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REVIEW ARTICLE: HYBRID MATERIALS BASED ON CARBON NANOTUBES

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ABSTRACT

Carbon nanotubes-based hybrid and composite materials, recently, are a hot topic in research about advanced materials. Nanotubes are functionalized and hybridized with both organic and inorganic compounds for designed applications. Hybrid materials can be fabricated by direct or in-direct method. Some investigations about electrical, optical and photocatalytic properties of hybrid materials would be discussed.

Keywords: CNT, hybrid material, metal oxide semiconductor.

1. INTRODUCTION

Since discovered by Iijima in 1991 [1], carbon nanotubes (CNTs), due to its outstanding electrical, mechanical properties, are one of the most attractive nanostructure materials in recent decades. Because of the limit of technology, CNT-based electronic devices, however, is only fabricated and tested in laboratory. To make the most of CNTs' outstanding properties for real applications, recently, researchers have given lot efforts to study CNT-based hybrid materials for real applications such as energy storage, supercapacitor, biosensor, gas sensor, cooling material… [2 - 20]. The CNTs-based hybrid material, for a designed application, was synthesized by corresponding method with the suitable functional material. This paper will give an overview of recent reports on developing CNTs-based hybrid materials.

2. CNT-BASED HYBRID MATERIALS

2.1. CNT-based hybrid materials: recent researches and potential applications

In studying about hybrid materials, researchers hope to combine the advantages of different components and widen the potential applications of materials. CNTs walls are inert with chemical reaction, so it is very hard to use in chemical or bio-application. To use CNTs in bio-application, ligands or functional organic agents were attached or covered on CNTs wall. These hybrid materials have both the large surface area, high conductivity of CNTs and the selectivity of organic agents. Recently, A.L. Yost et al. functionalized CNT with organic ligands in microfluidic platform to selectively detect expected organic compound [2]. Using the conductivity and high efficiency of absorbing light of CNTs, Strano et al. combined MWCNT with chloroplast to enhance the photosynthesis efficiency of Arabidopsis thaliana's leaf [3].

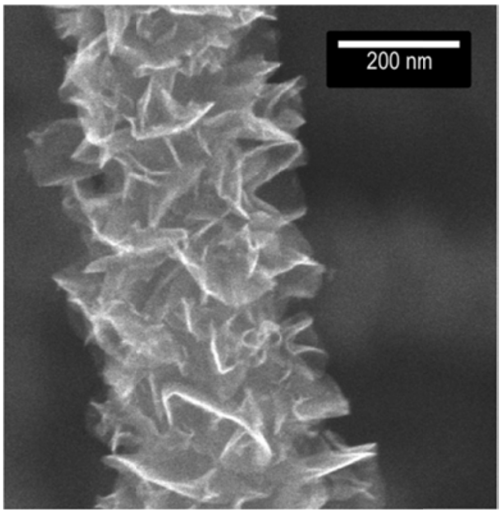

Figure 1. SEM image of foliate-like graphenated CNT [14] (Reprinted from [14] with permission of Cambridge University Press. Copyright © 2012 Cambridge University Press).

Also to use up the outstanding electric properties of CNT in energy storage application or supercapacitor, CNT is modified with graphene which has larger surface area and the same crystal structure with CNTs [12-16]. Figure 1 shows the foliate-like graphenated CNT, which was developed by C.B. Parker et al. to improve the operation of CNT-based capacitor [14]. Using the similar structure, Chen et al. aimed to enhance the performance of CNT-based electric and optoelectronic devices [15]. In these structures, researchers combined the high mobility of carriers in CNT with the high density of carrier in graphene's edge.

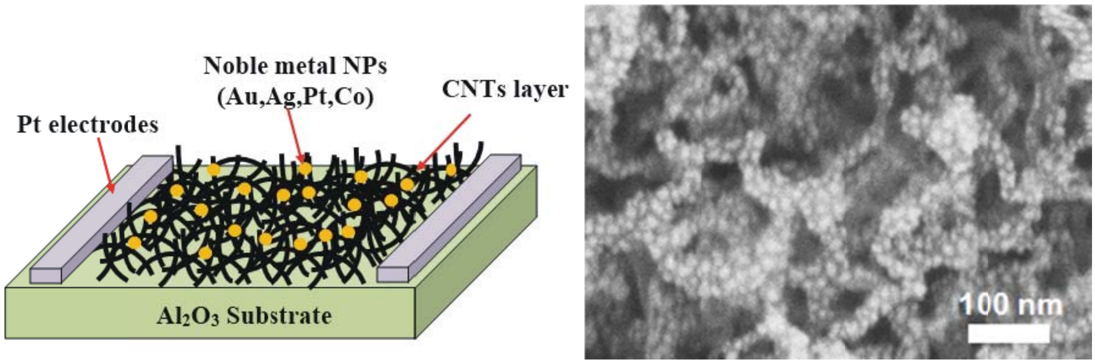

Figure 2. A diagram noble metal-decorated CNTs-based gas sensor device (left) and FESEM image of CNT layer coated with 4 nm Ag (right).

CNTs not only are modified with graphene which has similar structure with CNTs, but also are made composite with different nanostructures of metal [21 - 28], metal oxide semiconductor [29 - 36, 39 - 54], and pure/compound semiconductor [37, 38]. The remarkable advantage of

CNT-based materials is mostly showed in gas sensor application, photocatalytic activity. In Figure 2, there is a simple configuration of gas sensor using noble metal-coated CNT and the FESEM image of CNT layer coated with 4 nm Ag. By using Ag or Pt nanoparticles, N.H. Lam et al. clearly improved the NH3 sensitivity of gas sensor (Figure 3) [27]. The similar results are observed in researches using the hybrid materials of CNT and metal oxide semiconductor nanostructures. N. V. Hieu et al. combined multi-walled CNTs (MWCNTs) with SnO_2 and ZnO nanostructures which showed the gas sensitivity at high temperature 500 ^oC [36].

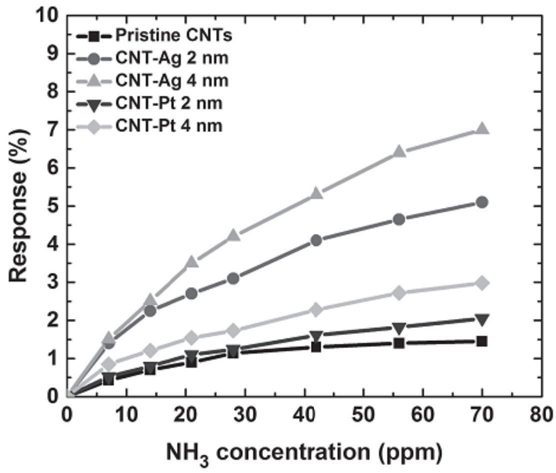

Figure 3. Comparison of responses of pristine CNT-, CNT/Pt- and CNT/Ag- based sensors under NH_3 gas concentration ranging from 0-70 ppm [27].

To utilize CNT for optical, electrical applications, CNTs have been mostly hybridised with nanostructures of semiconductor oxides, especially wide bandgap semiconductor oxides such as ZnO [31, 33, 39, 40], TiO2 [41 - 48], WO_3 [48 - 54], SnO_2 [32, 36]… The wide bandgap semiconductor oxides such as ZnO (3.37 eV), TiO_2 (3.2-3.4 eV), WO3 (2.4 - 3.2 eV) have been studied for a long time because of their distinguish properties, and their high potential in electronics, gas sensor, environmental controlling and recently in electrochromic applications [55 - 62]. ZnO, TiO_2, and WO_3, due to the lack of oxygen atom, are natural n-type semiconductors. In combination with CNT, they are hoping to create p-n junctions between CNT and semiconductor oxides.

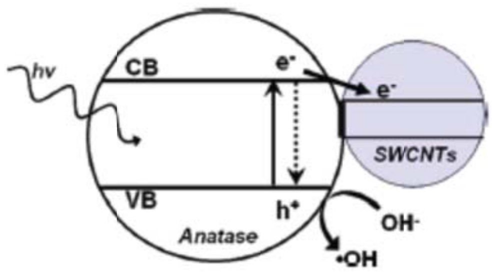

Figure 4. Schematic of a proposed model for SWCNT-enhanced photocatalysis of TiO2 [43] (Reprinted with permission from [43]. Copyright © 2008 American Chemical Society).

Moreover, ZnO, TiO_2, and WO_3 are wide bandgap semiconductors with the bandgaps are closed to near UV range (~ 360 nm, 385 nm, 480 nm, respectively). Recently, the photocatalytic activities of TiO2, WO3 were investigated in degradation measurements with methylene blue and phenol with UV light. To enhance the photocatalytic activity of TiO_2 and WO_3, researchers combined them with CNTs [43-48]. Figures 4 illustrates the interaction between CNT and nanostructure of semiconductor oxides - TiO_2 in enhancement of photocatalytic activities. In this combination, researchers also hope to use the high efficiency of absorbing light of CNT to create photocatalytic materials which work properly with visible light.

2.1. Synthesis CNT-based hybrid materials

To synthesize CNT-based hybrid materials, there are two main methods. The 1st method is to mix the component with CNT in solution, then deposit the solution on substrate or interdigitated electrodes – the indirect method [19 - 26, 29 - 31]. In the 2nd method – direct method, CNT scaffold/net is grown on substrate, then functional component is deposited directly on as-grown CNT scaffold/net [27, 31 - 35, 39, 41]. J.M. Tulliani et al. used both two methods and concluded that the gas sensitivity of ZnO/CNT hybrid materials fabricated by 1st method is lower than the one fabricated by 2nd method. Moreover, with the 1st method, it is very hard to make the sustainable contact between hybrid material and substrate [31].

2.2. Characterizing CNT-based hybrid materials

In studying about CNT-based hybrid materials, questions about the role of each component and the interaction between components are still not answered clearly. To get more knowledge about these problems, some efforts have been made. Some groups used the XPS measurement [15, 31, 41], others used Raman microscopy [15, 18, 21, 29] to get the information from hybrid materials. M. Baro et al. used Raman spectroscopy to evaluate the effect of different nanoparticles on MWCNT [21]. In Figure 5, there are Raman spectra of pristine MWCNT and different metal/alloy/metal oxide semiconductor nanoparticles – coated MWCNTs. The ratio I_D/I_G of coated MWCNTs is higher than pristine MWCNT (I_D: the intensity of signal from dis-ordered carbon; I_G: The intensity of signal from graphitic carbon). It is explained by the contact between nanoparticles and CNTs. These contacts act as defects on CNTs' walls, which results to increase the ratio of I_D/I_G.

To investigate the electric properties of hybrid materials, researchers used the impedance spectroscopy to evaluate the role of each component and effect of the interactions between components in hybrid materials [15, 34]. E. Llobet et al. built the equivalent circuit and measure the impedance spectrum of simple configuration sensor using plasma-treated MWCNTs. The resistance and capacitor of plasma-treated MWCNTs are used to examine the sensitivity of sensor with volatile organic compound [34].

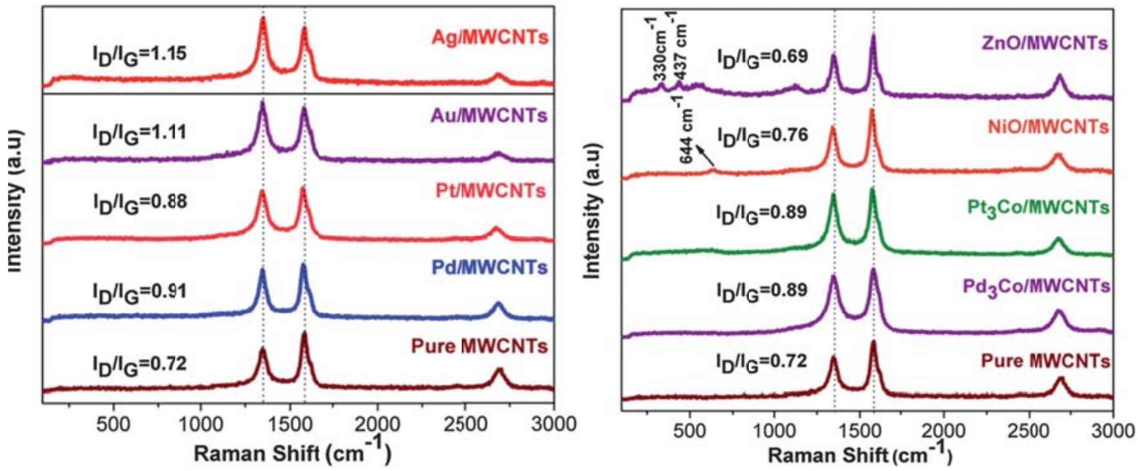

Figure 5. The Raman spectra of pure MWCNTs and different metal-, alloy-, metal oxide semiconductor-decorated MWCNTs [21]. (Reproduced from [21] with permission of The Royal Society of Chemistry).

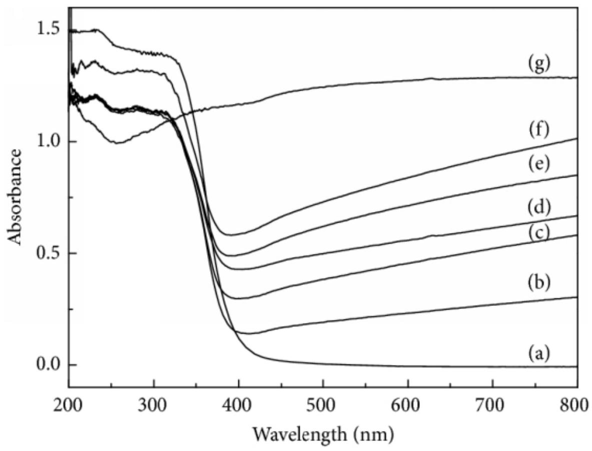

Figure 6. DRS patterns of MWCNT, TiO_2, and MWCNT-TiO_2 with different MWCNT content. (a) TiO_2; (b) 1.25 wt%; (c) 2.5 wt%; (d) 5 wt%; (e) 10 wt%; (f) 20 wt%; (g) MWCNT. (Reproduced from [63] with permission of Hindawi Publishing Corporation. Copyright © 2014 Ke Dai et al.).

The optical properties of CNT-based hybrid materials are also investigated [5, 15, 28, 33, 35, 41]. P.V. Kamat et al. measured the photoluminescence spectra and the time-integrated photoluminescence intensity of ZnO nanoparticles in solution with different CNT concentrations [33]. P.V. Kamat et al. observed that PL intensity of ZnO nanoparticles (NPs) and relaxation/emission time decreases when CNT concentration increases. These phenomena are explained by the contacts between nanoparticles and CNT. These contacts act as bridge to transfer carriers from nanoparticles to CNT. When ZnO NPs are excited by suitable light, electron-hole pairs are created in NPs. If there is no contact with CNT, the electron-hole will recombine in very short time and emit photons (radiative recombination). But because of the contact, carriers can transfer easily from NPs to CNTs and do not participate the radiative recombination. It means that the contact acts as a non-radiative recombination channel. When the concentration of CNTs increases, the number of contacts increases and, then, increases the contribution of non-radiative recombination and increase the number of channels participating recombination process (both radiative and non-radiative). It causes the less radiative recombination (lower PL intensity), and shorter life time of carriers (shorter relaxation or decay time). This mechanism also explained the increase of the Diffuse Reflectance Spectra (DRS) with the concentration of MWCNT concentration as shown in Figure 6.

4. CONCLUSIONS

In conclusion, the CNTs-based hybrid materials are very attractive and promising topic. By functionalized with different materials: organic, metal, semiconductor, polymer… the potential application of CNTs was widened. The large surface area of CNTs is used in biotechnology; the high mobility of carriers is used in supercapacitors; the high efficiency of light absorbing was used in photosynthesis and photocatalytic... There is still plenty work for researchers to develop applications of CNTs.

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TÓM TẮT

BÀI BÁO TỔNG QUAN: VẬT LIỆU LAI HÓA DỰA TRÊN NỀN ỐNG NANÔ CÁCBON

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Vật liệu lai hóa và vật liệu composit dựa trên nền ống nanô cácbon đang là một hướng nghiên cứu thu hút được nhiều sự quan tâm của các nhà khoa học trên thế giới. Ống nanô các bon được chức năng hóa hay được lai hóa với cả các hợp chất hữu cơ và vô cơ cho các ứng dụng khác nhau. Vật liệu lai hóa có thể được tổng hợp bằng phương pháp trực tiếp hay gián tiếp. Một số nghiên cứu về tính chất điện, tính chất quang và tính chất quang xúc tác của vật liệu lai hóa sẽ được thảo luận trong bài báo.

Từ khóa: CNT, vật liệu lai hóa, bán dẫn ôxít kim loại.