Scientific Reviews
&
Chemical Communications

Sci. Revs. Chem. Commun.: 6(4), 2016, 102-108
ISSN 2277-2669

STUDY OF CNT DECORATED SEMICONDUCTOR NANOPHOTOCATALYSTS FOR WATER PURIFICATION

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(*Received : 27.08.2016; Revised : 07.09.2016; Accepted : 09.09.2016*)

ABSTRACT

Water pollution is a great concern for whole of the world population as indicated by EU25 barometer. Photocatalysis based on nanocrystals is a very promising method for the treatment of contaminated, polluted water. A photocatalyst (ex.g. TiO_2, ZnO, MoO_3, CeO_2, ZrO_2, WO_3, α-Fe_2O_3, SnO_2, ZnS, CdS, CdSe, WS_2, and MoS_2) uses U.V. and visible light radiation from sunlight and breakdowns different substances e.g. organic materials, organic acids, estrogens, pesticides, dyes, crude oil, microbes (including viruses), inorganic molecules (eg. NO_x), can also remove metals such as mercury. The use of CNTs in photocatalyst systems, not only enhances the optical properties of TiO_2 and PbS photocatalysts, but also improves their capability in photo degradation of organic pollutants. The photo sensitization of transition metal oxides is a promising approach for achieving effective visible light photo catalysis. Nanostructured photosensitizers such as quantum dots, plasmonic metal nanostructures and carbon nanostructures coupled with wide band gap transition metal oxides are used to design better visible-light active photocatalysts.

Key words: CNT, Photocatalysts, Carbon Nanostructure, Nanostructure sensitization, Quantum dots, Transition metal oxides, Plasmonic metal nanostructures.

INTRODUCTION

Water pollution is a great concern for whole of the world population as indicated by EU25 barometer. The UN Millennium Development Goals (MDG) are also committed to provide access to safe drinking water and basic sanitation by 2015. Global demand for water treatment products reached $ 44.6 billion in 2008 and it is predicted to increase annually by 5.7% reaching $79 billion by 2015. It was predicted to be large in vast developing countries like China and India due to rapid industrialization and increased efforts to expand access to safe water supplies and adequate sanitation facilities especially in rural areas. The challenges in treating waste and drinking water are organic pollutants, heavy loads of metals, microbe contamination etc. Amongst many strategies known, CNT decorated semiconductor nanophotocatalysis is a subject of vigorous academic research, now a days. Photo catalysis based on nanocrystals is a very promising method for the treatment of contaminated, polluted water. A photocatalyst (ex.g. TiO_2, ZnO, MoO_3, CeO_2, ZrO_2, WO_3, α - Fe_2O_3, SnO_2, ZnS, CdS, CdSe, WS_2, and MoS_2) uses U.V. and visible light radiation from sunlight and breakdowns different substances e.g. organic materials, organic acids, estrogens,

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pesticides, dyes, crude oil, microbes (including viruses), inorganic molecules (eg. NO_x), can also remove metals such as mercury. Owing to their unique and tunable structural, physical and chemical properties, Carbon Nano Tubes (CNTs) have exhibited great potential in water treatment. We can make 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 use of CNTs in photo catalyst systems, not only enhances the optical properties of TiO_2 and PbS photo catalysts, but also improves their capability in photo degradation of organic pollutants.

EXPERIMENTAL

Titania (TiO_2) is a widely used photocatalyst due to its high chemical stability, low cost, and nontoxic nature , but it can only absorb UV light with low quantum efficiency due to its wide bandgap (*ca.* 3.2 eV), which limits its application in visiblelight-driven photocatalysis. Due to the special structures and extraordinary mechanical and unique electronic properties, carbon nanotubes (CNTs) have the potential to extend the photoresponse range of TiO_2 to visible-light region by modification of bandgap and/or sensitization and increase the photoactivity of TiO_2 by contribution to high surface area and inhibition of electron hole recombination. Single-walled carbon nanotubes (SWCNTs) and multiwalled carbon nanotubes (MWCNTs) can enhance the visible-light-driven photoactivity of TiO_2 by acting as a photosensitizer in the MWCNT-TiO_2 : Ni composite. MWCNTTiO_2 nanocomposite with visible-light-driven photoactivity can be successfully synthesized via direct growth of TiO_2 nanoparticles on the surface of the functionalized MWCNTs by the hydrothermal process and can be characterized by X-ray diffraction, UV-vis diffuse reflectance spectroscopy, field emission scanning electron microscope, thermogravimetry analysis, and N_2 adsorption-desorption isotherms as such.

Pretreatment methods for MWCNTs

MWCNTs are to be chemically oxidized in a mixture of sulfuric acid and nitric acid (3/1, v/v) while being ultrasonicated for 2 h; the as received MWCNTs are treated in boiled nitrate solution (20 wt%) for 1 h for surface functionalization; the as-received MWCNTs are dispersed in 5.0 M HNO_3 solution and refluxed for 48 h at 140^{o}C. These functionalized MWCNTs are washed with water to neutral, dried under vacuum.

Preparation and characterization of MWCNT-TiO_2 nanocomposites

Pretreated MWCNTs are ultrasonically dispersed in deionized water, and then titanium sulfate ($Ti(SO_4)_2$) is added into the dispersion under stirring. The obtained mixture is added into cetyltrimethyl ammoniumbromide (CTAB) solution under the molar ratio of $Ti(SO_4)_2$: CTAB : H_2O is 1 : 0.12 : 100. After stirring, the resulting mixture (pH 0.2) is aged at room temperature for 12 h and then transferred into an autoclave for 72 h hydrothermal treatment at 100^{o}C. The resulting materials are collected using the centrifugation technique and mixed with a water and ethanol (molar ratio 1 : 1) solution of sodium chloride under stirring at 40^{o}C for 5 h. Resultant sample is washed with water and ethanol, dried at 80^{o}C overnight, and calcined at 400^{o}C for 5 h.

X-ray diffraction (XRD) patterns are obtained on a XRD-6000 diffractometer. Scanning electron microscope (SEM) observation was conducted on a JEOL-6700F electron microscope. Diffuse reflectance spectra (DRS) were recorded on a Cary 5000 UV-Vis-NIR spectrophotometer). Thermogravimetry (TG) curves are recorded on a STA 449C thermal analyzer. The Brunauer-Emmett-Teller (BET) surface areas were analyzed by nitrogen adsorption-desorption measurement using a Micromeritics ASAP 2020 apparatus after the samples are degassed at 180^{o}C.

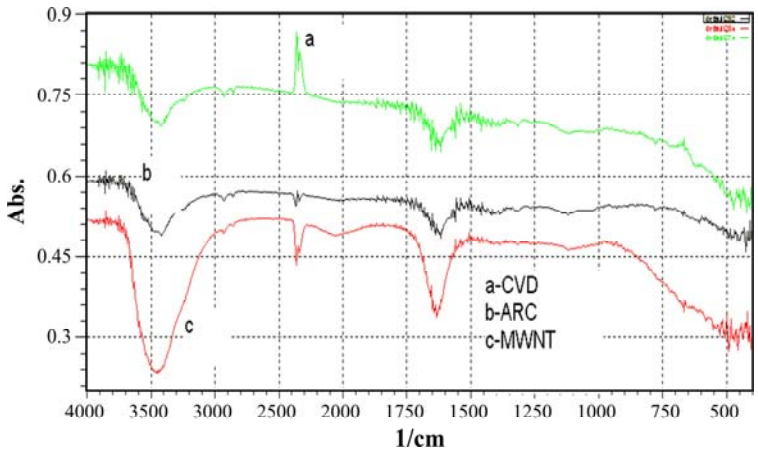

Fig. 1: Characterization of CNT (FT-IR spectra)

RESULTS AND DISCUSSION

Photocatalysis has been a hot topic in the degradation of organic pollutants for several decades. 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 have a large electron-storage capacity and it was estimated that every 32 carbon atoms in SWCNTs can store an electron. 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 $^{\bullet}OH$) which degrade and further mineralize organic pollutants. Recent research highlighted the euphoria of CNTs to TiO_2 nanoparticles.

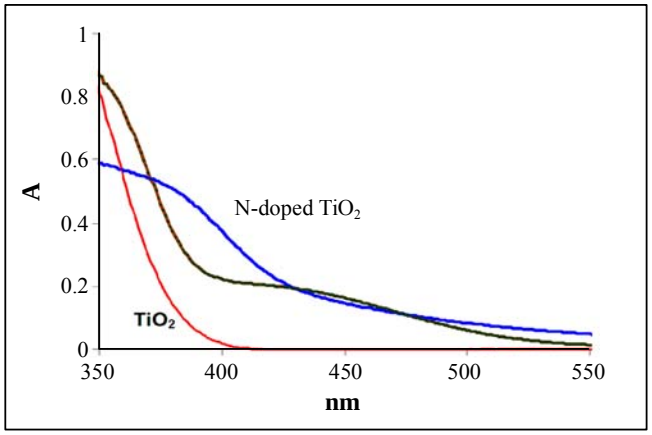

Fig. 2: The electronic absorption spectra of doped nanoparticles shows an absorption maximum centered at 435 nm and their absorption onset is ~550 nm

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. In addition to the inhibitation 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. Aqueous pollutants including dyes, benzene derivatives and carbamazepine 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. 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. Considering their semiconductor property, CNTs may also act as photosensitizers and inject the photo-excited electrons to the conducting band of TiO_2. 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. Applications of CNTs in photocatalysis also include using CNTs as pillars of reduced graphene oxide platelets for methylene blue (MB) degradation, and the preparation of Au NP@POM-CNT tricomponent hybrid photocatalyst.

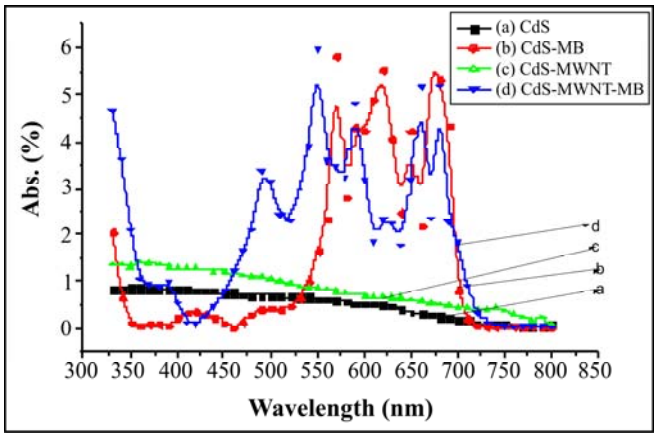

Fig. 3: Optical absorption spectra for CdS/MWNT/MB

Very interestingly, although Au nanoparticles are visible light photo-sensitizers, they donot 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. 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 used benzyl alcohol (BA) as surfactant in the preparation of CNT/TiO_2 composite. The addition of BA could improve the dispersion state of TiO_2 on CNTs through π–π interaction between BA and CNT and coordination between BA and titanium. Lee et al. synthesized N-doped CNT/TiO_2 nanowires through biomimetic mineralization, in which the direct contact between CNT and TiO_2 was the key for band gap narrowing. Some studies also emphasized on the contact resistance of CNT/TiO_2 in terms of electron transportation. SWCNT can enhance the photocatalytic activity of TiO_2 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/TiO_2. Duong et al. introduced indium tin oxide (ITO) thin films at the interface between SWCNTs and TiO_2. 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. 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. Qu et al. 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.

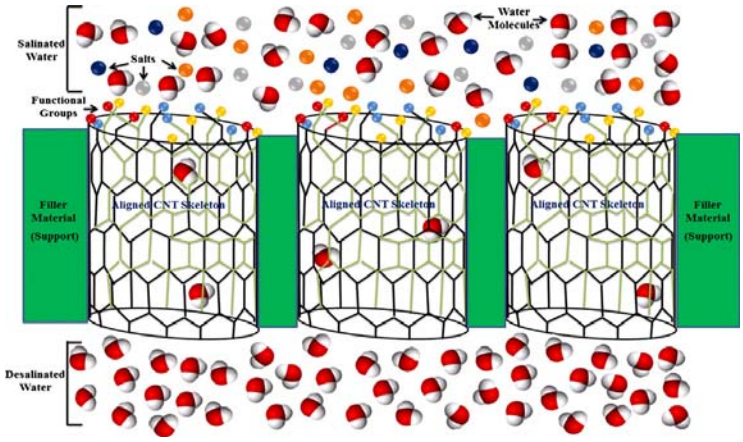

Fig. 4: CNT as Desalinating membrane

CONCLUSION

The unique and tunable physical, chemical, and electrical properties of cnts endow them the possibilities as novel and high-performance materials for water purification in the coming decades. Multi-functional materials could be fabricated by combining the virtues of different nanomaterials by using cnts as scaffolds, introducing synergistic effect into water treatment processes. Future design of CNT-based water-treatment materials should pay high attention to some practical aspects. Cost is often a limiting factor in large scale applications. Cnts are relatively expensive. 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/h can be achieved. The corporation of Hyperion-Mitsui projected that the cost of mwcnts produced on commercial scales in their plants will be about $80/kg, which could eventually be even reduced to $10/kg. The large scale manufacturing at low costs may pave a way to the wide applications of cnts. CNT based materials are especially suitable for point-of-use (POU) purposes. Studies have demonstrated that CNT filters can achieve high water flux at reasonably low pressure. The cytotoxicity of cnts can prohibit the formation of biofilm and make CNT filters more easily regenerated than the GAC-based filers. 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 term of the potential of CNT leakage into the drinking water. 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 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 manu facture CNT membrane for desalination purposes with high permeability and high salt rejection.

To date, however, many challenges still remain to synthesize the CNT membranes reproductively, cost effectively, and with uniform pore size distributions. For example, desalination membranes for > 95% salt rejection (a very modest number for desalination purposes) would require less than 1 pore in 100 over the size of 1-nm in diameter. Additional practical considerations include the potential fouling of CNT membranes by algae and other contaminants. It can be concluded that CNT based nanomaterials have advantages over conventional materials in 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. Indeed, the "Nano" era is approaching. CNTs will undoubtedly play a significant role in the field of water purification in the near future.

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