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Research paper

Evaluation of the physiochemical properties and catalytic performance of mixed metal oxides-carbon nanotubes nanohybrids containing carbon nanotubes with different diameters

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ABSTRACT

In this study, three types of oxided multi-wall carbon nanotubes (o-MWCNT) with different diameters and oxygen-containing group content were used to synthesize Layered double hydroxides/mixed metal oxides-carbon nanotubes (LDH/MMO-CNT) nanohybrids via a homogeneous urea precipitation method. The surface morphology, structure, graphitization of as-prepared nanohybrids were investigated by Scanning electron microscopy, X-ray diffraction and Raman measurements, etc. The results showed that 3D hierarchical honeycomb nano-structured MMO-CNT was obtained when adding o-MWCNT with a diameter <8 nm during preparation. And addition of o-MWCNT with a diameter >30 nm; resulted in formation of a structure in which 1D CNT coupled with layers of 2D LDH/MMO with a "line-face" morphology. The results of bisphenol A degradation showed that addition of o-MWCNT with a smaller diameter led to better catalytic performance of MMO-CNT nanohybrids. It may be attributed to the better graphitization and highly dispersed activated components in the catalyst.

1. Introduction

Carbon nanotubes (CNT) are hollow cylinders composed of one or several concentric layers of carbon atoms in a honeycomb lattice arrangement. They are currently considered as promising building blocks of the future nanoelectronic technology due to their excellent mechanical, electrical, thermal and magnetic properties (Heer et al., 1995). For example, the construction of hierarchical structures by arranging CNT and metal oxide nanoparticles with nanometer-scale precision has a wide application prospect (Grzelczak et al., 2010). Particularly, the combination of metal oxides and CNT endows the composites with the unique properties of each component, and sometimes could even produce a synergistic effect. The CNT network was found to be effective in facilitating the dispersion of the oxide nanoparticles. Moreover, the large surface area and the interaction between the functional groups of the CNT network and metal ions can provide more active sites for heterogeneous catalysis (Zhang et al., 2010; Huang et al., 2014). Delocalization of π electrons within the graphene layers (C-π) of CNT facilitates electrons transportation and thus accelerate the reactions (Zhang et al., 2010; Huang et al., 2014). On the other hand, the morphology, structure and composition of metal oxides could be affected by the introduction of CNT. Previous study in our lab found that a trace amount of carbon nanotubes was able to significantly facilitate the decomposition of PMS into radicals, thereby enhancing the oxidation of bisphenol A, and both 3D hierarchical honeycomb of nanohybrid and surface defects of carbon nanotubes played important roles in the catalytic degradation process(Li et al., 2015a).

Despite the potential of CNT as ideal reinforcing agents with the abovementioned advantages, the research work evaluating the effects of CNT with different properties in the heterogeneous catalysis is still rather lacking (Liu and Gao, 2005). Especially, with the development of different synthetic routes, such as arc discharge, laser ablation, and solvothermal processing etc., and modification methods, such as covalent modification and noncovalent modification, mass production of CNT with finely tuned and desired characteristic and performance has been achieved in recent years; e.g., Peng prepared CNT with the smallest diameter (0.4 nm) by mass-selected carbon ion beam deposition (Peng et al., 2000); and functionalized CNT with different surface oxygen-

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Table 1
Details of the o-MWCNT.

Sample	Diameter, d (nm)	Length, L (μm)	Aspect ratio, L/d	Oxygen-containing group	Functional group content (wt%)
CNT-8	<8	0.5–2	>62.5	–COOH	3.86
CNT-30	30–50	0.5–2	10–66.67	–COOH	0.73
CNT-50	>50	0.5–2	<66.67	–OH	0.71

containing groups including carboxylic acids, ketones and alcohols were customized by different methods (Mawhinney et al., 2000). It is interesting to note that the diameter and functionality can affect the physical and chemical properties of CNT. It was reported that CNT with different diameters and special electronic structure exhibit different quantum properties, and CNT with a smaller diameter displayed more obvious quantum effects (Alaei-Shahmiri et al., 1999). Other scientists also suggested that the band gap energy of CNT which is required by electrons to transit from the valence band to the conduction band depends on the diameter and chirality (Schönenberger et al., 1999; Avouris, 2002), therefore CNT with different diameter displayed either metallic or semiconductive properties. Recently, it was demonstrated that the surface groups, surface charge properties, dispersability, aspect ratio of CNT will be affected by functionality; with increasing functionalization degree, the tubes can eventually convert into insulating material (Karousis et al., 2010).

However, up till now, to our best knowledge, there is no other report concerning the effect of diameter and functionality of CNT on the structure and catalytic performance of CNT/metal oxides hybrids. In our previous study (Li et al., 2015b), CoMnAl-mixed metal oxides (MMO) derived from LDH was synthesized as heterogeneous catalysts, which showed superior catalytic performance for bisphenol (BPA) degradation by using potassium monopersulfate (PMS) as oxidant. LDH are a family of common inorganic materials and are facile to be synthesized in the laboratory. A key structural characteristic of LDHs is that the M^{II} and M^{III} cations are distributed in a uniform manner in the hydroxide layers (He et al., 2013). Therefore, LDHs can be

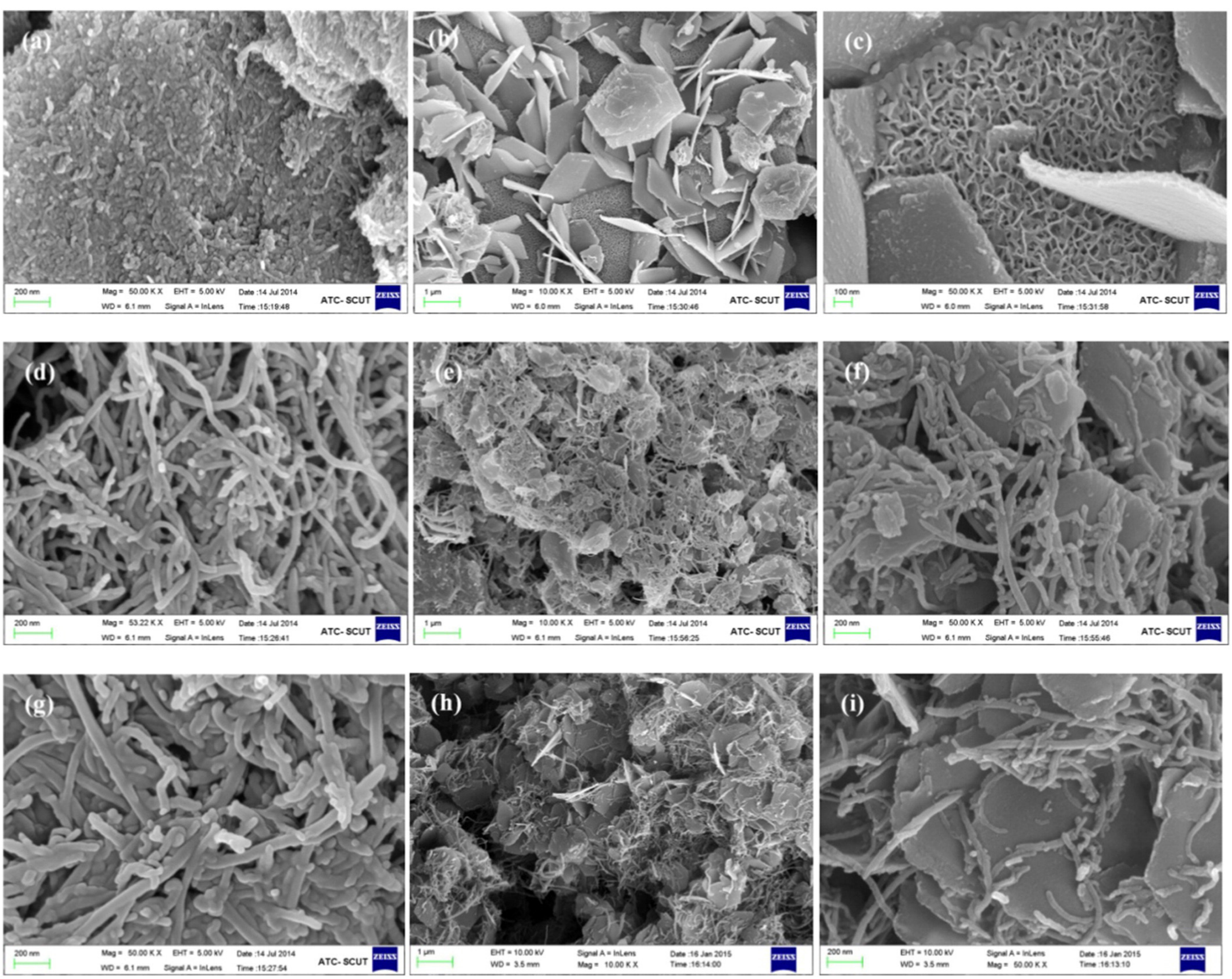

Fig. 1. SEM images of sample: (a) CNT-8; (b) and (c) LDH-CNT-8; (d) CNT-30; (e) and (f) LDH-CNT-30; (g) CNT-50; (h) and (i) LDH-CNT-50.

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