ~29° was achieved after only 50 ALD cycles, and kept unchanged with more ALD cycles. Similarly, the WCAs of the hybrid metal oxides modified CNT membranes were maintained around ~27° (Fig. 4c). The ALD-modified CNT membranes exhibit significantly enhanced affinity towards water, which is very much desired for their applications as functionalized materials in aqueous environments.

3.3. Photocatalytic activity of ALD-modified CNT membranes

Methylene blue (MB) was used as the model synthetic dye molecule to investigate the photocatalytic activity of ALD-modified CNT membranes. The self-degradation of MB and the pristine CNT membrane catalyzed degradation were also conducted. As shown in Fig. 5a, the MB degradation efficiencies for all samples were gradually enhanced with the increasing irradiation time, and the degradation efficiencies were changed with different loading amounts of ZnO. After 150 min irradiation, the degradation efficiency of pristine CNT membrane (15.2%) was comparable to that of the self-degradation of MB (13.1%), which means that the pristine CNT membranes have barely no photocatalytic activity. The degradation efficiency increased appreciably and reached a maximum value of 94.1% for 50 cycles ZnO-deposited membranes. However, when the ZnO loading amount is further increased, the degradation efficiency reduced to 79.4% and 47.5% for 70 and 90 cycles deposited membranes, respectively. With the increasing loading amount of the ZnO, the nanoparticulates were approaching each other and formed an intact layer, the specific surface area and number of
photocatalytic active sites were reduced on one hand, and the synergistic effect between CNTs and ZnO was hindered on the other [36,37], thus the photocatalytic activity of the modified CNT membranes is reduced. The photocatalytic performance of TiO2-deposited CNT membranes under UV light irradiation has a similar trend as that of ZnO-deposited membranes (as shown in Fig. 5b). For TiO2-deposited CNT membranes, the MB degradation efficiency reached a maximum value of 79.6% with 150 cycles TiO2 deposited CNT membranes, which demonstrated that the TiO2 photocatalytic activity was lower than the ZnO. We also examined the degradation efficiency of hybrid metal oxides deposited CNT membranes, as shown in Fig. 5c, after 90 min irradiation, the optimal degradation efficiency was achieved by the (30ZnO + 30TiO2) samples and the value is 85.1%. This result was much higher than that of 50 ALD ZnO-deposited and 150 ALD TiO2-deposited membranes after 90 min (Fig. 5d).

To further investigate the degradation efficiency difference between the ZnO, TiO2 and hybrid metal oxides deposited CNT membranes, the first-order kinetic model was used to explain the MB degradation behavior on different CNT membranes (Fig. 6a–c). It can be seen that the MB degradation for three types of modified CNT membranes all followed first-order kinetics. The rate constants of the pristine CNT membrane and MB self-degeneration were 0.0012 and 0.0010 min⁻¹, respectively. However, the rate constants for 50 ALD ZnO-deposited and 150 ALD TiO2-deposited membranes were 0.0195 and 0.0109 min⁻¹, which were 16 and 9 times higher than that of the pristine CNT membranes. The rate constant for the (30ZnO + 30TiO2) deposited CNT membrane was 0.0203 min⁻¹, indicating MB degradation was mainly performed by photocatalysis rather than photolysis [38]. These results further confirmed that the photocatalytic performance of (30ZnO + 30TiO2) deposited CNT membranes was superior than the other two modified CNT membranes.

According to the results above, a possible mechanism of the MB photodegradation was illustrated in Fig. 7. The higher photocatalytic activity of hybrid metal oxides deposited CNT membranes could be ascribed to the increased number of photocatalytic active sites, namely the photo-generated electrons and holes, which were participated in the photocatalytic reaction [37]. Under UV light irradiation, the electrons are excited from the valence band (VB) of metal oxides to the conduction band (CB), and then these photo-induced electrons transfer from the CB of metal oxides to CNTs. On the other hand, the MB dye can act as a sensitizer of light, and excited electrons transfer to the CB of metal oxides via CNTs. Simultaneously, upon bandgap excitation, the photo-generated electrons would be transferred from the CB of ZnO to that of TiO2. The photo-generated holes on the VB of TiO2 would be transferred to that of ZnO. The effective separation of charge carriers accelerated oxidation-reduction reactions between electron-holes or oxygen radicals and adsorbed MB dye. In the whole electron transfer process, CNTs could efficiently enhance electron transfer and reduce electron-hole pair recombination, thereby leading to enhanced photocatalytic efficiency [37,39–41].

3.4. Recyclability of ALD-modified CNT membranes

The (30ZnO + 30TiO2) deposited CNT membranes with superior photocatalytic activity were selected to evaluate the reusability by repeated MB degradation process. As shown in Fig. 8a, after 100 min irradiation, the degradation efficiency of the MB solution was ~99%. It can be seen from Fig. 8b that the hybrid metal oxides deposited CNT membrane can be reused for multiple times without loss of photocatalytic activity. For example, after being reused for three times, the degradation efficiency of the hybrid metal oxides deposited CNT membrane towards the MB solution is still higher than 98%, indicating the stable reusability of the hybrid-oxides-deposited CNT membranes.

4. Conclusions

In summary, we have demonstrated the controllable modification of CNT membranes via atomic-layer-deposited ZnO-TiO2 hybrid metal oxides to produce photocatalytic membranes. The CNT surface coverage and metal oxide loading amount could be precisely regulated by the ALD cycle numbers. The wettability of the ALD-modified CNT membranes is dramatically transformed from strongly hydrophobic to hydrophilic. The photocatalytic performance of the newly formed hybrid metal oxides on CNTs surface was enhanced by hindering the recombination of photo-induced electron-holes. The MB photodegradation efficiency was significantly improved to ~99% by the (30ZnO + 30TiO2) deposited CNT membrane after 100 min irradiation and the membrane could be reused for many times. Considering the advantages of ALD-modified CNT membranes, they are expected to have great potential applications in wastewater treatments.

Acknowledgements

Financial supports from the National Basic Research Program of China (2015CB653001) and the Jiangsu Natural Science Foundation (BK20150063) are gratefully acknowledged. We also thank the support from the Program of Excellent Innovation Teams of Jiangsu Higher Education Institutions, and the Project of Priority Academic Program Development of Jiangsu Higher Education Institutions (PAPD).