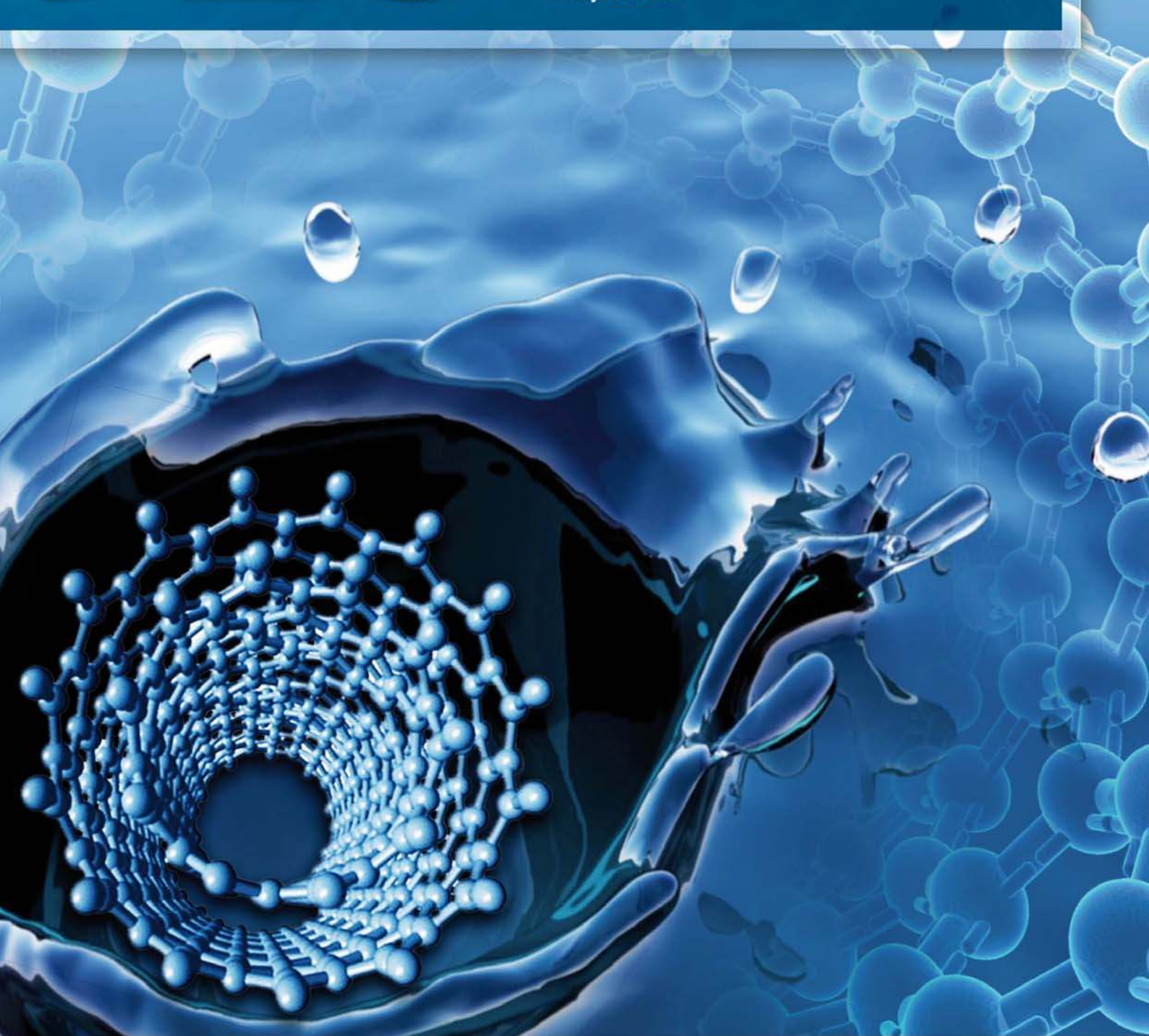


JES

JOURNAL OF
ENVIRONMENTAL
SCIENCES

ISSN 1001-0742
CN 11-2629/X

July 1, 2013 Volume 25 Number 7
www.jesc.ac.cn



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Application potential of carbon nanotubes in water treatment: A review

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Received 01 April 2013; revised 02 May 2013; accepted 09 May 2013

Abstract

Water treatment is the key to coping with the conflict between people's increasing demand for water and the world-wide water shortage. Owing to their unique and tunable structural, physical, and chemical properties, carbon nanotubes (CNTs) have exhibited great potentials in water treatment. This review makes an attempt to provide an overview of potential solutions to various environmental challenges by using CNTs as adsorbents, catalysts or catalyst support, membranes, and electrodes. The merits of incorporating CNT to conventional water-treatment material are emphasized, and the remaining challenges are discussed.

Key words: carbon nanotube; adsorption; catalysis; membrane; water treatment

DOI: 10.1016/S1001-0742(12)60161-2

Introduction

Water crisis is one of the greatest challenges of our time. The lack of fresh and clean water is a ubiquitous problem around the world. Water demand is growing rapidly as a result of increasing population and rapid urbanization. However, water resources are limited in populated areas and arid regions. The shortage of water resources calls for efficient technologies for waste water reclamation and seawater desalination. Meanwhile, pollution exacerbates the water shortage problems. Various contaminants are entering water resources from anthropogenic activities: from conventional pollutants, such as heavy metals and distillates, to emerging micropollutants, such as microcystins and antibiotics (Shannon et al., 2008). Some of these pollutants could not be removed from water efficiently via traditional water treatment methods. Moreover, more effective and low-cost technologies to decontaminate and disinfect water for point-of-use purposes are needed, especially in rural regions.

Since the first discovery in 1991 (Iijima, 1991), CNTs have attracted enormous research attention in various scientific communities. Owing to their tunable physical, chemical, electrical, and structural properties, CNTs can inspire innovative technologies to address the water shortage and water pollution problems. Carbon nanotube based nanotechnologies have found water-treatment applications in many fields, such as sorbents, catalyst, filters, or

membranes. Cost is often a limiting factor in large scale applications of CNT-based water-treatment materials. CNTs are relatively expensive, with current price around 75–250 dollars/g for single-walled carbon nanotubes and around 5–25 dollars/g for multi-walled carbon nanotubes (Cheap Tubes Inc., 2012). However, recent developments have demonstrated that it is possible to manufacture high quality CNTs at low prices. CNT can be mass produced using catalytic chemical vapor deposition in fluidized bed reactor and a production rate of 595 kg/hr can be achieved (Agboola et al., 2007). Mitsui projected that the cost of MWCNTs produced on commercial scales in their plants will be about 80 dollars/kg, and an eventual price of 10 dollars/pound seems to be achievable (Dalton et al., 2004). The large scale manufacturing at low costs may pave a way to the wide applications of CNTs. Through rational design and manipulation, CNTs can be incorporated into conventional water treatment materials, opening a new avenue to more efficient water purification and disinfection.

1 CNTs as adsorbents for removal of organic and inorganic pollutants

Adsorption is a simple and efficient method for the removal of organic and inorganic compounds in drinking water treatment. Among the various adsorbents, such as activated carbons (ACs), zeolites, and resins, ACs are one of the most widely used type of adsorbents in water treatment, because of their several merits: broad-spectrum removal

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capability toward pollutants, chemical inertness, and thermal stability. However, the application of ACs in water treatment also suffers from several bottlenecks, such as slow adsorption kinetics and difficulty for regeneration. To overcome the above problems, activated carbon fibers (ACFs) were developed as the second generation of carbonaceous adsorbents. The pores in ACFs are directly opening on the surface of carbon matrix, which shortens the diffusion distance of pollutants to adsorption sites. As a result, ACFs usually possess higher adsorption kinetics than ACs. CNTs, with one dimensional structure, like miniaturized ACFs. All adsorption sites locate on the inner and outer layer surface of CNTs. With the hollow and layered structures and tunable surface chemistry, theoretically, CNTs may be a promising third generation of carbonaceous adsorbents.

Adsorption study on CNT started several years later than its first report in 1991 (Mackie et al., 1997) and boomed in the past decade. As listed in **Table 1**, a wide spectrum of organic compounds or heavy metals has been studied as the target pollutants on CNTs with various physical structures and surface chemistry. The effects of solution chemistry, including solution pH, ionic strength, and co-existing matter, have also been investigated. Through these studies, adsorption mechanisms were elucidated at the molecular level.

In most cases, several driving forces act simultaneously, including hydrophobic effect, π - π interaction, π - π electron-donor-acceptor (EDA) interaction, electrostatic interaction, and hydrogen bonding. Because of the hydrophobic nature of their outer surfaces, CNTs have a strong affinity to organic chemicals, especially to nonpolar organic compounds, such as naphthalene (Gotovac et al., 2007b), phenanthrene, and pyrene (Yang et al., 2006). Meanwhile, the abundant π electrons on CNT surfaces enable a strong π - π coupling of aromatic pollutants with the CNT surface. Chen et al. (2007) investigated the adsorption of several polar and nonpolar pollutants onto CNTs and proposed that hydrophobic effect was not the dominant mechanism. For example, cyclohexane has a much higher K_{OW} (n-octanol-water partition coefficient, a parameter indicating the hydrophobicity of a chemical) value than nitrobenzene, but the adsorption affinity of cyclohexane was over 2 orders of magnitude weaker than the adsorption of nitrobenzene; the adsorption of nitrobenzene

was much stronger than that of benzene, toluene, and chlorobenzene, although it is less hydrophobic. In these cases, π - π EDA interaction between the nitroaromatics (π acceptors) and the grapheme sheets (π donors) of CNTs became the predominant mechanism. Within the groups of nitroaromatics, the adsorption affinity increased with the number of nitro groups.

In the light of the above mechanisms, the morphology of CNTs including nanoscale curvature and chirality of graphene layers is expected to have a great influence on the adsorption of organic pollutants, especially for those with π - π stacking as the interaction force. Gotovac et al. (2007a) observed remarkable difference between the adsorption capacities of tetracene and phenanthrene on the tube surface of CNTs because of the nanoscale curvature effect. The morphology difference of CNTs may also result in a difference in their aggregation tendency, which may further impact their adsorption ability. CNTs are prone to aggregation due to the strong van der Waals forces along the length axis. The aggregation tendency reduces with increased number of walls, or in other words, reduced nanocurvature. Generally, the aggregation of CNTs follows such an order: single-walled CNTs (SWCNTs) > double-walled CNTs (DWCNTs) > multi-walled CNTs (MWCNTs) (the interlayer spacing between the coaxial layers of MWCNTs was not available for adsorption). As shown in **Fig. 1**, SWCNTs usually exist as bundles or ropes while MWCNTs are randomly entangled as individual tubes. As a consequence of aggregation, the available outer surface was reduced while new adsorption sites appeared as interstitial channels and grooves between the tubes in CNT bundles. Zhang et al. (2009) developed equations to calculate the changes in pore volume and specific surface area caused by aggregation and found that aggregation of CNTs was unfavorable for the adsorption of several synthetic organic compounds (SOCs) on CNTs, since the surface area was more important than the pore volume in adsorption of SOC. Ultrasonication significantly enhanced the adsorption kinetics of SOC on CNTs, indicating that the dispersion status of CNTs affected the adsorption kinetics (Zhang et al., 2012).

Surface chemistry is another important factor influencing the CNTs adsorption behavior. Functional groups such as $-OH$, $-C=O$ and $-COOH$ could be intentionally introduced onto CNT surfaces by acid oxidation or air

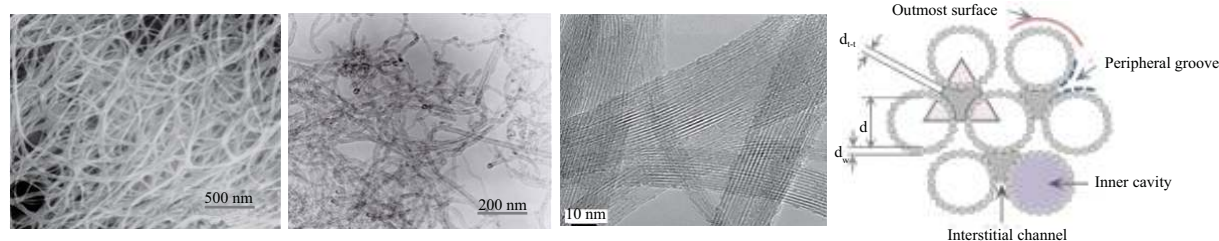


Fig. 1 SEM image of SWCNT, SEM image of MWCNT, TEM image of SWCNT, and schematic illustration of SWCNT bundle (from left to right) (Reprinted with permission from Zhang et al., 2009). Copyright 2009 American Chemical Society.

Table 1 Application of CNTs in removal of target pollutants from aqueous solutions

Adsorbents	Pollutants	Comments	Reference
As-grown CNTs and graphitized CNTs	1,2-Dichlorobenzene (DCB)	As-grown CNTs had rough surface which made adsorption of organics much easier. Graphitized CNTs became smooth and the adsorption of organics decreased. The removal efficiency of DCB by both as-grown CNTs and graphitized CNTs kept stable in the pH range 3–10. When pH exceeds 10, the removal dropped suddenly due to the adsorption of water molecules onto $-\text{COO}^-$ groups that could hinder the access of DCB.	Peng et al., 2003
CNTs purified by mixed HNO_3 and H_2SO_4	Polycyclic aromatic hydrocarbons (PAHs)	Adsorption capacity of phenanthrene by MWCNTs was related with surface area or micropore volume. SWCNTs exhibited a larger adsorption capacity toward PAHs than MWCNTs.	Yang et al., 2006
	PAHs	In low-concentration range, adsorption affinity of 13 PAHs was directly related to the solubility of their subcooled liquid.	Kah et al., 2011
	Phenolic compounds phenol, pyrogallol, 1-naphthol	Four possible solute-sorbent interactions, i.e., hydrophobic effect, electrostatic interaction, hydrogen bonding, and $\pi-\pi$ electron donor-acceptor interaction acted simultaneously. CNTs with smaller outer diameter had higher distribution coefficients (K_d). The K_d values of the three polar phenolics tended to increase with increasing pH and then decrease with pH over their pK_a value.	Pan and Xing, 2008
	Triton X-series surfactants	Hydrophobic and $\pi-\pi$ interactions between the surfactants and CNTs were the dominant mechanisms. The adsorption of Triton X-series surfactants facilitated suspending CNTs in water. Adsorption remained constant within pH 2–12, indicating that electrostatic interaction and hydrogen bonding were not the major mechanisms.	Bai et al., 2010
As-received CNTs	Uranium	Acid treatment increased the surface acidic functional groups of CNTs, therefore increased their colloidal stability and adsorption capacity for uranium.	Schierz and Zänker, 2009
	Atrazine and trichloroethylene	Hydrophobic interactions were the dominant adsorption mechanism. The impurities in SWCNTs contribute a significant mass but do not provide strong adsorption sites.	Brooks et al., 2012
CNTs activated by KOH etching	Pharmaceutical antibiotics: sulfamethoxazole, tetracycline, tylosin	KOH etching is an effective activation method to improve the adsorption affinity and adsorption reversibility of organic pollutants on carbon nanotubes. The activated CNTs showed an increased adsorption capacity toward antibiotics due to more interconnected pore structure and less pore deformation.	Ji et al., 2010
As-prepared and oxidized MWCNTs	Ionizable aromatic compounds (IACs): 1-naphthylamine, 1-naphthol, phenol	The adsorption capacity of MWCNTs toward IACs was higher than other common adsorbents such as natural bentonite, apatite and kaolinite. Oxidation of MWCNTs increased the surface area and added oxygen-containing functional groups to the surfaces of MWCNTs, which depressed the adsorption of IACs on MWCNTs. The adsorption was considerably hindered when $\text{pH} > \text{pK}_a$.	Sheng et al., 2010
MWCNTs grown by CVD	Antibiotic ciprofloxacin	The adsorption of ciprofloxacin was compared between AC, carbon xerogel and CNT. CNT exhibited the best adsorption performance per unit surface area.	Carabineiro et al., 2012
CNTs	Microcystins (MC)	CNTs showed higher adsorption affinity to MCs as compared to ACs. The pore size of CNTs was fit for the molecular dimension of microcystins. CNTs with smaller outside diameter could adsorb more MCs.	Yan et al., 2006
MWCNTs	Natural organic matter (NOM)	The higher molecular weight fraction of NOM was preferentially adsorbed, as proved by size exclusion chromatographic analysis.	Hyung and Kim, 2008
CNTs opened using hydrothermal opening method Amorphous Al_2O_3 supported on CNTs	Phenol	The influence of hydrothermal opening conditions on surface chemical composition and adsorption capacity of CNTs were investigated.	Wiśniewski et al., 2012
	Fluoride	The CNT supported Al_2O_3 had much higher adsorption capacity toward fluoride, which may be attributed to the nano-size Al_2O_3 clusters on CNTs and the intrinsic adsorption capacity of CNTs toward fluoride. The adsorption performs well at pH 5–9, which was a much broader range than that of the activated alumina (pH < 6).	Li et al., 2001
CNTs purified by HNO_3	Lead	The adsorption capacity of acid-refluxed CNTs (11.2 mg/g) was higher than that of ACs (about 5.5 mg/g). The surface oxygen-containing functional groups were the most important factor for lead adsorption. The higher adsorption capacity of CNTs at pH = 7 may be due to the cooperating role of adsorption and precipitation.	Li et al., 2002
Ceria nanoparticles supported on CNTs	Arsenate	The As(V)-loaded adsorbent can be efficiently regenerated. Ca^{2+} and Mg^{2+} ions in water enhanced the adsorption capacity of CeO_2 -CNTs toward arsenate due to the formation of ternary surface complex.	Peng et al., 2005
Iron(III) oxide coated ethylenediamine functionalized MWCNTs	Arsenate	Influence of pH, iron oxide loading and interfering ions were modeled using MINTEQA2 program.	Veličković et al., 2012

oxidation. Those functional groups make CNTs more hydrophilic and suitable for the adsorption of relatively low molecular weight and polar contaminants, such as phenol (Lin and Xing, 2008a) and 1,2-dichlorobenzene (Peng et al., 2003).

Figure 2 is an overview of the surface modification and effects of functional groups on the adsorption properties of CNTs (Pan and Xing, 2008). The adsorption of heavy metals on CNTs depends mainly on the specific complexation between metal ions and the hydrophilic functional groups of CNTs (Rao et al., 2007). Therefore, without doubt, surface functionalization of CNTs is favorable for the uptake of metal ions. Cho et al. (2010) reported that surface oxidation of CNTs enhanced the adsorption of zinc and cadmium ions from aqueous solutions. Using two-site Langmuir adsorption modeling, they found that the carboxyl-carbon sites of CNTs were over 20 times more energetic for Zn(II) uptake than the unoxidized carbon sites. Another direct consequence of surface modification of CNTs with hydrophilic groups is the improvement of CNT dispersion in aqueous media. Rosenzweig et al. (2013) reported that the alcohol (OH) and acid (COOH) moieties on CNTs can determine the aggregation state and accessible sites for copper adsorption. The surface functionalized CNTs had higher adsorption capacity for copper than pristine CNTs. It is worth noting that increasing the oxygen-containing functional groups is a double-edged sword. It may have an adverse effect on the adsorption of highly nonpolar chemicals like naphthalene (Cho et al., 2008). Wu et al. (2012) systematically investigated the influence of surface oxidation of MWCNT on the adsorption capacity and affinity of organic compounds in water, and found that surface oxidation of MWCNTs decreased the surface-area-normalized adsorption capacity

of organic compounds significantly because of the competition of water molecules; meanwhile, the adsorption affinity of organic chemicals were not altered because of the adsorption interactions (hydrophobic effect, π - π interaction and hydrogen bond) remained constant.

The complex mechanisms involved in CNT adsorption could be explained from two aspects: thermodynamics and kinetics. Thermodynamic parameters, including free energy change of adsorption (ΔG), enthalpy change (ΔH), entropy change (ΔS) and activation energy (E_a), provide an insight regarding the inherent energetic changes during adsorption. Adsorption of Pb^{2+} (Li et al., 2005), trihalomethanes (Lu et al., 2006), 1-naphthol and phenol (Sheng et al., 2010), methyl orange (Yao et al., 2011) were demonstrated to be spontaneous processes based on the negative ΔG and the positive ΔS . The positive ΔS values imply that the degree of freedom increased at the solid-liquid interface during the adsorption of contaminants onto CNTs. This could be attributed to the entropy increase of water molecules after the ordered water shells being destroyed in the adsorption process (Sheng et al., 2010).

In terms of adsorption kinetics, the ordered pore structure of CNTs makes it easier for the diffusion of pollutants to adsorption sites (Lu et al., 2005). This can be well reflected through the comparison with ACs. ACs is usually rich in micropores, which are sometimes not available for the access of relatively large organic molecules. Ji et al. (2009) investigated the adsorption of tetracycline to CNTs, graphite and AC and found that the adsorption affinity of tetracycline decreased in the order of graphite/SWNT > MWNT \gg AC upon normalization for adsorbent surface area. The weaker adsorption of tetracycline to AC indicated that adsorption affinity was greatly influenced by the accessibility of available adsorption sites. The remarkably

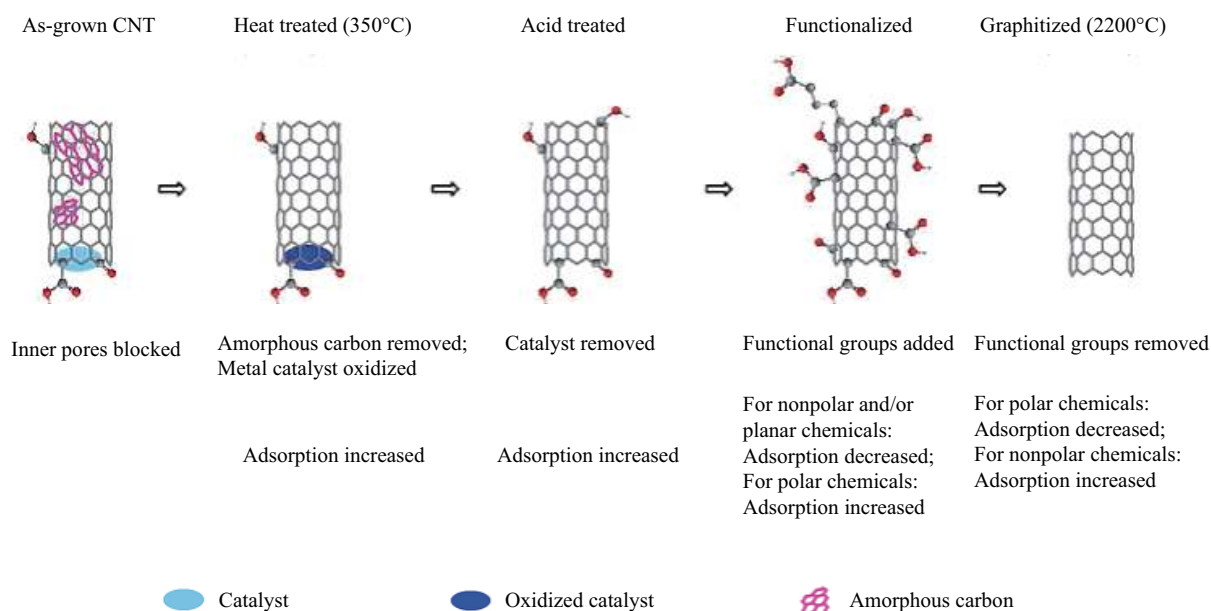


Fig. 2 Adsorption properties of CNTs as affected by the functional groups (Reprinted with permission from Pan and Xing, 2008). Copyright 2008 American Chemical Society.

strong adsorption of tetracycline to CNTs can be attributed to the strong adsorptive interactions (van der Waals forces, π - π EDA interactions, cation- π bonding) with the graphene surface of CNTs. From a kinetics point of view, Lu et al. (2005) studied the adsorption of trihalomethanes to CNTs and a powdered activated carbon (PAC). CNTs reached adsorption equilibrium much faster than the PAC. This may be explained by the different porous structures of CNTs and PAC. PAC had more micropores in which trihalomethanes have to move from the exterior surface to the inner pores of PAC to reach equilibrium. The more uniform pore structure of CNTs was beneficial for the diffusion of pollutants into the inner pores. Zhang et al. (2012) examined the adsorption kinetics of phenanthrene and biphenyl on a granular activated carbon (GAC) and CNTs. Fitting the kinetic data with intra-particle diffusion model indicated that external mass transfer controlled the adsorption of organic compound to CNTs, while intra-particle diffusion dominated in the adsorption of organic compounds onto ACs (Zhang et al., 2012). Therefore, in well mixed systems, CNTs are superior to ACs in terms of sorption kinetics.

Besides adsorption capacity and kinetics, adsorption selectivity or resistance to harsh environment is another important evaluation criterion for an adsorbent. A number of studies have examined the importance of aqueous chemistry conditions on the adsorption of SOCs by CNTs (Chen et al., 2008; Hyung and Kim, 2008; Lin and Xing, 2008b; Wang et al., 2008b, 2009c; Yang et al., 2008a). Effects of solution pH and ionic strength on SOC adsorption by CNTs were somewhat SOC-specific, the extent of which depends on the ionizability and electron-donor-acceptor ability of the involved SOCs (Chen et al., 2008; Lin and Xing, 2008a; Pan and Xing, 2008; Yang et al., 2008a). Zhang et al. (2009) observed that solution pH and ionic strength exhibited only slight or insignificant impacts on the adsorption of three representative SOCs (phenanthrene, biphenyl, and 2-phenylphenol), which are variant in planarity, polarity, and hydrogen/electron-donor/acceptor ability. The removal of Ni^{2+} and Zn^{2+} increased with solution pH in the range of 1–8, reached maximum in the range of 8–11, and decreased as pH over 12 (Lu and Chiu, 2006a, 2006b). The maximum adsorption in the pH range of 8–11 could be attributed to the negatively charged surface functional groups of CNTs and the formation of hydrated ion species such as $\text{M}(\text{OH})^{+1}$ and $\text{M}(\text{OH})_2^0$. At a pH higher than 12, the predominant metal species was $\text{M}(\text{OH})_3^{-1}$, and the heavy metal removal decreased due to the competition between OH^{-1} and $\text{M}(\text{OH})_3^{-1}$ and the repulsive force between the negatively charged CNT surface and $\text{M}(\text{OH})_3^{-1}$. The net impact of NOM on SOC adsorption by CNTs is a tradeoff between two opposite effects: increase in adsorption sites due to better dispersion of CNTs in the presence of NOM (Hyung et al., 2007; Lin and Xing, 2008b) and decrease in adsorption sites due to

competition and/or blockage by NOM (Wang et al., 2008b, 2009c). Under identical conditions, minimal NOM effects occurred on a macroporous MWNT while severe NOM effects were observed on a GAC (HD4000) and an ACF, of which the dominant structures are microporous (Zhang et al., 2011a). Although the single-solute adsorption capacities of the SWNT were much lower than those of HD4000, in the presence of NOM the SWNT possessed adsorption capacities similar to or even higher than those of HD4000.

Recently, quantum chemical calculations have been successfully applied to assess and predict the adsorption of pollutants by CNTs. Woods et al. (2007) studied the adsorption of benzene derivatives by CNT using density functional theory and found that physical adsorption dominated through the interactions between the π orbitals of benzene derivatives and CNT. Tournus and Charlier (2005) carried out an *ab initio* study of benzene adsorption on CNTs and found that the adsorption energies varied with the chiral angle of CNT. Zou et al. (2012) systematically investigated the adsorption of cyclohexane, benzene derivatives, and polycyclic aromatic hydrocarbons on CNT using M05-2X of density-functional theory. The contribution of different functional groups on CNT to adsorption was quantified, and the calculated ΔG correlated well with the experiment values (Fig. 3). With the development of molecular simulation methods, the adsorption of pollutants by CNTs can be predicted effectively using chemical calculations.

With the number of aforementioned advantages: stronger chemical-nanotube interactions, tailored surface chemistry, rapid equilibrium rates, and high sorption capacity, CNTs were considered as superior sorbents for a wide range of organic chemicals and inorganic contaminants than the conventional ACs. However, for practical application in water treatment, the small particle size of

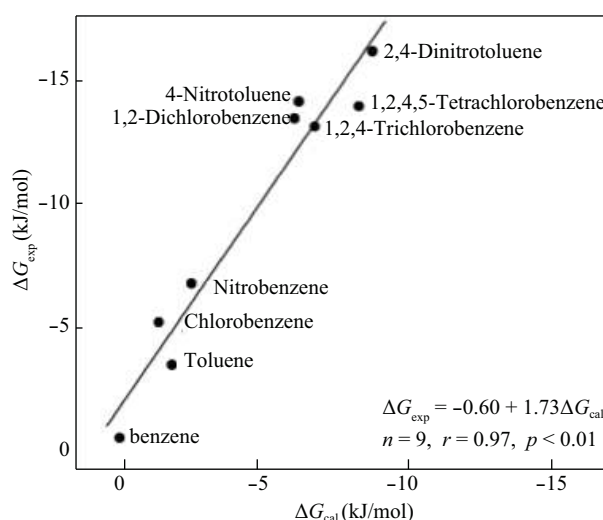


Fig. 3 Regression of calculated ΔG_{cal} with experimental ΔG_{exp} values for 9 aromatic compounds on SWCNT (Reprinted with permission from Zou et al. 2012). Copyright 2012 American Chemical Society.

CNTs will cause excessive pressure drops and the recovery of spent CNTs is a true challenge. The macroscopic manipulation of CNT monolithic blocks via appropriate methods provide breakthrough for this bottleneck. Gui et al. (2010) made a monolithic CNT sponge by chemical vapor deposition using ferrocene as precursor. The as-made CNT sponge had a randomly intertwined three-dimensional structure and displayed high porosity and very low density. The CNT sponge can float on oil-contaminated water and remove oil with a large adsorption capacity (80 to 180 times their own weight for a wide range of solvents and oils) (Fig. 4). The sponge had a tendency to move to the oil film area due to its high hydrophobicity, leading to the unique “floating-and-cleaning” capability that is very useful for spill cleanup.

In addition to serving as direct adsorbents, CNTs can also be utilized as excellent scaffold for macromolecules or metal oxides with intrinsic adsorption ability. The tunable surface chemistry and controllable pore size make CNTs good support for composite adsorbents. Examples of CNTs as scaffolds for pollutant removal include CNT decoration with iron oxide for europium adsorption (Chen et al., 2009), chitosan for methyl orange adsorption (Zhu et al., 2010), polyaniline for malachite green adsorption (Zeng et al., 2013) and ceria nanoparticles for chromium adsorption (Di et al., 2006). Maggini et al. (2013) synthesized a supermolecular adsorbent by coating magnetic CNT with poly(vinylpyridine), which exhibited excellent removal capacity of divalent metals from water, and the exhausted material can be separated using magnetic field and regenerated by acid treatment. The unique electrical properties of CNTs could be utilized for enhanced adsorption with electrochemical assist (Li et al., 2011b).

The mechanical flexibility and robustness, thermal stability and resistance to harsh environment endow CNTs with excellent application potential in water treatment. CNTs have the potential to serve as superior adsorbents for removal of both organic and inorganic contaminants from water systems. Nevertheless, there are several aspects that need to be evaluated prudently before the real application in water treatment facilities, including cost, reusability and the possibility of leakage into the environment.

2 CNTs as catalysts or co-catalysts for biorefractory and persistent organic pollutants

CNTs have been demonstrated as excellent catalyst-support (Table 2) due to several reasons: (1) CNTs have a large specific surface area, generally $> 150 \text{ m}^2/\text{g}$ (Peigney et al., 2001). Heterogeneous catalysis degradation of aqueous pollutants is best modeled by the Langmuir-Hinshelwood mechanism, which requires the adsorption of chemicals before the chemicals are degraded on the catalyst. The large specific surface area is helpful for the adsorption of pollutants. It should be noted that the specific surface area of CNT is smaller than that of AC, so the following merits of CNT are more important; (2) CNT could be easily functionalized with carbonyl and hydroxyl moieties via acid treatment, and these groups could be further modified to improve the adsorption affinity toward some specific chemicals, leading to “selective degradation” processes, like degradation of pollutants over benign species, and highly-toxic pollutants over low-toxic pollutants; (3) the uniform porous structure of CNTs reduces the mass-transfer limitations of reactants from solution to active sites on the catalyst; (4) CNTs have good thermal stability and resistance to acidic and basic media thus could be used in severe conditions.

2.1 CNTs in photocatalysis

Photocatalysis has been a hot topic in the degradation of organic pollutants for several decades (Hoffmann et al., 1995). Traditional photocatalysts include TiO_2 , CdS, Fe_2O_3 , ZnO etc. These semiconductors suffer from some disadvantages: TiO_2 has a large band gap and can only be excited by ultraviolet light, thus could not effectively harvest the spectrum of sunlight; CdS and ZnO hold the drawback of photocorrosion and cause the decrease in photoactivity and stability; in addition, all the semiconductors have the bottleneck of low quantum efficiency due to the rapid recombination of photo-generated electrons and holes, i.e., most charges quickly recombine without participating in photocatalytic reactions.

Owing to their excellent mechanical, electrical and optical properties, CNTs can serve as an ideal building block in hybrid catalysts and improve the performance of photocatalysts. CNT can be either semiconducting or metallic depending on their diameter and chirality. CNTs

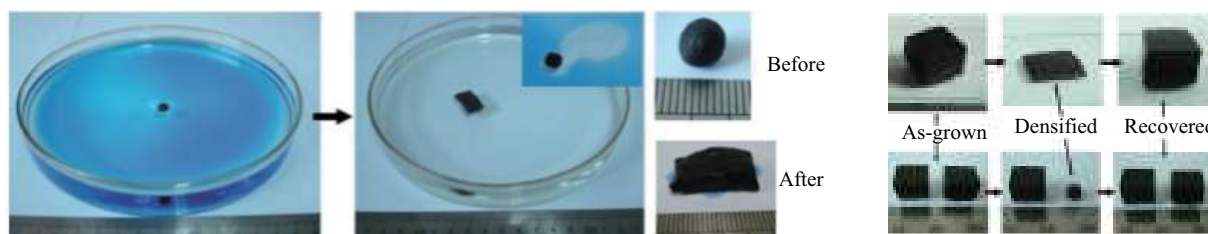


Fig. 4 Application of CNT sponge in the cleanup of oil on water and densification of cubic-shaped sponges into small pellets and full recovery to original structure upon ethanol absorption (Reprinted with permission from Gui et al., 2010). Copyright 2010 Wiley-VCH.

have a large electron-storage capacity and it was estimated that every 32 carbon atoms in SWCNTs can store an electron (Kongkanand and Kamat, 2007). When in contact with TiO_2 nanoparticles, CNTs prompt electron transfer from the conducting band of TiO_2 to the CNT surface due to their lower Fermi level. Thus, CNTs accept and store photogenerated electrons and inhibit the recombination of electrons and holes. Those electrons can be transferred to another electron acceptor, such as molecular oxygen, forming reactive oxygen species (O_2^- , H_2O_2 and $\cdot\text{OH}$) which degrade and further mineralize organic pollutants.

Recent research highlighted the euphoria of CNTs to TiO_2 nanoparticles. CNT/ TiO_2 composites showed enhanced photocatalytic oxidation activity to phenol due to reduced charge recombination as evidenced by the diminished photoluminescence intensity, and SWCNT enhanced the photocatalytic activity of TiO_2 better than MWCNT because there are more individual contact between the SWCNT and the TiO_2 nanoparticle surface (Yao et al., 2008). In addition to the inhibition of charge recombination, the introduction of CNTs increases the amount of hydroxyl groups on the catalyst surface, which can be oxidized by h^+ and generate hydroxyl radicals, as proved by EPR results (Yu et al., 2005b). Aqueous pollutants including dyes (Li et al., 2011c; Yu et al., 2005a), benzene derivatives (Silva and Faria, 2010), and carbamazepine (Martinez et al., 2011) were efficiently photodegraded by CNT- TiO_2 composites. More practically, CNT/ TiO_2 composite has found application in the degradation of nitro phenols from real wastewater under sunlight and the composite held repetitive photocatalytic activity (Wang et al., 2009b).

The addition of CNT to TiO_2 may change the absorption spectrum of the catalyst. Annealing of CNTs coated with

thin and uniform TiO_2 results in carbon diffusion into oxide phase via oxygen lattice substitution. Carbon doping produced a mid band-gap state close to the TiO_2 valence band and extended light absorption to the visible region (Fig. 5) (Cong et al., 2011; Lu et al., 2010). Considering their semiconductor property, CNTs may also act as photosensitizers and inject the photo-excited electrons to the conducting band of TiO_2 (Wang et al., 2005a).

CdS is a visible light-responsive photocatalyst, but it suffers from photocorrosion. Anchoring CdS onto CNTs inhibited the photocorrosion phenomenon, and the author attributed it to the enhanced adsorption capacity toward reducing agents in the solution, which can capture holes and stabilize CdS (Ma et al., 2008).

Applications of CNTs in photocatalysis also include using CNTs as pillars of reduced graphene oxide platelets for rhodamine B (RhB) degradation (Zhang et al., 2010), and the preparation of Au NP@POM-CNT tri-component hybrid photocatalyst (Li et al., 2011a). Very interestingly, although Au nanoparticles are visible light photo-sensitizers, they do not hold photocatalytic activity, due to the fast rate of charge recombination. The excellent electron-conducting ability of CNTs made the Au NP@POM-CNT hybrid an effective visible light photocatalyst.

It is worth noting that CNTs can absorb the incident light, thus excess CNTs may have an adverse impact on the activity of the composite photocatalyst. Therefore, it is critical to control the dosage of CNTs to photocatalysts (Yu et al., 2005b). Moreover, the interfacial contact between CNTs and metallic semiconductors dictate the performance of the hybrid photocatalyst. Appropriate synthetic approaches are needed for the improvement of the CNT/ TiO_2 interface. Eder and Windle (2008) used benzyl

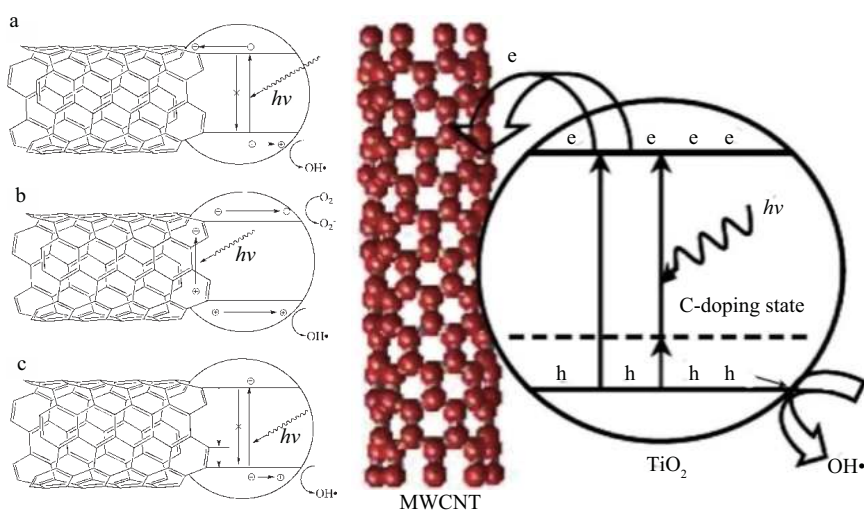


Fig. 5 Proposed mechanisms of synergistic enhancement in TiO_2 -CNT composites. Left panel: (a) CNTs inhibit charge recombination by acting as sinks for photogenerated electrons in TiO_2 ; (b) photosensitizing mechanism based on electron-hole pair generation in the CNT. Depending on the relevant positions of the bands, the electron or hole may be injected into the TiO_2 , generating reactive oxygen species; (c) CNTs act as dopants through the Ti-O-C bonds (Reprinted with permission from Woan et al., 2009). Copyright 2009 Wiley. Right panel: enhancement of visible light photocatalytic activity in carbon-doped TiO_2 coating on CNTs (Reprinted with permission from Cong et al., 2011). Copyright 2011 Elsevier.

Table 2 CNTs as photocatalyst support for the degradation of organic pollutants

Hybrid photocatalyst	Target pollutants	Highlights	Reference
CNT/TiO ₂	Azo dye	Enhancement of adsorption of dye; Inhibition of charge recombination.	Yu et al., 2005a
CNT/mesoporous TiO ₂	Acetone	Inhibition of charge recombination; More hydroxyl groups on the catalyst and more hydroxyl radicals generated.	Yu et al., 2005b
CNT/TiO ₂ nanowire film and CNT/P25 film	Methyl Orange	CNT/TiO ₂ nanowire film was more suitable for photocatalytic filtration application owing to its less pore blockage.	Daranyi et al., 2011
CNT/TiO ₂	Rhodamine B	Electrospinning method was employed to fabricate CNT/TiO ₂ composite.	Im et al., 2012
SWCNT/TiO ₂	Congo Red	The addition of silica promoted the coating of TiO ₂ on CNT. Imitate contact between CNT and TiO ₂ were needed to achieve enhanced photocatalytic activity.	Jafry et al., 2011
CNT/TiO ₂	Phenol	SWCNTs were better support for TiO ₂ than MWCNTs due to more interfacial contact.	Yao et al., 2008
CNT/TiO ₂ heterojunction array	Phenol	The thickness of TiO ₂ layer could be controlled by varying the deposition time.	Yu et al., 2008
MWCNT/TiO ₂	2,6-Dinitro-p-cresol	No obvious decline in efficiency of the composite photocatalysts was observed after 5 repeated cycles.	Wang et al., 2009a
MWCNT/TiO ₂	2,4-Dinitrophenol	The composite was very effective in decolorization and COD reduction of real wastewater from DNP manufacturing.	Wang et al., 2009b
MWCNT/TiO ₂	Eosin Yellow	Nitrogen was doped to enhance visible photoactivity, and palladium was doped to reduce charge recombination.	Kuvarega et al., 2012
MWCNT/TiO ₂	Acid Blue 92	MWCNT prevented the agglomeration of TiO ₂ particles.	Zarezade et al., 2011
CNT/TiO ₂	Aniline, nitrobenzene, benzoic acid	The presence of oxygen-containing functional groups had a positive effect on the photocatalytic activity of the composite.	Silva and Faria, 2010
CNT/TiO ₂	Methyl Orange	CNT also acted as a dispersing template to control the morphology of TiO ₂ .	Xu et al., 2010
CNT/titanium silicate	4-Nitrophenol, Rhodamine B	Ball milling removing the physical contact between CNT and titanium silicate greatly reduced the photocatalytic activity, indicating the significance of interfacial charge transfer	Krissanasaeeraneet et al., 2010
MWCNT/TiO ₂	Atrazine	Microwave was used to enhance the photocatalytic activity; CNT had a beneficial effect on absorbing microwave energy.	Chen et al., 2011
TiO ₂ -CeO ₂ /CNT Titania nanotube/CNT	Phenol derivatives Acetaldehyde	Presence of mesopores in composite matrix. Visible light photoactivity was caused by Ti-O-C bond, which was confirmed by XPS and EPR	Wilson et al., 2012 Vijayan et al., 2012
CNT/ZnS	Methylene Blue	Post-refluxing treatment played a key role in the improvement of the interaction between ZnS nanocrystals and CNTs	Feng et al., 2008
CNT/ZnS	Methyl Orange	Microwave assisted synthesis promote the dispersion of ZnS and the size of ZnS nanospheres were easily tunable.	Wu et al., 2008
CNT/CdS	Azo dye	CNTs hampered the photocorrosion of CdS.	Ma et al., 2008
CNT/WO ₃	Rhodamine B	Mass ratio of CNTs and WO ₃ were optimized.	Wang et al., 2008a

alcohol (BA) as surfactant in the preparation of CNT/TiO₂ composite. The addition of BA could improve the dispersion state of TiO₂ on CNTs through π - π interaction between BA and CNT and coordination between BA and titanium. Lee et al. (2012) synthesized N-doped CNT/TiO₂ nanowires through biomimetic mineralization, in which the direct contact between CNT and TiO₂ was the key for band gap narrowing. Some studies also emphasized on the contact resistance of CNT/TiO₂ in terms of electron transportation. SWCNT can enhance the photocatalytic activity of TiO₂ more than MWCNT due to more individual contact, but the resistance of SWCNT is high, so there is a need to reduce the interface charge transfer resistance of SWCNT/TiO₂. Duong et al. (2011) introduced indium tin oxide (ITO) thin films at the interface between SWCNTs and TiO₂. The transparent conducting ITO films remarkably reduced the contact resistance and played a key role in enhancing photoelectrochemical activity.

CNTs can also act a photocatalyst directly. Yan et al. (2011) reported that the loading of Ag to CNTs obviously enhanced the photocatalytic activity of CNTs. The Ag/CNT composite exhibited photocatalytic degradation activity toward RhB and the mechanisms are shown in **Fig. 6** (Yan et al., 2011). Qu et al. (2013) reported that CNTs synthesized from poplar leaves could photocatalytically degrade bisphenol A, and the photocatalytic activity was caused by CNT and the metal oxide on the surface of

CNT.

2.2 CNTs in catalytic wet air oxidation

Wet air oxidation, a process that utilize the oxygen in air to oxidize dissolved and suspended organic matter in water, has been commercially used as an effective method for wastewater treatment for around 60 years. However, severe reaction conditions and high operating costs impede its application for treating the industrial wastewater. Using catalysts (usually noble metals) in wet air oxidation process helps to promote the oxidation efficiency and reduce costs. Several studies used CNT as catalyst support in wet air oxidation for the treatment of organic and toxic wastewaters (Garcia et al., 2005, 2006; Gomes et al., 2004; Taboada et al., 2009; Yang et al., 2007, 2008b). CNT supported Pt, Pd and Ru catalysts have found applications in wet air oxidation of organic pollutants like phenol and aniline (Garcia et al., 2006; Yang et al., 2008b). As compared to AC, the mesoporous nature of CNTs is more advantageous for the diffusion of pollutants to the surface of catalyst.

CNTs themselves can act as effective catalyst in wet air oxidation processes. MWCNTs display catalytic activity in the wet air oxidation of phenol, and the mechanisms are shown in **Fig. 7** (Yang et al., 2007). Molecular oxygen in water adsorbed on the surface of functionalized CNTs, and then was dissociated on the graphite layers to produce dis-

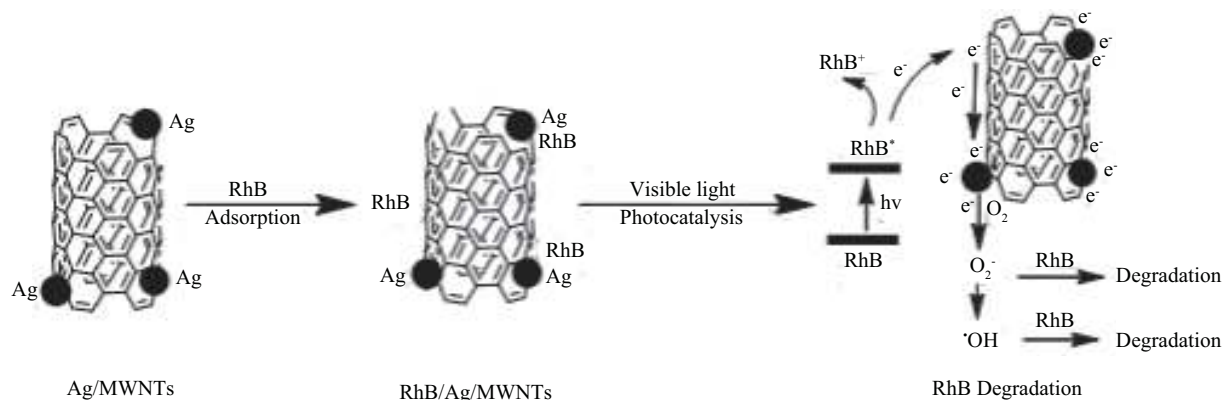


Fig. 6 Photocatalytic mechanism of RhB degradation on Ag/CNT (Reprinted with permission from Yan et al., 2011). Copyright 2011 Elsevier.

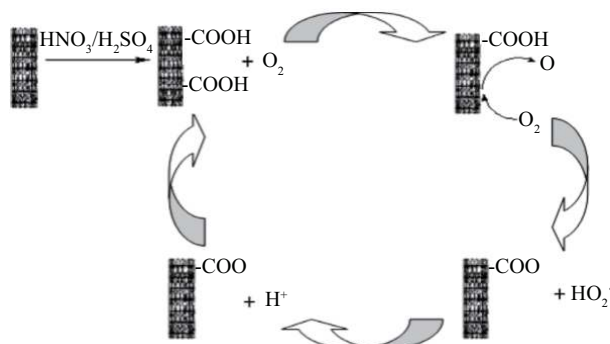


Fig. 7 HO₂· radical producing mechanisms in catalytic wet air oxidation of phenol over MWCNTs (Reprinted with permission from Yang et al., 2007). Copyright 2007 Elsevier.

sociated oxygen atoms. Thereafter, the carboxylic groups on CNTs and the oxygen atoms formed $\text{HO}_2\cdot$ radicals through hydrogen bonding, leading to the degradation of organic pollutants.

3 CNT membranes for water purification

Membrane technologies, including microfiltration, ultrafiltration, nanofiltration and reverse osmosis, constitute vital units of many water treatment systems. Polymer membranes are widely used in water treatment facilities and have chemical and mechanical stability, but they are hydrophobic in nature and have a propensity for adsorption of organic foulants. The irreversible adsorption of organic, inorganic and biological substances onto the membrane surface leads to membrane fouling and consequently continuous flux-decline. Studies have demonstrated that CNT filters can achieve high water flux at reasonably low pressure (Brady-Estévez et al., 2008). CNTs owing to the several merits: strong antimicrobial activity, higher water flux than other porous materials of comparable size, tunable pore size and surface chemistry, and electrical conductivity, are promising materials for filtration and separation.

3.1 CNT filters as anti-microbial materials

Millions of people die each year from water related diseases. The removal of bacteria and other organisms from drinking water is an extremely important process. CNTs, especially SWCNTs, exhibit strong antimicrobial activity (Kang et al., 2007). Direct contact with SWCNTs causes severe membrane damage and subsequently cell death. SWCNT filter showed high bacterial retention (Brady-Estévez et al., 2008), and MWCNT filter exhibited high viral removal at low pressure (Brady-Estévez et al., 2010b), both through size exclusion effect. To combine their advantages, SWCNT-MWCNT hybrid filter achieved efficient bacterial inactivation and viral retention at low pressure (Brady-Estévez et al., 2010a). By applying external electric field, viral removal by CNT filter was markedly enhanced as a result of increased viral particle trans-

port (Rahaman et al., 2012). In combination with silver nanoparticles (Akhavan et al., 2011) or silver nanowires (Schoen et al., 2010), enhanced antibacterial ability were achieved.

The above-mentioned CNT filters were prepared by simple filtration of CNT suspensions through a porous substrate. Srivastava et al. (2004) fabricated a monolithic uniform macroscopic hollow cylinder having radially aligned CNT walls by using a continuous spray pyrolysis method. The CNT aligns had a uniform nanoporous structure which was favorable for filtration with low blockage. The cylinder also had high mechanical strength and thermal stability. **Figure 8** shows the application of a CNT filter in the removal of *E. coli* bacteria from water. The CNT filter had a major advantage over conventional membrane filters: it can be cleaned repeatedly by simple ultrasonication and autoclaving. After regeneration, the filter regained its full filtering efficiency.

3.2 CNTs as additives for anti-fouling membranes

Fouling of polymer membranes depends on the interaction between membrane surface and foulants, which is related to the membrane morphology and chemistry as well as the properties of foulants. Tuning the membrane surface chemistry is an effective method to control membrane fouling. It is generally accepted that increasing the surface hydrophilicity offers a better fouling resistance because many organic foulants are hydrophobic. CNTs, although hydrophobic in nature, can be changed to hydrophilic via acid treatment. It has been demonstrated that CNT blended polysulfone membrane (Choi et al., 2006) and polyethersulfone membrane (Celik et al., 2011) are more hydrophilic and have an enhanced fouling resistance due to the hydrophilic carboxylic groups of functionalized CNTs. Other functional groups can also be introduced onto CNT surface, such as hydrophilic isophthaloyl chloride groups (Qiu et al., 2009) and amphilic-polymer groups with protein-resistant ability (Liu et al., 2010). The property of CNT has an influence on the performance of CNT-blended membrane. The study by Ajmani et al. (2012) revealed that CNT-membrane constructed with larger diameter CNTs

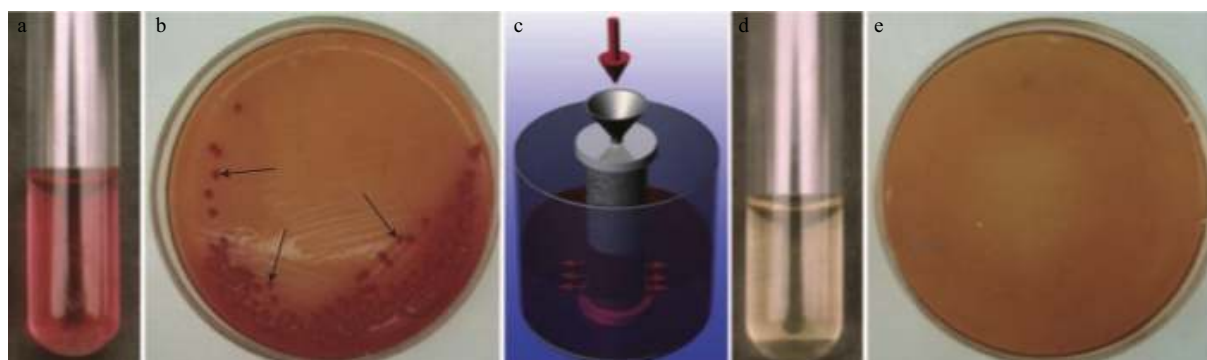


Fig. 8 Removal of *E. coli* bacteria using CNT filter. (a) *E. coli*-ridden solution; (b) colonies of *E. coli* bacteria (marked by arrows) grown by the culture of the polluted water; (c) cylindrical CNT filter; (d) filtrate; (e) no bacterial colonies grown by the culture of the filtrate (Reprinted with permission from Srivastava et al., 2004). Copyright 2004 Nature Publishing Group.

was more effective for fouling control compared with membrane made from smaller diameter CNTs, which can be explained by the superior ability of larger-diameter CNT to remove large organic foulants.

Biofouling, the growth of a biofilm on membrane surfaces, can also be alleviated by the incorporation of CNTs. As mentioned before, CNTs have anti-bacterial properties, so the introduction of CNTs to polymer membranes could impart biocidal properties to the membrane, resulting in a better biofouling resistance (Tiraferri et al., 2011). CNT can also be used to improve the dispersion of other antimicrobial agents, like Ag nanoparticles (Gunawan et al., 2011). The Ag nanoparticles loaded on MWCNTs achieved an excellent dispersion with size around 2–5 nm, leading to more direct contact with bacteria and more effective antibacterial activity.

There are several other benefits for blending CNTs with conventional polymer membranes. Due to the superior mechanical strength of CNTs, the CNT-blended membranes can have an improved tensile strength than the pristine membranes. The tensile strength of the MWCNT/polyacrylonitrile membranes (Majeed et al., 2012) and MWCNT/chitosan composite membranes (Tang et al., 2009) at 2 wt.% MWCNTs loading increased 97% and 90%, respectively, compared to the neat ones.

CNTs also help to increase the water permeability of the polymer membrane. Wang et al. (2005b) developed a high flux filtration membrane by introducing surface-oxidized MWCNTs in the coating layer. Increasing the MWCNT dosage could improve the water flux while retaining the total organic rejection. The improved flux rate was attributed to the generation of more effective hydrophilic nanochannels for water passage in the composite membranes (Majeed et al., 2012; Zhao et al., 2013).

3.3 Aligned CNT membranes for future seawater desalination

In the context of global water crisis, seawater desalination is playing an important role in providing a seemingly unlimited, steady supply of fresh water. Current desalination relies on polymer reverse-osmosis membranes to filter out dissolved salts and fine solids. High pressure and thus significant energy is needed to drive the desalination process. There is also a trade-off between high water flux and high selectivity in the membrane design process.

In the past decade, it has been proved by theoretical calculations (Hummer et al., 2001) and experiments (Majumder et al., 2005) that water transports several orders of magnitude faster in CNTs than in other porous materials of comparable size. This high fluid velocity is attributed to the smooth and hydrophobic inner walls of CNTs. Ordered hydrogen bonds are created in water-CNT interface and they introduce a vapor phase barrier between the chain of water molecules and the nonpolar CNT wall, so water molecules move almost frictionless inside the walls.

Aligned CNT membranes have the potential to act as high-flux desalination membranes. Holt et al. (2006) developed sub-2-nm aligned nanotube membranes using catalytic chemical vapor deposition followed by laser etching to uncap the nanotubes. Water permeabilities of these nanotube-based membranes were several orders of magnitude higher than those of commercial polycarbonate membranes, despite having smaller pore sizes. To fully take advantage of the inner pores of CNTs, high density and vertically aligned CNT membranes were fabricated by Yu et al. (2009). The CNT arrays made by chemical vapor deposition were soaked into an organic solvent like n-hexane, and then the layers were dried at room temperature. Evaporation of solvents shrank the layer to approximately 5% of its original area, leading to a high density, vertically aligned CNT forest membrane.

Via tip functionalization, CNT membranes can acquire ion exclusion ability. Gong et al. (2010) designed a controllable ion-selective nanopore based on SWCNTs with specially arranged carbonyl oxygen atoms modified inside the nanopores. The different patterns of carbonyl oxygen atoms determined the hydration structure of K^+ and Na^+ within the nanopores, leading to a tunable ionic selectivity. Majumder et al. (2007) modified the tips of CNTs using electrochemical grafting of diazonium salts, and suggested the separation coefficient of the CNT membranes can be tuned by changing the voltage apply (Fig. 9). In the work of Fornasiero et al. (2008), negatively charged groups introduced by plasma treatment made aligned CNT membranes reject as high as 98% ions, and the ion exclusion was dominated by charge exclusion mechanism.

However, in high ion-strength environment like seawater and blackish water, the efficiency of charge exclusion mechanism may be declined significantly. Another ion-rejection mechanism, size exclusion effect, needs more attention. To date, the diameter of CNTs has reached as small as 0.3 nm (Zhao et al., 2004), which nearly

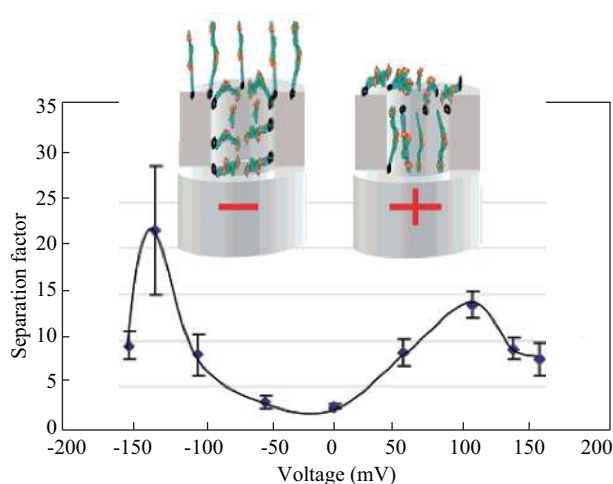


Fig. 9 Change in separation coefficient with voltage applied to the CNT-SG-spacer (polypeptide)-dye membrane (Reprinted with permission from Majumder et al., 2007). Copyright 2007 American Chemical Society.

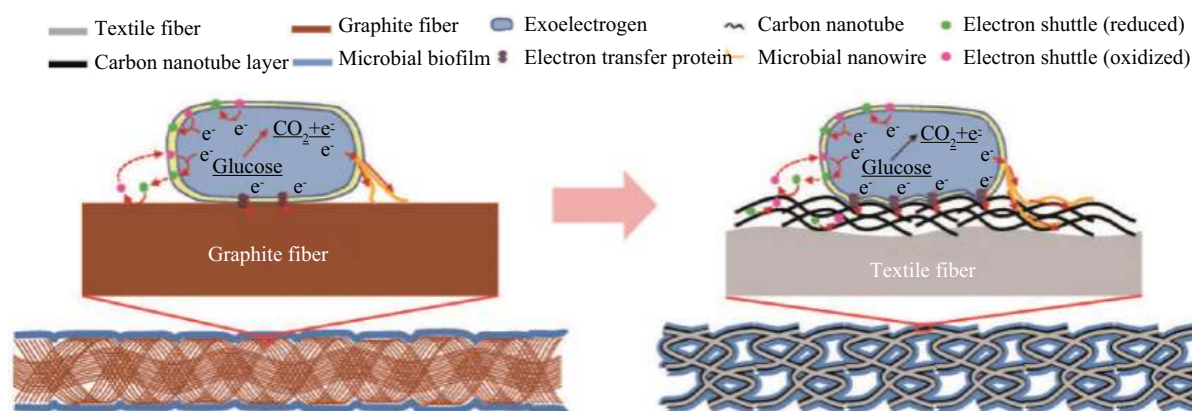


Fig. 10 Schematic diagram of the electrode configuration and electron-transfer mechanisms for the CNT-textile anode (right), compared with the widely used carbon cloth anode (left) (Reprinted with permission from Xie et al., 2011). Copyright 2011 American Chemical Society.

approaches the hydrated radius of sodium ions, ranging from 0.178 to 0.358 nm depending on environment conditions (Carrillo-Tripp et al., 2006; Tansel et al., 2006). By calculating the potential of mean force for ion and water translocation, Corry (2008) proposed that ions face a large energy barrier and will not pass through the narrower tubes ((5,5) and (6,6) “armchair” type tubes) but can pass through the wider (7,7) and (8,8) nanotubes. Water, however, faces no such impediment due to the formation of stable hydrogen bonds and crosses the tubes at very large rates. Thus, the manufacture of defect-free CNT membranes with sub-nanometer pores can shine light on future desalination technologies.

4 CNT electrodes for microbial fuel cell

Microbial fuel cell (MFC) is an environmental friendly method for wastewater treatment with self-sustained electricity generation using microorganisms. The performances of MFCs, including COD (chemical oxygen demand, an index of organic matter concentration) removal and electricity generation, depend on several factors, such as reactor design, pH, microbial species and electrode material.

In anode, the organic matter in wastewater is oxidized by mediation of exoelectrogens, microorganisms that transfer electrons to an electrode. The anode material requires large specific area for microbe colonization, high conductivity, stability and catalytic activity. To date, carbon materials such as carbon cloth, carbon paper, and carbon foam are applied in most MFC anodes. However, they have little electro-catalytic activity for the electrode microbial reactions. CNTs with high conductivity and high surface-to-volume ratio can be promising anode materials. However, CNTs have cellular toxicity which lead to proliferation inhibition and cell death and could not be used directly. Coated with conductive polymers, such as polyaniline (Qiao et al., 2007), polypyrrole (Zou et al., 2008), CNTs can be used as anode material and are favorable for increasing the specific surface area of the

electrode and enhancing the charge transfer efficiency. The biocompatibility of CNT could also be improved by surface oxidation. A microsized (1.5 μL) MFC has been successfully fabricated using vertically grown oxidized-MWCNT as the anode (Mink et al., 2012). CNTs can also be used to fabricate electrodes with novel configurations. A three dimensional structure was achieved by uniformly coating CNT on macroscale porous substrate (e.g., textile or sponge) (Xie et al., 2011, 2012). The 3D CNT anode exhibits strong interaction with the microbial biofilm and facilitates electron transfer from exoelectrogens to the electrode surface, thus remarkably decreases the charge transfer resistance and enhances the performance of MFC (Fig. 10) (Xie et al., 2011).

In cathode of MFC, electrons are accepted usually by oxygen, the most sustainable terminal electron acceptor. However, poor oxygen reduction reactions under common operation conditions undermine the performance of MFC. Some bacteria have the ability to catalyze oxygen reduction reactions in cathode. Because of their size and shape, CNTs have good contact with the redox active center of redox proteins inside those bacteria, thus CNT-based cathode will facilitate the electron transfer and enhance oxygen reduction reaction (Liu et al., 2011). CNT can also act as excellent support for some oxygen-reduction-reaction electro-catalyst, such as manganese dioxide (Chen et al., 2012; Zhang et al., 2011b). In all, the unique and tunable structure and electrical properties make CNTs promising in acting as the future MFC electrodes.

5 Conclusions

CNT based nanomaterials have advantages over conventional materials in various environmental applications. The development of cost-effective and highly efficient manufacturing routes may find the entry point to integrate CNTs into traditional water treatment processes. Surface modification and macroscopic manipulation of CNTs are often effective ways to fully take advantage of CNTs' unique physical, chemical, and electrical properties. Despite the

euphoria, the potential threat of CNTs to the environment and human health should be taken into consideration before large scale applications.

CNT based materials are especially suitable for point-of-use (POU) purposes. The cytotoxicity of CNTs can prohibit the formation of biofilm and make CNT filters more easily regenerated than the GAC-based filters. CNT filters have removal ability toward a wide range of organic and inorganic pollutants together with bacteria and viruses, thus they have the potential to substitute conventional adsorbents and disinfection agents in POU systems. Nevertheless, CNT filters should be evaluated carefully before wide applications in terms of the potential of CNT leakage into the drinking water.

For CNT supported catalysts, the studies have been focused on the improvement in catalytic activity by using some model pollutants, such as phenol and dyes. More attention should be paid to the degradation ability toward more recalcitrant organic pollutants by using CNT composite catalysts. The degradation products and pathways need to be elucidated to fully assess the application feasibility of these catalysts. If some products and intermediates are even more toxic than the original compound, additional methods to degrade these toxic products must be used subsequently.

CNT membranes represent an emerging branch of membrane science with myriad opportunities in filtration and seawater desalination. Their exceptional mechanical strength, thermal stability, and electrical conductivity can be useful in the regeneration process. In conventional cellulose nitrate/acetate membranes, strong bacteria adsorption on the membrane surface undermines their reusability in water filtration. CNT based membranes can be cleaned efficiently by using some physical methods like sonication and autoclaving. Their electrical conductivity could also be useful for flux regeneration using principles of electrochemistry. Based on the findings on the high water flux within CNT pores, it is very attractive to manufacture CNT membrane for desalination purposes with high permeability and high salt rejection. To date, however, many challenges still remain to synthesize the CNT membranes reproducibly, cost effectively, and with uniform pore size distributions. Additional practical considerations include the potential fouling of CNT membranes by algae and other contaminants.

In brief, the following conclusions can be drawn based on the above discussions: (1) CNTs can act as more effective adsorbent than activated carbon in terms of larger adsorption capacity, superior adsorption selectivity, shorter equilibrium time and easier regeneration. The adsorption potential of CNTs can be predicted using molecular simulations. (2) CNTs can serve as efficient catalyst support owing to their high electrical conductivity, high strength and adsorption capacity. The combination of TiO₂ and CNT can achieve better charge separation and improved

visible photoactivity. (3) CNTs have great potential in filtration application. Bacteria and viruses can be effectively removed by CNT filters through adsorption and microbe killing. CNT blended polymeric membranes exhibit better anti-fouling ability, higher strength and water permeability. The most attractive virtue lies in the potential of using CNT membrane for water desalination with both high flux and high selectivity. Challenges still remain in the precise control of CNTs in terms of vertically align, uniform dispersion and tip opening and functionalization. Cost is another concern in industry-level manufacture of CNT membranes. (4) Before using CNTs in real water treatment devices, the potential risk of CNT leaking should be evaluated prudently, since CNTs have been shown to exhibit cytotoxicity.

Acknowledgments

The authors would like to thank the financial support from the Program for the New Century Excellent Talents in Universities of China (No. NCET-10-0489), the Natural Science Foundation of China (No. 21107045), and the Natural Science Foundation of Jiangsu Province of China (No. BK2011575).

References

- Agboola A E, Pike R W, Hertwig T A, Lou H H, 2007. Conceptual design of carbon nanotube processes. *Clean Technologies and Environmental Policy*, 9(4): 289–311.
- Ajmani G S, Goodwin D, Marsh K, Fairbrother D H, Schwab K J, Jacangelo J G et al., 2012. Modification of low pressure membranes with carbon nanotube layers for fouling control. *Water Research*, 46(17): 5645–5654.
- Akhavan O, Abdollahad M, Abdi Y, Mohajrzadeh S, 2011. Silver nanoparticles within vertically aligned multi-wall carbon nanotubes with open tips for antibacterial purposes. *Journal of Materials Chemistry*, 21(2): 387–393.
- Bai Y C, Lin D H, Wu F C, Wang Z Y, Xing B S, 2010. Adsorption of Triton X-series surfactants and its role in stabilizing multi-walled carbon nanotube suspensions. *Chemosphere*, 79(4): 362–367.
- Brady-Estévez A S, Kang S, Elimelech M, 2008. A single-walled-carbon-nanotube filter for removal of viral and bacterial pathogens. *Small*, 4(4): 481–484.
- Brady-Estévez A S, Schnoor M H, Kang S, Elimelech M, 2010a. SWNT-MWNT hybrid filter attains high viral removal and bacterial inactivation. *Langmuir*, 26(24): 19153–19158.
- Brady-Estévez A S, Schnoor M H, Vecitis C D, Saleh N B, Elimelech M, 2010b. Multiwalled carbon nanotube filter: Improving viral removal at low pressure. *Langmuir*, 26(18): 14975–14982.
- Brooks A J, Lim H N, Kilduff J E, 2012. Adsorption uptake of synthetic organic chemicals by carbon nanotubes and activated carbons. *Nanotechnology*, 23(29): 294008.
- Carabineiro S A C, Thavorn-amornsri T, Pereira M F R, Serp P, Figueiredo J L, 2012. Comparison between activated carbon, carbon xerogel and carbon nanotubes for the ad-

- sorption of the antibiotic ciprofloxacin. *Catalysis Today*, 186(1): 29–34.
- Carrillo-Tripp M, San-Román M L, Hernández-Cobos J, Saint-Martin H, Ortega-Blake I, 2006. Ion hydration in nanopores and the molecular basis of selectivity. *Biophysical Chemistry*, 124(3): 243–250.
- Celik E, Park H, Choi H, Choi H, 2011. Carbon nanotube blended polyethersulfone membranes for fouling control in water treatment. *Water Research*, 45(1): 274–282.
- Cheap Tubes Inc., 2012. <http://www.cheaptubesinc.com/carbon-nanotubes-prices.htm>
- Chen C L, Wang X K, Nagatsu M, 2009. Europium adsorption on multiwall carbon nanotube/iron oxide magnetic composite in the presence of polyacrylic acid. *Environmental Science and Technology*, 43(7): 2362–2367.
- Chen G C, Shan X Q, Wang Y S, Pei Z G, Shen X E, Wen B et al., 2008. Effects of copper, lead, and cadmium on the sorption and desorption of atrazine onto and from carbon nanotubes. *Environmental Science and Technology*, 42(22): 8297–8302.
- Chen H Z, Yang S G, Yu K, Ju Y M, Sun C, 2011. Effective photocatalytic degradation of atrazine over titania-coated carbon nanotubes (CNTs) coupled with microwave energy. *The Journal of Physical Chemistry A*, 115(14): 3034–3041.
- Chen W, Duan L, Zhu D Q, 2007. Adsorption of polar and nonpolar organic chemicals to carbon nanotubes. *Environmental Science and Technology*, 41(24): 8295–8300.
- Chen Y F, Lv Z S, Xu J M, Peng D Q, Liu Y X, Chen J X et al., 2012. Stainless steel mesh coated with MnO₂/carbon nanotube and polymethylphenyl siloxane as low-cost and high-performance microbial fuel cell cathode materials. *Journal of Power Sources*, 201: 136–141.
- Cho H H, Smith B A, Wnuk J D, Fairbrother D H, Ball W P, 2008. Influence of surface oxides on the adsorption of naphthalene onto multiwalled carbon nanotubes. *Environmental Science and Technology*, 42(8): 2899–2905.
- Cho H H, Wepasnick K, Smith B A, Bangash F K, Fairbrother D H, Ball W P, 2010. Sorption of aqueous Zn[II] and Cd[II] by multiwall carbon nanotubes: The relative roles of oxygen-containing functional groups and graphenic carbon. *Langmuir*, 26(2): 967–981.
- Choi J H, Jegal J, Kim W N, 2006. Fabrication and characterization of multi-walled carbon nanotubes/polymer blend membranes. *Journal of Membrane Science*, 284(1-2): 406–415.
- Cong Y, Li X K, Qin Y, Dong Z J, Yuan G M, Cui Z W et al., 2011. Carbon-doped TiO₂ coating on multiwalled carbon nanotubes with higher visible light photocatalytic activity. *Applied Catalysis B: Environmental*, 107(1-2): 128–134.
- Corry B, 2008. Designing carbon nanotube membranes for efficient water desalination. *The Journal of Physical Chemistry B*, 112(5): 1427–1434.
- Dalton A B, Collins S, Razaal J, Munoz E, von Ebron H, Kim B G et al., 2004. Continuous carbon nanotube composite fibers: Properties, potential applications, and problems. *Journal of Materials Chemistry*, 14(1): 1–3.
- Darányi M, Csesznok T, Kukovecz A, Konya Z, Kiricsi I, Ajayan P M et al., 2011. Layer-by-layer assembly of TiO₂ nanowire/carbon nanotube films and characterization of their photocatalytic activity. *Nanotechnology*, 22(19): 195701.
- Di Z C, Ding J, Peng X J, Li Y H, Luan Z K, Liang J, 2006. Chromium adsorption by aligned carbon nanotubes supported ceria nanoparticles. *Chemosphere*, 62(5): 861–865.
- Duong T T, Nguyen Q D, Hong S K, Kim D, Yoon S G, Pham T H, 2011. Enhanced photoelectrochemical activity of the TiO₂/ITO nanocomposites grown onto single-walled carbon nanotubes at a low temperature by nanocluster deposition. *Advanced Materials*, 23(46): 5557–5562.
- Eder D, Windle A H, 2008. Carbon-inorganic hybrid materials: The carbon-nanotube/TiO₂ interface. *Advanced Materials*, 20(9): 1787–1793.
- Feng S A, Zhao J H, Zhu Z P, 2008. The manufacture of carbon nanotubes decorated with ZnS to enhance the ZnS photocatalytic activity. *New Carbon Materials*, 23(3): 228–234.
- Fornasiero F, Park H G, Holt J K, Stadermann M, Grigoropoulos C P, Noy A et al., 2008. Ion exclusion by sub-2-nm carbon nanotube pores. *Proceedings of the National Academy of Sciences of the United States of America*, 105(45): 17250–17255.
- Garcia J, Gomes H T, Serf P, Kalck P, Figueiredo J L, Faria J L, 2006. Carbon nanotube supported ruthenium catalysts for the treatment of high strength wastewater with aniline using wet air oxidation. *Carbon*, 44(12): 2384–2391.
- Garcia J, Gomes H T, Serp P, Kalck P, Figueiredo J L, Faria J L, 2005. Platinum catalysts supported on MWNT for catalytic wet air oxidation of nitrogen containing compounds. *Catalysis Today*, 102-103: 101–109.
- Gomes H T, Samant P V, Serp P, Kalck P, Figueiredo J L, Faria J L, 2004. Carbon nanotubes and xerogels as supports of well-dispersed Pt catalysts for environmental applications. *Applied Catalysis B: Environmental*, 54(3): 175–182.
- Gong X J, Li J C, Xu K, Wang J F, Yang H, 2010. A controllable molecular sieve for Na⁺ and K⁺ ions. *Journal of the American Chemical Society*, 132(6): 1873–1877.
- Gotovac S, Honda H, Hattori Y, Takahashi K, Kanoh H, Kaneko K, 2007a. Effect of nanoscale curvature of single-walled carbon nanotubes on adsorption of polycyclic aromatic hydrocarbons. *Nano Letters*, 7(3): 583–587.
- Gotovac S, Song L, Kanoh H, Kaneko K, 2007b. Assembly structure control of single wall carbon nanotubes with liquid phase naphthalene adsorption. *Colloids and Surfaces, A: Physicochemical and Engineering Aspects*, 300(1-2): 117–121.
- Gui X C, Wei J Q, Wang K L, Cao A Y, Zhu H W, Jia Y et al., 2010. Carbon nanotube sponges. *Advanced Materials*, 22(5): 617–621.
- Gunawan P, Guan C, Song X H, Zhang Q Y, Leong S S J, Tang C Y et al., 2011. Hollow fiber membrane decorated with Ag/MWNTs: Toward effective water disinfection and biofouling control. *ACS Nano*, 5(12): 10033–10040.
- Hoffmann M R, Martin S T, Choi W Y, Bahnemann D W, 1995. Environmental applications of semiconductor photocatalysis. *Chemical Reviews*, 95(1): 69–96.
- Holt J K, Park H G, Wang Y M, Stadermann M, Artyukhin A B, Grigoropoulos C P et al., 2006. Fast mass transport through sub-2-nanometer carbon nanotubes. *Science*, 312(5776): 1034–1037.

- Hummer G, Rasaiah J C, Noworyta J P, 2001. Water conduction through the hydrophobic channel of a carbon nanotube. *Nature*, 414(6860): 188–190.
- Hyung H, Fortner J D, Hughes J B, Kim J H, 2007. Natural organic matter stabilizes carbon nanotubes in the aqueous phase. *Environmental Science and Technology*, 41(1): 179–184.
- Hyung H, Kim J H, 2008. Natural organic matter (NOM) adsorption to multi-walled carbon nanotubes: Effect of NOM characteristics and water quality parameters. *Environmental Science and Technology*, 42(12): 4416–4421.
- Iijima S, 1991. Helical microtubules of graphitic carbon. *Nature*, 354(6348): 56–58.
- Im J H, Yang S J, Yun C H, Park C R, 2012. Simple fabrication of carbon/TiO₂ composite nanotubes showing dual functions with adsorption and photocatalytic decomposition of Rhodamine B. *Nanotechnology*, 23(3): 035604.
- Jafry H R, Liga M V, Li Q L, Barron A R, 2011. Single walled carbon nanotubes (SWNTs) as templates for the growth of TiO₂: The effect of silicon in coverage and the positive and negative synergies for the photocatalytic degradation of Congo red dye. *New Journal of Chemistry*, 35(2): 400–406.
- Ji L L, Chen W, Duan L, Zhu D Q, 2009. Mechanisms for strong adsorption of tetracycline to carbon nanotubes: A comparative study using activated carbon and graphite as adsorbents. *Environmental Science and Technology*, 43(7): 2322–2327.
- Ji L L, Shao Y, Xu Z Y, Zheng S R, Zhu D Q, 2010. Adsorption of monoaromatic compounds and pharmaceutical antibiotics on carbon nanotubes activated by KOH etching. *Environmental Science and Technology*, 44(16): 6429–6436.
- Kah M, Zhang X R, Jonker M T O, Hofmann T, 2011. Measuring and modeling adsorption of PAHs to carbon nanotubes over a six order of magnitude wide concentration range. *Environmental Science and Technology*, 45(14): 6011–6017.
- Kang S, Pinault M, Pfefferle L D, Elimelech M, 2007. Single-walled carbon nanotubes exhibit strong antimicrobial activity. *Langmuir*, 23(17): 8670–8673.
- Kongkanand A, Kamat P V, 2007. Electron storage in single wall carbon nanotubes. Fermi level equilibration in semiconductor-SWCNT suspensions. *ACS Nano*, 1(1): 13–21.
- Krissanasraerane M, Wongkasemjit S, Cheetham A K, Eder D, 2010. Complex carbon nanotube-inorganic hybrid materials as next-generation photocatalysts. *Chemical Physics Letters*, 496(1-3): 133–138.
- Kuvarega A T, Krause R W M, Mamba B B, 2012. Multiwalled carbon nanotubes decorated with nitrogen, palladium co-doped TiO₂ (MWCNT/N, Pd co-doped TiO₂) for visible light photocatalytic degradation of Eosin Yellow in water. *Journal of Nanoparticle Research*, 14(4): 776–791.
- Lee W J, Lee J M, Kochuveedu S T, Han T H, Jeong H Y, Park M et al., 2012. Biomineralized N-doped CNT/TiO₂ core/shell nanowires for visible light photocatalysis. *ACS Nano*, 6(1): 935–943.
- Li S W, Yu X L, Zhang G J, Ma Y, Yao J N, Keita B et al., 2011a. Green chemical decoration of multiwalled carbon nanotubes with polyoxometalate-encapsulated gold nanoparticles: Visible light photocatalytic activities. *Journal of Materials Chemistry*, 21(7): 2282–2287.
- Li X N, Chen S, Quan X, Zhang Y B, 2011b. Enhanced adsorption of PFOA and PFOS on multiwalled carbon nanotubes under electrochemical assistance. *Environmental Science and Technology*, 45(19): 8498–8505.
- Li Y H, Di Z C, Ding J, Wu D H, Luan Z K, Zhu Y Q, 2005. Adsorption thermodynamic, kinetic and desorption studies of Pb²⁺ on carbon nanotubes. *Water Research*, 39(4): 605–609.
- Li Y H, Wang S G, Cao A Y, Zhao D, Zhang X F, Xu C L et al., 2001. Adsorption of fluoride from water by amorphous alumina supported on carbon nanotubes. *Chemical Physics Letters*, 350(5-6): 412–416.
- Li Y H, Wang S G, Wei J Q, Zhang X F, Xu C L, Luan Z K et al., 2002. Lead adsorption on carbon nanotubes. *Chemical Physics Letters*, 357(3-4): 263–266.
- Li Z, Gao B, Chen G Z, Mokaya R, Sotiropoulos S, Puma G L, 2011c. Carbon nanotube/titanium dioxide (CNT/TiO₂) core-shell nanocomposites with tailored shell thickness, CNT content and photocatalytic/photoelectrocatalytic properties. *Applied Catalysis B: Environmental*, 110: 50–57.
- Lin D H, Xing B S, 2008a. Adsorption of phenolic compounds by carbon nanotubes: Role of aromaticity and substitution of hydroxyl groups. *Environmental Science and Technology*, 42(19): 7254–7259.
- Lin D H, Xing B S, 2008b. Tannic acid adsorption and its role for stabilizing carbon nanotube suspensions. *Environmental Science and Technology*, 42(16): 5917–5923.
- Liu X W, Sun X F, Huang Y X, Sheng G P, Wang S G, Yu H Q, 2011. Carbon nanotube/chitosan nanocomposite as a biocompatible biocathode material to enhance the electricity generation of a microbial fuel cell. *Energy and Environmental Science*, 4(4): 1422–1427.
- Liu Y L, Chang Y, Chang Y H, Shih Y J, 2010. Preparation of amphiphilic polymer-functionalized carbon nanotubes for low-protein-adsorption surfaces and protein-resistant membranes. *ACS Applied Materials and Interfaces*, 2(12): 3642–3647.
- Lu C, Chiu H S, 2006a. Adsorption of zinc(II) from water with purified carbon nanotubes. *Chemical Engineering Science*, 61(4): 1138–1145.
- Lu C, Chung Y L, Chang K F, 2005. Adsorption of trihalomethanes from water with carbon nanotubes. *Water Research*, 39(6): 1183–1189.
- Lu C, Chung Y L, Chang K F, 2006. Adsorption thermodynamic and kinetic studies of trihalomethanes on multiwalled carbon nanotubes. *Journal of Hazardous Materials*, 138(2): 304–310.
- Lu C, Liu C T, 2006b. Removal of nickel(II) from aqueous solution by carbon nanotubes. *Journal of Chemical Technology and Biotechnology*, 81(12): 1932–1940.
- Lu S Y, Tang C W, Lin Y H, Kuo H F, Lai Y C, Tsai M Y et al., 2010. TiO₂-coated carbon nanotubes: A redshift enhanced photocatalysis at visible light. *Applied Physics Letters*, 96(23): 231915.
- Ma L L, Sun H Z, Zhang Y G, Lin Y L, Li J L, Yu K W Y et al., 2008. Preparation, characterization and photocatalytic properties of CdS nanoparticles dotted on the surface of carbon nanotubes. *Nanotechnology*, 19(11): 115709.
- Mackie E B, Wolfson R A, Arnold L M, Lafdi K, Migone A D, 1997. Adsorption studies of methane films on catalytic car-

- bon nanotubes and on carbon filaments. *Langmuir*, 13(26): 7197–7201.
- Maggini L, Raquez J M, Marega R, Ahrens J J, Pineux F, Meyer F et al., 2013. Magnetic poly(vinylpyridine)-coated carbon nanotubes: An efficient supramolecular tool for wastewater purification. *Chemosphere*, 6(2): 367–373.
- Majeed S, Fierro D, Bühr K, Wind J, Du B, Boschetti-De-Fierro A et al., 2012. Multi-walled carbon nanotubes (MWCNTs) mixed polyacrylonitrile (PAN) ultrafiltration membranes. *Journal of Membrane Science*, 403–404: 101–109.
- Majumder M, Chopra N, Andrews R, Hinds B J, 2005. Nanoscale hydrodynamics: enhanced flow in carbon nanotubes. *Nature*, 438(7064): 44–44.
- Majumder M, Zhan X, Andrews R, Hinds B J, 2007. Voltage gated carbon nanotube membranes. *Langmuir*, 23(16): 8624–8631.
- Martinez C, Canle M, Fernandez M I, Santaballa J A, Faria J, 2011. Kinetics and mechanism of aqueous degradation of carbamazepine by heterogeneous photocatalysis using nanocrystalline TiO₂, ZnO and multi-walled carbon nanotubes-anatase composites. *Applied Catalysis B: Environmental*, 102(3–4): 563–571.
- Mink J E, Rojas J P, Logan B E, Hussain M M, 2012. Vertically grown multiwalled carbon nanotube anode and nickel silicide integrated high performance micro-sized (1.25 μl) microbial fuel cell. *Nano Letters*, 12(2): 791–795.
- Pan B, Xing B S, 2008. Adsorption mechanisms of organic chemicals on carbon nanotubes. *Environmental Science and Technology*, 42(24): 9005–9013.
- Peigney A, Laurent C, Flahaut E, Bacsa R R, Rousset A, 2001. Specific surface area of carbon nanotubes and bundles of carbon nanotubes. *Carbon*, 39(4): 507–514.
- Peng X J, Li Y H, Luan Z K, Di Z C, Wang H Y, Tian B H et al., 2003. Adsorption of 1,2-dichlorobenzene from water to carbon nanotubes. *Chemical Physics Letters*, 376(1–2): 154–158.
- Peng X J, Luan Z K, Ding J, Di Z H, Li Y H, Tian B H, 2005. Ceria nanoparticles supported on carbon nanotubes for the removal of arsenate from water. *Materials Letters*, 59(4): 399–403.
- Qiao Y, Li C M, Bao S J, Bao Q L, 2007. Carbon nanotube/polyaniline composite as anode material for microbial fuel cells. *Journal of Power Sources*, 170(1): 79–84.
- Qiu S, Wu L G, Pan X J, Zhang L, Chen H L, Gao C J, 2009. Preparation and properties of functionalized carbon nanotube/PSF blend ultrafiltration membranes. *Journal of Membrane Science*, 342(1–2): 165–172.
- Qu J, Cong Q, Luo C Q, Yuan X, 2013. Adsorption and photocatalytic degradation of bisphenol a by low-cost carbon nanotubes synthesized using fallen leaves of poplar. *RSC Advances*, 3(3): 961–965.
- Rahaman M S, Vecitis C D, Elimelech M, 2012. Electrochemical carbon-nanotube filter performance toward virus removal and inactivation in the presence of natural organic matter. *Environmental Science and Technology*, 46(3): 1556–1564.
- Rao G P, Lu C, Su F S, 2007. Sorption of divalent metal ions from aqueous solution by carbon nanotubes: A review. *Separation and Purification Technology*, 58(1): 224–231.
- Rosenzweig S, Sorial G A, Sahle-Demessie E, Mack J, 2013. Effect of acid and alcohol network forces within functionalized multiwall carbon nanotubes bundles on adsorption of copper(II) species. *Chemosphere*, 90(2): 395–402.
- Schierz A, Zänker H, 2009. Aqueous suspensions of carbon nanotubes: Surface oxidation, colloidal stability and uranium sorption. *Environmental Pollution*, 157(4): 1088–1094.
- Schoen D T, Schoen A P, Hu L B, Kim H S, Heilshorn S C, Cui Y, 2010. High speed water sterilization using one-dimensional nanostructures. *Nano Letters*, 10(9): 3628–3632.
- Shannon M A, Bohn P W, Elimelech M, Georgiadis J G, Mariñas B J, Mayes A M, 2008. Science and technology for water purification in the coming decades. *Nature*, 452(7185): 301–310.
- Sheng G D, Shao D D, Ren X M, Wang X Q, Li J X, Chen Y X et al., 2010. Kinetics and thermodynamics of adsorption of ionizable aromatic compounds from aqueous solutions by as-prepared and oxidized multiwalled carbon nanotubes. *Journal of Hazardous Materials*, 178(1–3): 505–516.
- Silva C G, Faria J L, 2010. Photocatalytic oxidation of benzene derivatives in aqueous suspensions: Synergic effect induced by the introduction of carbon nanotubes in a TiO₂ matrix. *Applied Catalysis B: Environmental*, 101(1–2): 81–89.
- Srivastava A, Srivastava O N, Talapatra S, Vajtai R, Ajayan P M, 2004. Carbon nanotube filters. *Nature Materials*, 3(9): 610–614.
- Taboada C D, Batista J, Pintar A, Levec J, 2009. Preparation, characterization and catalytic properties of carbon nanofiber-supported Pt, Pd, Ru monometallic particles in aqueous-phase reactions. *Applied Catalysis B: Environmental*, 89(3–4): 375–382.
- Tang C Y, Zhang Q, Wang K, Fu Q, Zhang C L, 2009. Water transport behavior of chitosan porous membranes containing multi-walled carbon nanotubes (MWNTs). *Journal of Membrane Science*, 337(1–2): 240–247.
- Tansel B, Sager J, Rector T, Garland J, Strayer R F, Levine L F et al., 2006. Significance of hydrated radius and hydration shells on ionic permeability during nanofiltration in dead end and cross flow modes. *Separation and Purification Technology*, 51(1): 40–47.
- Tiraferrri A, Vecitis C D, Elimelech M, 2011. Covalent binding of single-walled carbon nanotubes to polyamide membranes for antimicrobial surface properties. *ACS Applied Materials & Interfaces*, 3(8): 2869–2877.
- Tournus F, Charlier J C, 2005. *Ab initio* study of benzene adsorption on carbon nanotubes. *Physical Review B*, 71(16): 165421.
- Veličković Z, Vuković G D, Marinković A D, Moldovan M S, Perić-Grujić A A, Uskoković P S et al., 2012. Adsorption of arsenate on iron(III) oxide coated ethylenediamine functionalized multiwall carbon nanotubes. *Chemical Engineering Journal*, 181–182: 174–181.
- Vijayan B K, Dimitrijevic N M, Finkelstein-Shapiro D, Wu J S, Gray K A, 2012. Coupling titania nanotubes and carbon nanotubes to create photocatalytic nanocomposites. *ACS Catalysis*, 2(2): 223–229.
- Wang H, Wang H L, Jiang W F, 2009a. Solar photocatalytic degradation of 2,6-dinitro-p-cresol (DNPC) using multi-walled carbon nanotubes (MWCNTs)-TiO₂ composite photocatalysts. *Chemosphere*, 75(8): 1105–1111.
- Wang H, Wang H L, Jiang W F, Li Z Q, 2009b. Photocatalytic degradation of 2,4-dinitrophenol (DNP) by multi-walled

- carbon nanotubes (MWCNTs)/TiO₂ composite in aqueous solution under solar irradiation. *Water Research*, 43(1): 204–210.
- Wang S, Shi X L, Shao G Q, Duan X L, Yang H, Wang T G, 2008a. Preparation, characterization and photocatalytic activity of multi-walled carbon nanotube-supported tungsten trioxide composites. *Journal of Physics and Chemistry of Solids*, 69(10): 2396–2400.
- Wang W D, Serp P, Kalck P, Faria J L, 2005a. Visible light photodegradation of phenol on MWNT-TiO₂ composite catalysts prepared by a modified sol-gel method. *Journal of Molecular Catalysis A: Chemical*, 235(1-2): 194–199.
- Wang X F, Chen X M, Yoon K, Fang D F, Hsiao B S, Chu B, 2005b. High flux filtration medium based on nanofibrous substrate with hydrophilic nanocomposite coating. *Environmental Science and Technology*, 39(19): 7684–7691.
- Wang X L, Lu J L, Xing B S, 2008b. Sorption of organic contaminants by carbon nanotubes: Influence of adsorbed organic matter. *Environmental Science and Technology*, 42(9): 3207–3212.
- Wang X L, Tao S, Xing B S, 2009c. Sorption and competition of aromatic compounds and humic acid on multiwalled carbon nanotubes. *Environmental Science and Technology*, 43(16): 6214–6219.
- Wilson D, Wang W, Lopes R J G, 2012. Ceria-doped and TiO₂ nanocomposite coating on multiwalled carbon nanotubes for the photocatalytic remediation of agro-industrial wastewaters. *Applied Catalysis B: Environmental*, 123-124: 273–281.
- Wiśniewski M, Terzyk A P, Gauden P A, Kaneko K, Hattori Y, 2012. Removal of internal caps during hydrothermal treatment of bamboo-like carbon nanotubes and application of tubes in phenol adsorption. *Journal of Colloid and Interface Science*, 381(1): 36–42.
- Woan K, Pyrgiotakis G, Sigmund W, 2009. Photocatalytic carbon-nanotube-TiO₂ composites. *Advanced Materials*, 21(21): 2233–2239.
- Woods L M, Bădescu Ș C, Reinecke T L, 2007. Adsorption of simple benzene derivatives on carbon nanotubes. *Physical Review B*, 75(15): 155415.
- Wu H Q, Wang Q Y, Yao Y Z, Qian C, Zhang X J, Wei X W, 2008. Microwave-assisted synthesis and photocatalytic properties of carbon nanotube/zinc sulfide heterostructures. *Journal of Physical Chemistry C*, 112(43): 16779–16783.
- Wu W H, Chen W, Lin D H, Yang K, 2012. Influence of surface oxidation of multiwalled carbon nanotubes on the adsorption affinity and capacity of polar and nonpolar organic compounds in aqueous phase. *Environmental Science and Technology*, 46(10): 5446–5454.
- Xie X, Hu L B, Pasta M, Wells G F, Kong D S, Criddle C S et al., 2011. Three-dimensional carbon nanotube-textile anode for high-performance microbial fuel cells. *Nano Letters*, 11(1): 291–296.
- Xie X, Ye M, Hu L B, Liu N, McDonough J R, Chen W et al., 2012. Carbon nanotube-coated macroporous sponge for microbial fuel cell electrodes. *Energy and Environmental Science*, 5(1): 5265–5270.
- Xu Y J, Zhuang Y B, Fu X Z, 2010. New insight for enhanced photocatalytic activity of TiO₂ by doping carbon nanotubes: A case study on degradation of benzene and methyl orange. *Journal of Physical Chemistry C*, 114(6): 2669–2676.
- Yan H, Gong A J, He H S, Zhou J, Wei Y X, Lv L, 2006. Adsorption of microcystins by carbon nanotubes. *Chemosphere*, 62(1): 142–148.
- Yan Y, Sun H P, Yao P P, Kang S Z, Mu J, 2011. Effect of multi-walled carbon nanotubes loaded with Ag nanoparticles on the photocatalytic degradation of rhodamine B under visible light irradiation. *Applied Surface Science*, 257(8): 3620–3626.
- Yang K, Wu W H, Jing Q F, Zhu L Z, 2008a. Aqueous adsorption of aniline, phenol, and their substitutes by multi-walled carbon nanotubes. *Environmental Science and Technology*, 42(21): 7931–7936.
- Yang K, Zhu L Z, Xing B S, 2006. Adsorption of polycyclic aromatic hydrocarbons by carbon nanomaterials. *Environmental Science and Technology*, 40(6): 1855–1861.
- Yang S X, Li X, Zhu W P, Wang J B, Descorme C, 2008b. Catalytic activity, stability and structure of multi-walled carbon nanotubes in the wet air oxidation of phenol. *Carbon*, 46(3): 445–452.
- Yang S X, Zhu W P, Li X, Wang H B, Zhou Y R, 2007. Multi-walled carbon nanotubes (MWNTs) as an efficient catalyst for catalytic wet air oxidation of phenol. *Catalysis Communications*, 8(12): 2059–2063.
- Yao Y J, He B, Xu F F, Chen X F, 2011. Equilibrium and kinetic studies of methyl orange adsorption on multiwalled carbon nanotubes. *Chemical Engineering Journal*, 170(1): 82–89.
- Yao Y, Li G H, Ciston S, Lueptow R M, Gray K A, 2008. Photoreactive TiO₂/carbon nanotube composites: Synthesis and reactivity. *Environmental Science and Technology*, 42(13): 4952–4957.
- Yu H T, Quan X, Chen S, Zhao H M, Zhang Y B, 2008. TiO₂-carbon nanotube heterojunction arrays with a controllable thickness of TiO₂ layer and their first application in photocatalysis. *Journal of Photochemistry and Photobiology A: Chemistry*, 200(2-3): 301–306.
- Yu M, Funke H H, Falconer J L, Noble R D, 2009. High density, vertically-aligned carbon nanotube membranes. *Nano Letters*, 9(1): 225–229.
- Yu Y, Yu J C, Chan C Y, Che Y K, Zhao J C, Ding L et al., 2005a. Enhancement of adsorption and photocatalytic activity of TiO₂ by using carbon nanotubes for the treatment of azo dye. *Applied Catalysis B: Environmental*, 61(1-2): 1–11.
- Yu Y, Yu J C, Yu J G, Kwok Y C, Che Y K, Zhao J C et al., 2005b. Enhancement of photocatalytic activity of mesoporous TiO₂ by using carbon nanotubes. *Applied Catalysis A: General*, 289(2): 186–196.
- Zarezaide M, Ghasemi S, Gholami M R, 2011. The effect of multiwalled carbon nanotubes and activated carbon on the morphology and photocatalytic activity of TiO₂/C hybrid materials. *Catalysis Science and Technology*, 1(2): 279–284.
- Zeng Y, Zhao L J, Wu W D, Lu G X, Xu F, Tong Y et al., 2013. Enhanced adsorption of malachite green onto carbon nanotube/polyaniline composites. *Journal of Applied Polymer Science*, 127(4): 2475–2482.
- Zhang L L, Xiong Z G, Zhao X S, 2010. Pillaring chemically exfoliated graphene oxide with carbon nanotubes for photocatalytic degradation of dyes under visible light irradiation. *ACS Nano*, 4(11): 7030–7036.

- Zhang S J, Shao T, Bekaroglu S S K, Karanfil T, 2009. The impacts of aggregation and surface chemistry of carbon nanotubes on the adsorption of synthetic organic compounds. *Environmental Science and Technology*, 43(15): 5719–5725.
- Zhang S J, Shao T, Karanfil T, 2011a. The effects of dissolved natural organic matter on the adsorption of synthetic organic chemicals by activated carbons and carbon nanotubes. *Water Research*, 45(3): 1378–1386.
- Zhang S J, Shao T, Kose H S, Karanfil T, 2012. Adsorption kinetics of aromatic compounds on carbon nanotubes and activated carbons. *Environmental Toxicology and Chemistry*, 31(1): 79–85.
- Zhang Y P, Hu Y Y, Li S Z, Sun J, Hou B, 2011b. Manganese dioxide-coated carbon nanotubes as an improved cathodic catalyst for oxygen reduction in a microbial fuel cell. *Journal of Power Sources*, 196(22): 9284–9289.
- Zhao X, Liu Y, Inoue S, Suzuki T, Jones R O, Ando Y, 2004. Smallest carbon nanotube is 3 Å in diameter. *Physical Review Letters*, 92(12): 125502.
- Zhao Y F, Xu Z W, Shan M J, Min C Y, Zhou B M, Li Y L et al., 2013. Effect of graphite oxide and multi-walled carbon nanotubes on the microstructure and performance of PVDF membranes. *Separation and Purification Technology*, 103: 78–83.
- Zhu H Y, Jiang R, Xiao L, Zeng G M, 2010. Preparation, characterization, adsorption kinetics and thermodynamics of novel magnetic chitosan enwrapping nanosized γ -Fe₂O₃ and multi-walled carbon nanotubes with enhanced adsorption properties for methyl orange. *Bioresource Technology*, 101(14): 5063–5069.
- Zou M Y, Zhang J D, Chen J W, Li X H, 2012. Simulating adsorption of organic pollutants on finite (8,0) single-walled carbon nanotubes in water. *Environmental Science and Technology*, 46(16): 8887–8894.
- Zou Y J, Xiang C L, Yang L N, Sun L X, Xu F, Cao Z, 2008. A mediatorless microbial fuel cell using polypyrrole coated carbon nanotubes composite as anode material. *International Journal of Hydrogen Energy*, 33(18): 4856–4862.

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Journal of Environmental Sciences (Established in 1989)

Vol. 25 No. 7 2013

Supervised by	Chinese Academy of Sciences	Published by	Science Press, Beijing, China
Sponsored by	Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences	Distributed by	Elsevier Limited, The Netherlands
Edited by	Editorial Office of Journal of Environmental Sciences P. O. Box 2871, Beijing 100085, China Tel: 86-10-62920553; http://www.jesc.ac.cn E-mail: jesc@263.net , jesc@rcees.ac.cn	Domestic	Science Press, 16 Donghuangchenggen North Street, Beijing 100717, China Local Post Offices through China
Editor-in-chief	Hongxiao Tang	Foreign	Elsevier Limited http://www.elsevier.com/locate/jes
CN 11-2629/X	Domestic postcode: 2-580	Printed by	Beijing Beilin Printing House, 100083, China
		Domestic price per issue	RMB ¥ 110.00

ISSN 1001-0742

