GROWING CARBON NANOTUBE ON ALUMINUM OXIDES
An Inherently Safe Approach for Environmental Applications

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Abstract: Using micron-sized Al_2O_3 particles as carriers to grow carbon nanotubes (CNTs) under 700°C atmosphere of methane and hydrogen after pre-planted catalysts of Fe–Ni nanoparticles, those composite CNTs (CCNTs) have demonstrated several unique properties compared to CNTs—medium specific surface area and zeta potential, high adsorption capacity for metal ions, high recovery rate by acids, low decomposition heat for exothermal reaction, and so on. The adsorption behaviours of Pb^{2+}, Cu^{2+} and Cd^{2+} in aqueous solutions by CCNTs are in good agreement with the Langmuir adsorption isotherm and second order kinetic model with maximum individual adsorption capacities of 67.11, 26.59 and 8.89 mg g^{-1}. The individual and competitive adsorption behaviours indicated that the preference order of adsorption were $Pb^{2+} > Cu^{2+} > Cd^{2+}$ for aluminum oxides, activated carbon, commercial CNTs, and CCNTs as well as other researchers' CNTs. We suggest that future development of CNTs to combine with metals and/or other materials, such as TiO_2, should consider attached to carriers or surface in order to avoid concerns on environment, health and safety. Thus, growing CNTs on Al_2O_3 particles to form CCNTs is an inherently safe approach for many promising environmental applications.

Keywords: carbon nanotube; aluminum oxide carrier; metal ion adsorption; environmental application.

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INTRODUCTION

Since carbon nanotubes (CNTs) were discovered by Iijima (Iijima, 1991), many applications have used their exceptional mechanical properties, unique electrical property, high chemical stability and large specific surface area. With hollow and layered nano-sized structures, CNTs also have potential as adsorber with high adsorption capacities for many pollutants, including metals (Li *et al.*, 2002, 2003a, b; Tsai, 2005; Hsieh *et al.*, 2006), fluorides (Li *et al.*, 2003c), chlorinated organics of dichlorobenzene (Peng *et al.*, 2003) and dioxin (Long and Yang, 2001). In addition, acid and/or oxidation were used to modify CNTs and to improve their effectiveness and capacities for metal adsorption (Li *et al.*, 2003a, b). Other types of nano-material could also be useful in environmental applications.

There have been extensive studies on using Fe metals, Fe/Ni bimetals, and their nanoparticles on treating ground-water containing toxic chlorinated organics (Leah and Paul, 1994; Schrick *et al.*, 2002; Hsieh, and Horng, 2006; Hsieh, 2006). Other applications are also abundant, such as char-supported nano Fe catalyst was studied for integrated function of chemical heat pumping, hot gas cleaning, pollutant abatement and water–gas-shift reaction catalysis (Yu *et al.*, 2006). Owing to these catalytic or reduction–oxidation reactions could form a film of iron oxide on the surface of nano-iron particles in the dechlorination process, the capacity and reactivity of nano-Fe would gradually lower. Therefore, the use of Fe/Ni, Fe/Pd and other bimetals to improve the effectiveness was popular among researchers. In addition, several researches have already developed ways to combine CNTs and metal nanoparticles for catalyst in order to expand the use of metal nanoparticles and CNTs (Tanaka *et al.*, 2004; Huang, 2006). The usefulness of those composite nanoparticles/CNTs/fibres would be the subject of many current and future researches.

Although nanotechnology could offer many beneficial applications in energy, medical and environmental fields, nanoparticles present large and somewhat unknown risks yet to be identified in environmental, health and safety (EHS) management (Thayer, 2006). One report is concerned about that the single-walled carbon nanotubes (SWCNTs) would ignite when exposed to a conventional photographic flash (Ajayan *et al.*, 2002). On the other hand, Kashiwagi *et al.*, (2004) analysed the thermal and flammability properties of polypropylene/multi-walled carbon nanotubes (PP/MWCNTs) nanocomposites and found an increase in the radiation in-depth absorption coefficient by the addition of MWCNTs to PP. Yu *et al.*, (2005) studied the thermal decomposition process of CNT/SiO_2 precursor powders prepared by rapid sol–gel method and found that the faster heating rate as CNTs combusting would generate higher temperature. Pritchard (2004) further concluded that an increasing range of materials as nanopowders would be capable of generating explosive dust clouds. Thus, growing concerns over the impacts of nanoparticles were probably due to 'massive disconnect[ion]' between EHS efforts of research and business development (Ajayan *et al.*, 2002).

In sum, CNTs were demonstrated as good adsorbents for pollutants and Fe/Ni particles were as good catalysts in may recent researches. As their dimensions were reduced to nano-sizes, they also posed concerns and threats to EHS management during their life cycle of usage. Hence, if micro-sized carriers could support those CNTs and Fe/Ni nanoparticles in order to maintain highly effective functions and to reduce potential EHS at the same time, the applications of these new composite materials would be vary desirable. This study will discuss several environmental applications of innovative composite materials of growing CNTs and Fe/Ni on micro-sized aluminum oxides (α-Al_2O_3). Those composite CNTs (CCNTs), combining Fe/Ni nanoparticles, CNTs and carrier of α-Al_2O_3, have demonstrated some unique properties—medium specific surface area and zeta potential, high adsorption capacity for metal ions, high recovery rate by acids, low decomposition heat for exothermal reaction, and so on (Horng and Hsieh, 2005; Horng *et al.*, 2006a, b; Horng and Hsieh, 2005; Hsieh *et al.*, 2006). By integrating the results from several recent studies, the benefits and shortcomings of CCNTs applications will be discussed in this paper.

EXPERIMENTAL

CCNTs Preparation

The carrier particles of micro-sized Al_2O_3 particles are initially cleaned in acid aqueous solution with ultrasonic vibration. After cleaning, the Al_2O_3 particles are sensitized in sensitization solution ($SnCl_2$ +HCl) and then activated in activation solution ($PdCl_2$ +HCl). After sensitization and activation, a film of Fe–Ni nanoparticles can be electrolessly deposited on the Al_2O_3 particles in an aqueous solution containing Fe^{2+} and Ni^{2+} ions. The composition of the electroless plating bath and the its operation parameters are reported elsewhere (Hsieh *et al.*, 2006; Hsieh, 2006).

The Al_2O_3 carrier particles, on the surface of which had been deposited a film of Fe–Ni nanoparticles, were heated to 700°C and held at this temperature for a half hour in a N_2 atmosphere with a flow rate of 120 cc min^{-1}. The N_2 atmosphere was then replaced by CH_4 gas, the flow rate of which was also 120 cc min^{-1}. In the CH_4 atmosphere CNTs were grown on the surface of Al_2O_3 particles with the Fe–Ni nanoparticles as catalyst. The characteristics of CNTs, Fe–Ni nanoparticles and Al_2O_3 were measured and observed by electron microscopy for morphology, BET method for special surface area and Zeta potential test for surface charge (Hsieh *et al.*, 2006; Hsieh, 2006).

The weight percents of CNTs, Fe–Ni nanoparticles and Al_2O_3 particles were 32, 12 and 56%, respectively. The specific surface area of CCNT and Al_2O_3 particles was 31.58 and 9.30 $m^2\,g^{-1}$. From the weight percent of CNTs, we deduced that the specific surface area of CNTs alone would be 98.69 $m^2\,g^{-1}$ (Hsieh *et al.*, 2006). For comparison, active carbon powders (denoted C) from Merk, commercial multi-wall CNT of MWCNT 2040 from ConYuan Biochemical Technology Co. Ltd, Taiwan (denoted CBT), and α-Al_2O_3 particles with Fe–Ni nanoparticles were also tested.

Those CCNTs were observed by TEM and FE-SEM (Figure 1). It shows clearly that the growth mechanism of

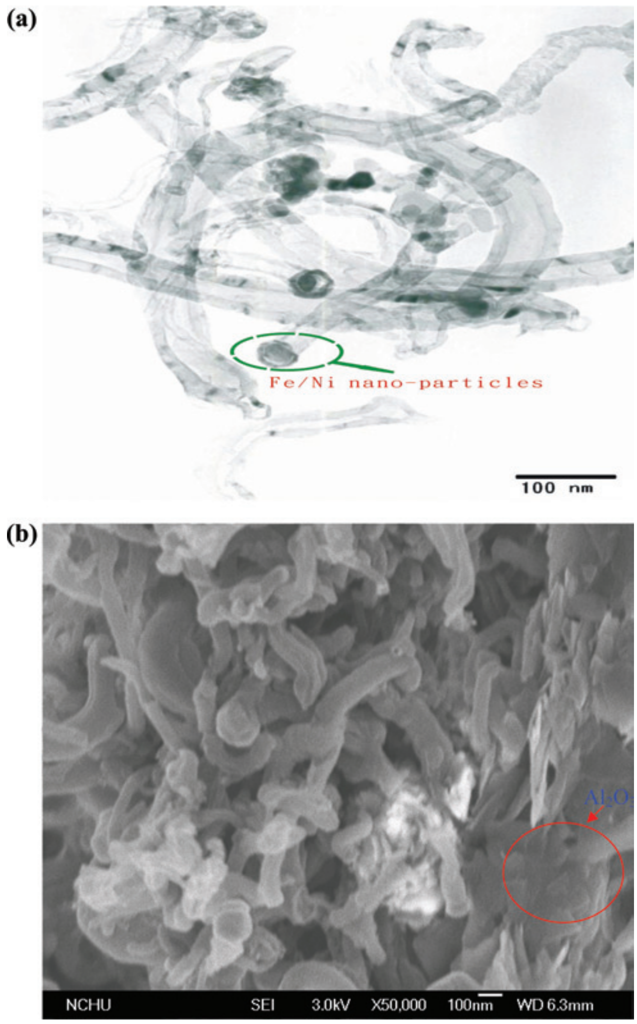

Figure 1. TEM image of CNTs on CCNTs and SEM image of aggregated CCNTs. (a) TEM image of CNTs with Fi–Ni particles on tips on CCNTs. (b) SEM image of aggregated CCNTs.

CNTs on Al_2O_3 particles with Fe–Ni nanoparticles as catalyst was 'top growth'. The CNTs grown on the surface of Al_2O_3 particles were curved and tangled with each other and had multi-walled structure micrometers in length and nanometers in diameter. The contents of CCNTs that adsorbed Pb^{+2} was also analysed by XRD and found the existence of Al_2O_3, graphite, Ni and Fe/Ni alloy (Figure 2; Horng *et al.*, 2006). The Zeta potential tests indicated that the iso-electric point (IEP) value of CCNTs is about 7.0—between the CBT (about 5) and the pure α-Al_2O_3 (about 9.5). From these IEP values it can reasonably deduced that CNTs growing on α-Al_2O_3 would modify surface charges and distribution on α-Al_2O_3 (Tsai, 2005).

Adsorption Tests

The individual and competitive adsorption capacities of Pb^{2+}, Cu^{2+} and Cd^{2+} from aqueous solutions were studied for the adsorbents of α-Al_2O_3, powdered activated carbon (C), and commercial CNTs (CBT) and CCNTs (Hsieh *et al.*, 2006; Tsai, 2005). All adsorption experiments were carried out in aqueous solutions containing Pb^{2+}, Cu^{2+} and Cd^{2+} at room temperature, at pH 5, and for 30, 60, 120, 180, 240, 300 and 360 min. In adsorption experiments, the concentrations of Pb^{2+}, Cu^{2+} and Cd^{2+} were prepared by nitrate salts and the concentrations of the adsorbents were prepared at 0.05, 0.1, 0.15, 0.2, 0.25 and 0.3 g per 100 ml. The pHs of the solutions were set at 5 and were adjusted by 0.1 M HNO_3 and 0.1 M NaOH. For regeneration tests, the adsorbed metals were desorbed by 0.5 eq/L g nitric acid by magnetic stirring of 120 rpm. After four–hour on a rotary vibrator (TS-580 batch shaker) for adsorption equilibriums, the filtrates were obtained and analysed by filtering through 0.45 μm filters. Concentrations of metal ions before and after adsorption were measured in solutions by an inductively coupled plasma atomic emission spectrometer (ICP-AES) on GBC Integra XMP and the adsorbed quantities of heavy metals were calculated from the differences.

Tests by Differential Scanning Calorimetry (DSC)

Scanning experiments were performed on a Mettler TA8000 system coupled with a DSC821^e measuring cell that can withstand pressure up to about 100 bar. STAR^e software was used for acquiring curve traces. An aluminum standard pan was used to avoid evaporation of the CNTs during scanning. The scanning rates chosen for the temperature range from 30–640°C were 2°C min^{-1} and 4°C min^{-1} (for accuracy purposes) under atmospheric air. The amounts of materials that tested were 1.28 mg for C and CBT, 4.00 mg for CCNTs (with carbon content 1.28 mg same as for C and CBT) and 2.72 mg for Al_2O_3 as reported elsewhere (Horng *et al.*, 2006).

RESULTS AND DISCUSSION

Adsorption of Metal Ions by CCNTs and Others

The growing of CNTs on α-Al_2O_3 was successful and the resultant CCNTs were used to adsorb Cd^{+2}, Cu^{+2} and Pb^{+2}. The equilibrium of metal adsorption reached their maximum capacities after around 240 min (4 h) as shown in Figure 3. Removals g metal ions were determined to be maximum by CCNTs, followed by powdered activated carbon (C), commercial CNTs (CBT) and α-Al_2O_3 for Pb^{+2}, Cu^{+2} and Cd^{+2} [Figure 4(a)–(c)]. For CCNTs with 40 mg L^{-1} of adsorbates, the maximum adsorption capacities for Pb^{+2}, Cu^{+2} and Cd^{+2} are 36, 22 and 8.4 mg g^{-1} (Figure 3). These results indicate that the adsorption preference order is $Pb^{+2} > Cu^{+2} > Cd^{+2}$ and the adsorption of those metal ions by CCNTs is superior to those of CBT and C. In addition, a sedimentation test for CCNTs and CBT was performed in order to observe operational convenience (Tsai, 2005). CCNTs would disperse in solutions but would centrifuge or filter easier than that of CBT.

The isothermal adsorption model of Pb^{+2}, Cu^{+2} and Cd^{+2} onto adsorbents of CCNTs, CBT, C and Al_2O_3 were analysed by following the equations in Table 1.

$$\text{Langmuir isotherm}\ \frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{q_m K_e C_e} \quad (1)$$

$$\text{Freundlich isotherm}\ q_e = K_f C_e^{1/n} \quad (2)$$

where K_e and K_f are the Langmuir and Freundlich constants.

By comparing the R^2, the Langmuir isotherms were the best fit models for all absorbents on adsorbing metal ions and the maximum capacities (*gm*) of adsorbents were determined. Thus, the results implied that one atomic layer of adsorbates (Pb^{+2}, Cu^{+2} and Cd^{+2}) formed on the surface of adsorbents (Tsai, 2005).

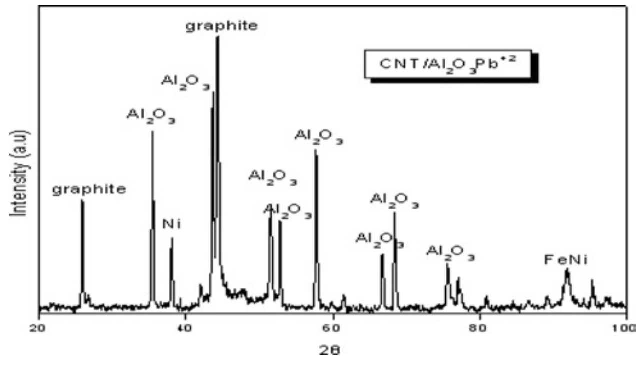

Figure 2. The XRD diagram of CCNT with no detection of adsorbed Pb^{+2} (Horng *et al.*, 2006).

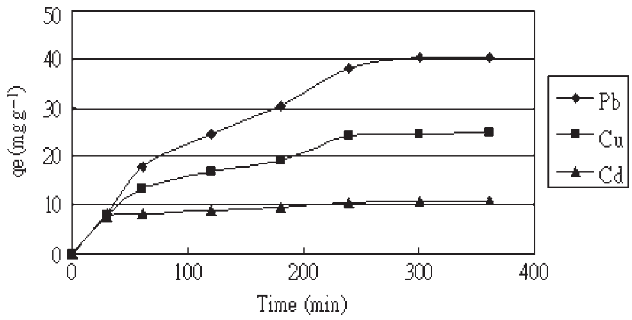

Figure 3. Adsorption capacities and equilibrium time for Pb^{+2}, Cu^{+2} and Cd^{+2} adsorption on CCNTs.

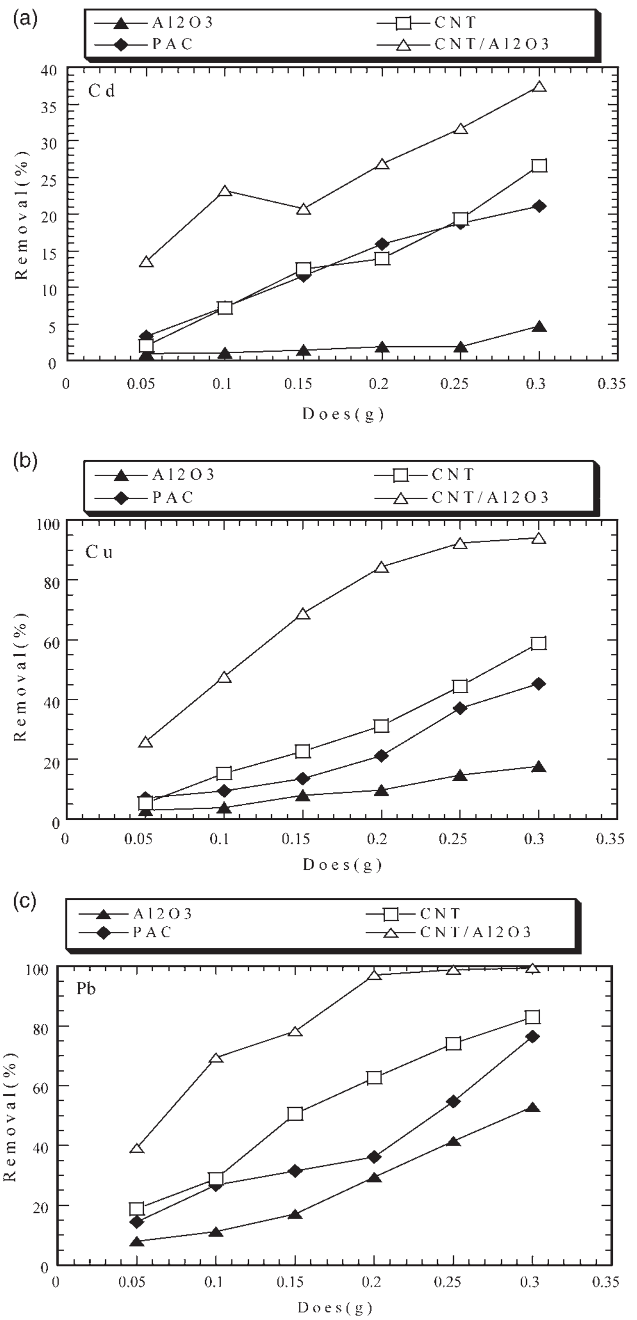

Figure 4. Removal percentages of (a) Cd^{+2}, (b) Cu^{+2} and (c) Pb^{+2} adsorption on different dosages of α-Al_2O_3, C, CBT and CCNTs.

The kinetic behaviours of adsorption were also fitted with two models: The first order kinetic model can be expressed by

$$\frac{dq_t}{dt} = k_1(q_e - q_t), \tag{3}$$

where q_e and q_t, in mg g^{-1}, are the metal quantities adsorbed by adsorbent at time $t = \infty$ and $t = t$, respectively. The equation transformed into

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \tag{4}$$

The second order kinetic model is expressed by

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \tag{5}$$

and it can be transformed into

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{6}$$

The data were transformed to log ($q_e - q_t$) versus *ı* and t/q_t versus *ı* and the regression results are shown in Table 2. By comparing regression coefficients (R^2) and $q_{e,exp}$ with $q_{e,cal}$, the results of the kinetic behaviours matched better with the second order model (Tsai, 2005).

Several problems would associate with inherent properties of nanoparticles, such as large, reactive and charged surfaces. Those CCNTs yielded preference adsorption order of s $Pb^{2+} > Cu^{2+} > Cd^{2+}$ and higher than those for aluminum oxides, powder activated carbon and commercial CNTs. Those results of preference order were similar to the results by other researchers (Li *et al.*, 2003a). In sum, the adsorption behaviours of Pb^{2+}, Cu^{2+} and Cd^{2+} in aqueous solutions by as-grown CNTs on α-Al_2O_3 particles (CCNTs) are in good agreement with the Langmuir adsorption isotherm and second order kinetic model with maximum individual adsorption capacities of 67.11, 26.59 and 8.89 mg g^{-1} (as shown in Table 3). Those results were slightly lower than acid/oxidation modified surface of CNTs by Li *et al.* (2003a) but higher than as grown CNTs (Li *et al.*, 2002).

The adsorption of metal ions on CCNTs could be desorbed by various concentrations of HCl and HNO_3 solution—performed for 10 mg l^{-1} Pb^{+2} solution in Figure 5. With six regeneration cycles, the capacity of CCNTs still maintained above 20 mg g^{-1}. In addition, the recovery ratios reach above 85% for 0.15 eq/L of HCl and were above 90% for 0.2 eq/L of HNO_3. In those regeneration processes, the catalytic Fe-Ni nanoparticles would dissolve by the regenerant acids in the first cycle. In the later cycles, concentrations of Fe and Ni dissolved in acid regenerants would be very small as shown elsewhere (Horng *et al.*, 2006a; Tsai, 2005).

Thermal Decomposition of CCNTs by DSC Testing

Recent researches indicated that MWNT even could retard flame by uniform laying on polypropylene surface (Kashiwagi *et al.*, 2004). We used the non-isothermal method of DSC to determine the thermal decomposition hazards of different types of carbon—α-Al_2O_3, C, CBT and CCNTs (Figure 6). Although CBT had the highest onset temperature, its heat of decomposition is only moderate (about 70 mass% of powdered activated carbon, C). Those results were somewhat compatible with the results of MWNT and CNT/SiO_2 precursor powders by Yu *et al.* (2005). They obtained the peak temperature of MWNT at 5°C min^{-1} to be 659°C (738°C at 10°C min^{-1}) and experienced thermal delayed effects. Kashiwagi *et al.* (2004) further observed that with 7.1 mass% catalyst iron particles in MWCNTs would show no effect on heat release but smoldering at the end of combustion. They concluded that the thermal conductivity of MWCNTs on PP surface would somewhat reflect the incident radiation and hence reduce the transmitted flux. Those CCNTs (Figure 6) demonstrated a similar deflection

Table 1. The isothermal adsorption models for adsorption of Pb^{+2}, Cu^{+2} and Cd^{+2} by various adsorbents (Tsai, 2005; Horng *et al.*, 2006a).

		Langmuir			Freundlich			
Adsorbent	Metal ion	qm (mg g^{-1})	K_e (l mg^{-1})	R^2	n	K_f (l mg^{-1})	R^2	pH range
αAl_2O_3	Pb	8.92	0.09	0.997	2.12	1.30	0.953	5.87–6.01
	Cu	6.97	0.16	0.997	2.08	1.22	0.971	5.80–6.29
	Cd	2.00	0.16	0.994	1.84	0.34	0.984	6.30–6.53
C[1]	Pb	33.78	0.01	0.983	1.09	0.49	0.977	5.85–6.02
	Cu	11.79	0.06	0.998	1.48	0.86	0.988	5.97–6.17
	Cd	5.89	0.17	0.996	1.76	0.98	0.987	6.63–6.86
CBT[2]	Pb	11.23	0.04	0.993	1.52	0.68	0.979	5.08–5.14
	Cu	7.14	0.12	0.996	1.86	0.99	0.980	4.82–5.11
	Cd	6.19	0.18	0.997	1.94	1.94	0.964	5.12–5.19
CCNTs	Pb	67.11	0.04	0.989	1.39	3.22	0.974	5.05–5.34
	Cu	26.59	0.10	0.987	1.66	2.91	0.980	5.25–5.52
	Cd	8.89	0.13	0.956	1.55	1.17	0.926	5.28–5.78

[1]Active carbon powders; [2]commercial CNTs.

Table 2. Kinetic adsorption model of adsorption of Pb^{+2}, Cu^{+2} and Cd^{+2} (Tsai, 2005; Horng *et al.*, 2006a).

		First-order kinetic model				Second-order kinetic model		
Adsorbent	Metal ion	$q_{e,exp}$ (mg g^{-1})	$q_{e,cal}$ (mg g^{-1})	k_1*10^2 (1 min^{-1})	R^2	$q_{e,cal}$ (mg g^{-1})	k_2*10^2 (1 min^{-1})	R^2
α-Al_2O_3	Pb	7.37	5.27	1.11	0.977	7.59	0.63	0.994
	Cu	6.43	4.57	1.01	0.940	6.49	0.79	0.993
	Cd	2.48	2.31	7.83	0.966	2.50	1.24	0.985
C[1]	Pb	11.09	9.91	1.17	0.871	11.36	0.35	0.989
	Cu	7.25	4.12	1.08	0.932	7.35	1.01	0.997
	Cd	4.48	3.90	8.98	0.976	4.67	0.55	0.979
CBT[2]	Pb	7.20	5.08	1.52	0.945	8.09	0.23	0.951
	Cu	6.41	4.17	1.11	0.953	6.93	0.31	0.972
	Cd	4.28	2.17	1.15	0.963	4.53	0.62	0.983
CCNTs	Pb	40.23	29.17	1.91	0.897	47.17	0.03	0.930
	Cu	24.96	17.14	1.52	0.946	28.17	0.07	0.956
	Cd	11.18	9.50	1.29	0.845	11.85	0.44	0.991

[1]Powder activeed carbon; [2]commercial CNTs.

Table 3. Comparison of Pb^{+2}, Cu^{+2} and Cd^{+2} adsorption capacities of different adsorbents.

	Langmuir isotherm model (qm)				
Adsorbent	Pb^{+2} (mg g^{-1})	Cu^{+2} (mg g^{-1})	Cd^{+2} (mg g^{-1})	Condition	Refs.
CCNTs	67.11	26.59	8.89	pH 5.0; room temperature	Tsai, 2005; Horng *et al.*, 2006a
Surface oxidized CNTs	97.08	24.49	10.86	pH 5.0; room temperature	Li *et al.*, 2003a
As grown CNTs	17.44	—	—	pH 5.0; room temperature	Li *et al.*, 2002
CBT	11.23	7.14	0.13	pH 5.0; room temperature	Tsai, 2005; Horng *et al.*, 2006a
C	33.78	11.79	5.89	pH 5.0; room temperature	Tsai, 2005; Horng *et al.*, 2006a

effect as lower peaks temperature of CCNTs appeared in DSC thermal scans (Horng *et al.*, 2006b).

By comparing the results for DSC thermal scans on α-Al_2O_3, C, CBT and CCNTs (Figure 6), CCNTs had medium starting temperature of exothermal reaction and lowest heat of decomposition and is a safer material (less heat hazard) than C and CBT. In addition, the heating exothermal reaction is the first order for CCNTs and had activation energy increase as the heating rate increases (Horng *et al.*, 2006). Moreover, our results implied that different types of carbon contained in C, CBT and CCNTs could yield different energies during thermal decomposition. Thus, those MWCNTs on CCNTs that yielded low heat of decomposition could be different and inherently safer material than commercial CNTs (CBT).

Integrating CNTs into Other Materials

Recently, several researches have used composite CNTs with metals, TiO_2 or other materials on potential applications (Tanaka *et al.*, 2004; Kashiwagi, 2004; Kedem *et al.*, 2005; Yu *et al.*, 2005; Huang, 2006). Kedem *et al.* (2005) prepared composite nanofibers containing nanometric TiO_2 particles and MWCNTs by the electrospinning technique for potential use as new photo-catalytic reactor elements. As Kyung *et al.* (2005) demonstrated that the simultaneous and

Table 4. CNTs properties, potential benefits, shortcomings and applications.

Property	Benefits	Shortcomings	Application
(1) Small particle size	• Large surface • Good for uniform surface coverage • Fast reactions • Better conservation of materials • Better green chemistry	• Threat to respiratory/membrane system • Threat to dust exploration • Easy aggregation and difficult heat dispassion • Difficult to detect/observe • Easy penetration on protective surfaces • Un-controllable Brownian movement	b,c,g
(2) Large surface area	• Good catalyst potential • Good for uniform surface coverage • High buoyancy in fluids • Strong related to small particle size	• Highly reactive /oxidative surface • Easy aggregation due to surface charges • Large impact at small amount	a,b,c,d,e,g
(3) High reactivity	• Good catalyst use • Better on specific reaction • Fast kinetics/quick heat generation • Good for process intensification • Related to large surface area	• Fast reaction, by-products coverage, and/or equilibrium • Reactive and explosive dangers due to fast reactions and large heat generation	a,b,c,d,e,f,g
(4) Electrical and magnetic properties	• Many applications in electronics and electrical engineering • Easy manipulation and manufacture by electrical or magnetic means	• Easy aggregation by magnetic or electrical forces • Strong and dense magnetic effect in small amount and short distance	b,g
(5) EHS applications/concerns	• Many environmental applications (pollutant degradation/adsorption) • Numerous applications in health and safety applications, such as sunscreen, and so on	• Threat to health and safety of operators or users due to small size, high reactivity and large surface area • Potential Impacts on EHS management and product's life cycle • Unknown/potential risks to environment	a,b,c,d,e,g

Note: (a) Chemical/accident treatment; (b) hazard protection; (c) air quality control; (d) chemical/toxics removal; (e) water quality control; (f) process intensification/green chemistry; (g) instrument analysis or interference. [From (a) to (e) were proposed by Koper *et al.*, 2006].

synergistic conversion of dyes and heavy metal ions in aqueous suspensions was possible, the author and co-workers successfully applied Fe/Ni/composite MWCNTs with TiO_2 (Figure 7; similar to CCNTs) to photo-catalyse the azo dye (Huang, 2006) Future environmental applications are still under investigation. However, new hazards or concerns might be raised on the combination of nanoparticles with nanofibres. This study showed that CCNTs were no-worse in performance comparing to CBT and other nanomaterials. The author believes that using micro-sized carriers to grow nanoparticles or -fibres would be a better approach without risking the unknown hazards of nanoparticles.

Environmental Applications for CNTs and CCNTs

Many properties of CNTs promote abundant researches and applications: small particle size, large surface area, high reactivity, as well as electrical and magnetic properties. On the other hand, the EHS concerns are also abundant and alarming. Those properties, potential benefits, shortcomings and applications are listed in Table 4. However, many

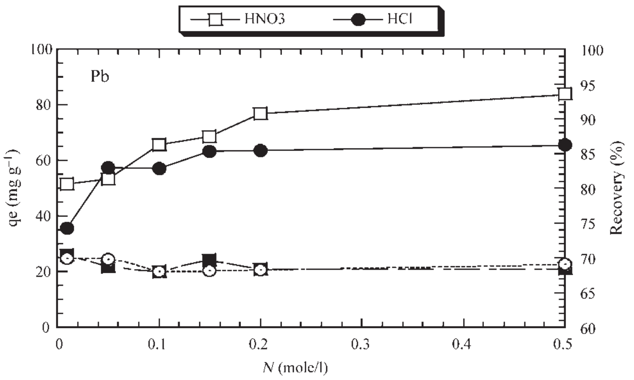

Figure 5. Recovery percentages and capacities of CCNTs with different concentrations (Normal as eq/L) of HNO_3 and HCl concentrations.

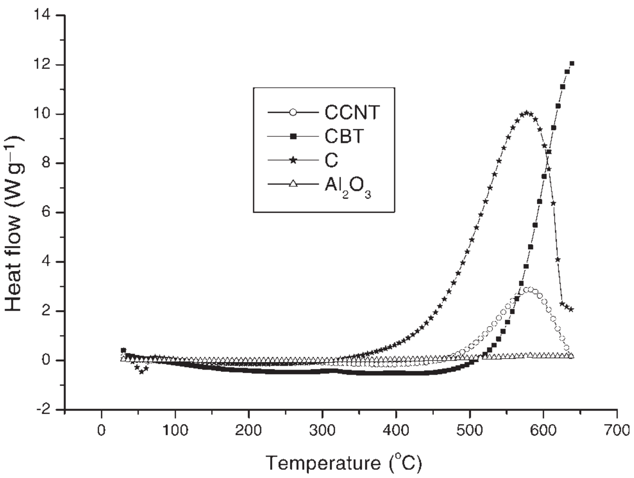

Figure 6. Comparison of heat flow versus temperature by DSC tests on CCNTs, CBT, C and α-Al_2O_3 at heating rate: 4°C min^{-1}.

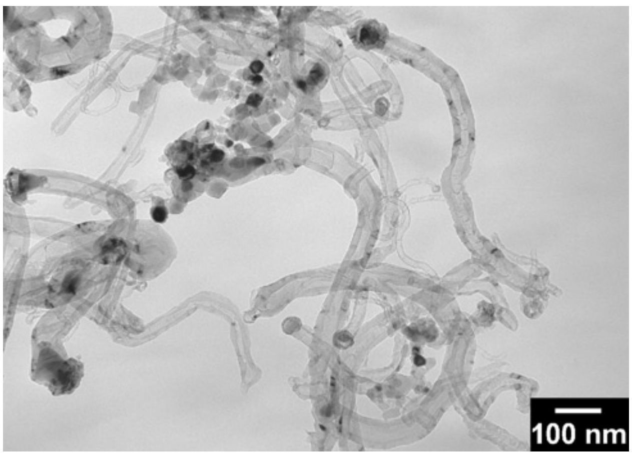

Figure 7. SEM image of CNTs/Fe-Ni with 20 nm TiO_2.

properties are related, such as small particle size, large surface area, high reactivity as well as EHS concerns. There are several environmental applications proposed for the nanocrystalline materials by Koper *et al.* (2006). However, applications on process (intensification) and instrumentation (analysis) should be included as indicated in Table 4.

Upon examination of those properties and applications with CCNTs' characteristics, we found some advantages. From the above results, the author concluded that an innovative type of CCNTs was developed. By growing MWCNTs onto α-Al_2O_3, CCNTs have not only a low decomposition heat but also a high adsorption capacity for metal ions. Those CCNTs not only exhibit good operational and separation properties from aqueous solutions but also indicate less hazard of EHS concerns because of heat reflection by their micro-sized carriers—α-Al_2O_3. In sum, with medium specific surface area and zeta potential, high adsorption capacity for metal ions, high recovery rate by acids, low decomposition heat for exothermal reaction, CCNTs developed by the author and co-workers (Tsai, 2005; Hsieh, 2006; Horng *et al.*, 2006a, b) would be inherently safer materials than other CNTs available commercially. Thus, the development of nanomaterials for environmental applications should have EHS concerns in mind such as growing nanoparticles or nanofibres on micro-sized carriers or surfaces to avoid possible EHS impacts. This study has demonstrated the development and evaluation of an innovative and inherently safer nanomaterial—CCNTs with more stable thermal and surface properties. However, many more tests still need for practical applications of CCNTs on environmental engineering—such as column tests, recovery tests, and so on. We would continue the development CCNTs on other carrier materials as well as practical applications.

CONCLUSIONS

Upon the development of nanoparticles and their applications, several problems would associate with their inherent properties, such as large, reactive and change able surfaces. These properties could represent benefits or shortcomings—depending on their applications (Pritchard, 2004; Hayer, 2006). This study has shown that by growing CNTs on α-Al_2O_3 to form CCNTs would hold several advantages—operational convenience, less potential EHS impacts, and better thermal properties (Horng and Hsieh, 2005; Horng *et al.*, 2006a, b; Hsieh and Horng, 2005; Hsieh *et al.*, 2006). With CCNTs' medium specific surface area and zeta potential, high adsorption capacity for metal ions, high regeneration rate by acids, low decomposition heat for exothermal reaction, they have high adsorption capacities for Pb^{2+}, Cu^{2+} and Cd^{2+}. The CCNTs exceeded the performance of the adsorbents of aluminum oxides, activated carbon and yielded preference adsorption order of $Pb^{2+} > Cu^{2+} > Cd^{2+}$ similar to others (Li *et al.*, 2003a).

The adsorption behaviours of Pb^{2+}, Cu^{2+} and Cd^{2+} in aqueous solutions by as-grown CCNTs are in good agreement with the Langmuir adsorption isotherm and second order kinetic model with maximum individual adsorption capacities of 67.11, 26.59 and 8.89 mg g^{-1} (Horng *et al.*, 2005; Hsieh *et al.*, 2006). Those results were compatible to modified CNTs by acid/oxidation of others (Li *et al.*, 2003a).

In order to broaden the applications of CCNTs, one recent study already attached TiO_2 on CCNTs with promising potential applications in catalytic reactions of dyes (Huang, 2006). The combination of CNTs with other materials and their application are under intensive studying by many researchers.

This study has proposed and evaluated several applications of CCNTs, which have medium specific surface area and zeta potential, high adsorption capacity for metal ions, high recovery rate by acids, low decomposition heat for exothermal reaction. Those CCNTs would be inherently safer materials than other CNTs available commercially. And, we hereby suggest that the development of nanomaterials for environmental applications should have EHS concerns in mind—such as growing nanoparticles or nanofibres on micro-sized carriers or surfaces to avoid possible EHS impacts. The growth of CNTs onto materials surface appears to be an inherently safe approach for many promising environmental applications on their stable surface and thermal properties.

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