Songklanakarin J. Sci. Technol.
40 (5), 1181-1185, Sep. - Oct. 2018

http://www.sjst.psu.ac.th

Short Communication

MWCNT/Silica aerogel: Preparation, characterization and applications in heterogeneous catalysis and decolorization of aqueous dye solutions

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Received: 23 April 2017; Revised: 23 June 2017; Accepted: 7 July 2017

Abstract

2.3 x 10^{-3} wt% multi-walled carbon nanotube incorporated silica aerogel (MWCNT/Silica aerogel) was synthesized by ambient pressure drying. The as-synthesized MWCNT reinforced silica aerogel was characterized by XRD, SEM, N_2-adsorption–desorption, etc. The MWCNT/Silica aerogel catalyzed a multicomponent reaction for synthesizing medicinally important benzylpyrazolyl coumarin derivative. And, in another application, the efficient decolorization of Eriochrome Black T and Methylene Blue from their respective aqueous solutions over MWCNT/Silica aerogel was also investigated using UV spectrophotometer. A comparison has also been made with decolorizing activities of silica gel and activated charcoal.

Keywords: MWCNT/Silica aerogel synthesis, ambient pressure drying, heterogeneous catalysis, dye decolorization

1. Introduction

Aerogel is an ultra-light synthetic porous material having unique microscopic (nanoscale skeleton) and macro-scopic (condensed state matter) structural features. An aerogel is derived from gel made through sol-gel chemistry when the liquid component inside the wet gel is exchanged by air without damaging the solid microstructure (Kistler, 1931; Du, Zhou, Zhang, & Shen, 2013). Aerogels are attractive materials for their applications in thermal insulation, adsorption, chemical sensors, catalysis, and space explorations. Usually silica aerogels have poor mechanical strength and are hygroscopic in nature. Off late, silica aerogels and metal-modified aerogels have been widely employed as catalyst support and catalysts (Müller, Schneider, Mallat, & Baiker, 2001). Carbon aerogels have interesting adsorption properties, structural stability, high thermal stability and most importantly the useful electronic conductivity for their applications in catalyst carriers, oil or organic solvents' adsorption and energy storage (Biener *et al*., 2011; White, Brun, Budarin, Clark, & Titirici, 2014). Multi Walled Carbon Nanotubes (MWCNTs) were used as reinforcement to improve the mechanical properties of silica aerogels (Bangi, Kavale, Baek, & Park, 2012). MWCNT/Silica aerogel composites are useful hybrid aerogels (Bargozin, Amirkhani, Moghaddas, &

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Ahadian, 2012; Chernov *et al*., 2016) and could be easily modified or fabricated than the pure carbon aerogels.

Herein, sol-gel method followed by ambient pressure drying was employed to prepare 2.3 x 10^{-3} wt% multi-walled carbon nanotube incorporated silica aerogel (MWCNT/ Silica aerogel). This nanocomposite was characterized by XRD, BET, SEM, etc. and was evaluated as active catalyst for synthesis of benzylpyrazolyl coumarin in a multicomponent reaction (MCR). MWCNT/Silica aerogel was also employed as a functional material in decolorization of Eriochrome Black T (EBT) and Methylene Blue (MB) dyes from their respective aqueous solutions.

2. Experimental

2.1 Preparation of MWCNT incorporated silica aerogel

In a typical experiment, the dispersion of MWCNTs (2.3 x 10^{-3} wt%) was carried out by subjecting the mixture of MWCNTs, de-ionized water and Tween 80 to ultrasonication for 4 hrs. Thereafter, the gel was formed by mixing sodium silicate, MWCNTs and citric acid. The citric acid (3M) catalyzed the MWCNT/Silica gel formation. During the synthesis, the H_2O:Na_2SiO_3 molar ratio and the concentration of MWCNTs were kept constant at 146.67 and 2.3 x 10^{-3} wt% respectively and gel aging, solvent exchange, silylation and ambient pressure drying were subsequently performed**.** The surface of MWCNTs is functionalized with non-covalent surfactant Tween 80 so as to disperse the CNTs in water and the precursor solution. Tween 80 is an aromatic compound with the ethylene oxide as hydrophilic group. These hydrophilic groups play an important role in the generation of effective repulsive force by electrical double layer interactions. The adsorption of Tween 80 to the surface of MWCNTs helps to de-bundle CNTs by steric or electrostatic repulsions. The functionalization of MWCNTs using Tween 80 forms the hydroxyl groups on the surface of nanotubes helping CNTs get dispersed in the water. The silylated gels were dried at 50 °C for one hour and then 200 °C for one hour in PID controlled oven. A combination of sodium silicate and ambient pressure drying provides low cost alternative to the development of silica aerogels overcoming the difficulties encountered in expensive supercritical CO_2 drying. Photographs of the MWCNT/Silica aerogel material are shown in Figure 1.

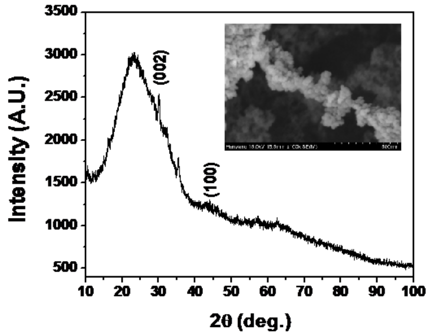

Figure 1. XRD pattern of MWCNT incorporated silica aerogel (Inset: FE-SEM image).

2.2 Characterization

Herein, low density (0.056 g/cc), highly porous (97%), semitransparent and super hydrophobic (148°) MW-CNT incorporated silica aerogel was synthesized. The X-ray diffraction (XRD) pattern determined the crystallinity and composition whereas the Scanning Electron Microscopy (SEM) analyzed the morphology of the MWCNT/Silica aerogel (Figure 2). Figure 2 depicts the XRD diffractogram of MWCNTs/silica aerogel. It clearly shows a broad peak which is due to the amorphous and insulating nature of the nano-structured material. But there are two small peaks at 2θ of around 30.04° and 43.9° corresponding to the (002) and (100) planes of MWCNTs (Stamatin *et al.*, 2007). The Figure 2 inset depicting the SEM image of MWCNTs/Silica aerogel confirms the formation of mesoporous network structure and the capping of silica particles on the side walls of MWCNTs. This coupling is considerably strong and they cannot be detached from each other. This could be due to the hydrogen bonding interactions between silanol and surface OH groups on the modified MWCNTs surface as reported (Bangi, Kavale, Baek, & Park, 2012) in the reactions.

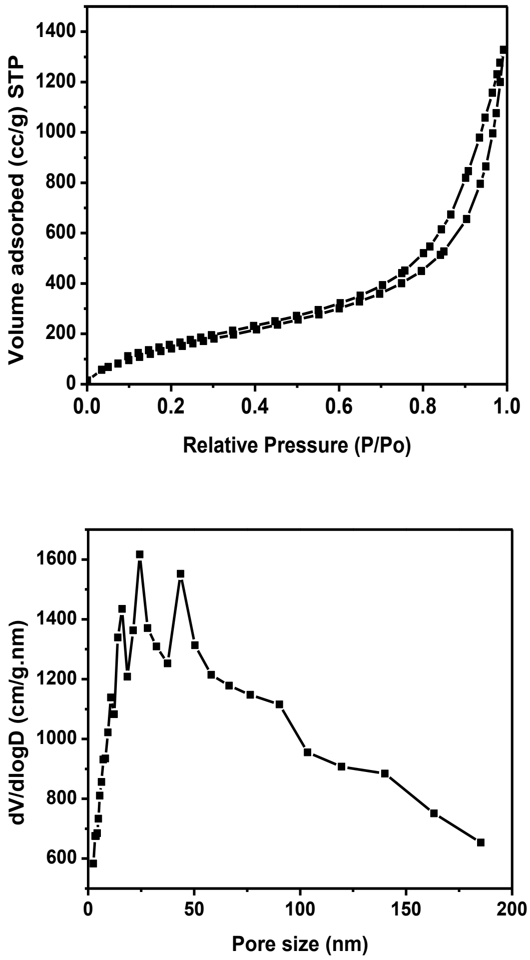

Figure 2. N_2 adsorption-desorption isotherm and pore size distribution.

The specific surface area, pore volume and pore size were derived from the N_2 adsorption–desorption isotherm at 77 K of the as-synthesized aerogel. As shown in Figure 3, the aerogel exhibited type IV isotherms with a type H1 hysteresis loop, typical for mesoporous materials. Further the material showed broad asymmetrical pore size distributions in the micro-mesopore range with more mesopores. The MW-CNT/Silica aerogel exhibits high BET surface area of 645.65 m^2/g, Langmuir surface area 1406.3 m^2/g, BJH surface area 740.60 m^2/g, pore volume 2.0113 cc/g and the average pore diameter of 12.46 nm.

Figure 3. Photographs of the MWCNT/Silica aerogel.

2.3 Applications

2.3.1 Catalyzed four-component organic reaction

The catalytic property of the MWCNT/Silica aerogel was studied by employing 15 mg of material in an MCR of phenyl hydrazine (1.0 mmol), ethyl acetoacetate (1.0 mmol), benzaldehyde (1.0 mmol) and 4-hydroxycoumarin (1.0 mmol) in the presence of acetonitrile as the solvent at room temperature and it afforded 60% yield of the desired benzyl-pyrazolyl coumarin product within 40 minutes. The catalyst was easily recovered and reused without any loss in activity. Figure 4 shows the mass spectrum of the MCR product namely 4-((4-hydroxy-2-oxo-2H-chromen-3-yl)(phe-nyl)me-thyl)-5-methyl-2-phenyl-1H-pyrazol-3(2H)-one.

2.3.2 Decolorization of Eriochrome Black T and Methylene Blue from aqueous solutions

Organic dyes induce water pollution and the cleaning of this dye-medium i.e. the aqueous solution of dye is one of the most serious environmental problems today (Brillas & Martínez-Huitle, 2015). Methylene Blue (or Methylthioninium chloride) is a potent cationic dye and is classified basic in nature by the Color Index International. MB (CAS Number 122965-43-9, Molecular Formula $C_{16}H_{18}ClN_3S{\cdot}xH_2O$, MW 319.85, Absorption λ_{max} 660-665 nm) with thiazine group as the chromophore has been extensively used to dyeing paper, wool, silk and cotton. An excessive MB exposure may lead to side-effects (Janani, Rani, Ellappan, & Miranda, 2016) including health-issues such as dizziness, severe headache, hypertension, serotonin toxicity, etc. Eriochrome Black T / EBT (CAS Number 1787-61-7, Molecular Formula $C_{20}H_{12}N_3NaO_7S$, MW 461.38, Absorption λ_{max} 503 nm) is an azo dye with -N=N- (azo) structure as the chromophore. A literature survey showed that only few reports have raised the removal of EBT (Luna, Flores, Genuino, Futalan, & Wan, 2013).

3. Results and Discussion

The present manuscript reports preliminary results with respect to catalytic application of MWCNT/Silica aerogel and environmental application while touching upon the chemical as well as thermal and mechanical pathways behind the decolorization (of dyes).

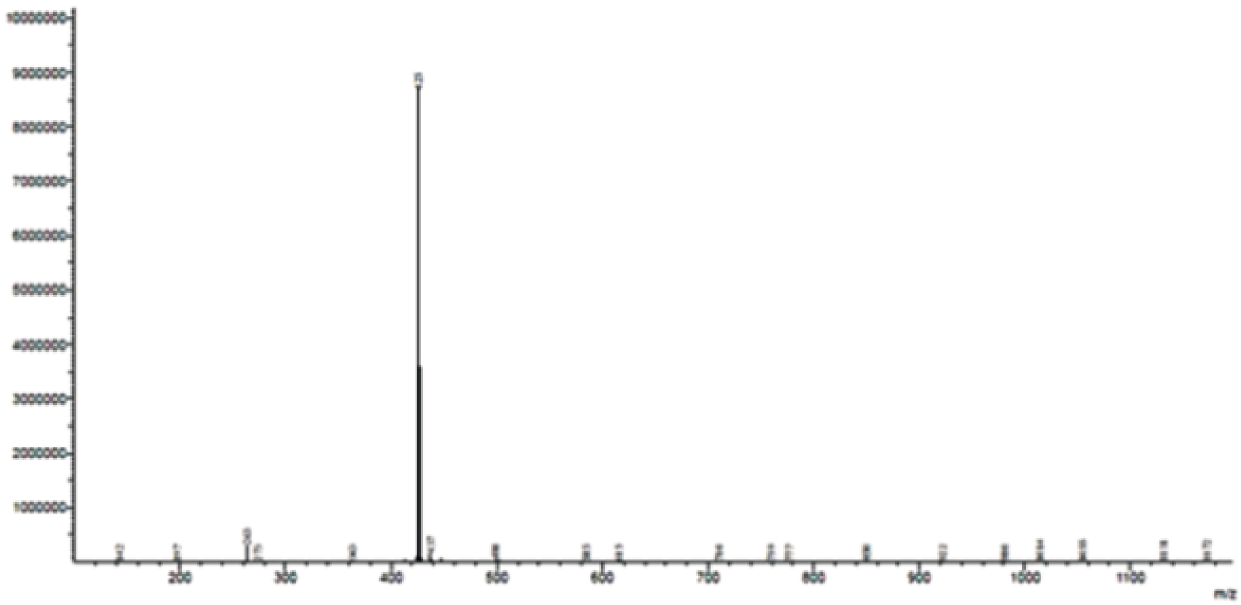

Figure 4. Mass spectrum of the MCR product.

3.1 MWCNT/Silica aerogel catalyzed synthesis of benzylpyrazolyl coumarin derivative

This MWCNT/Silica aerogel offered scope for its utility in organic reactions because of high silicon content and hydrophobic nature stemming from the surface -CH_3 groups. Active sites for the MCR on this catalytic material could have been generated by dehydroxylation of surface isolated hydroxyl groups or the strained siloxane bridge. Though we have no direct evidence of carbocatalysis or catalysis by MWCNTs as such, for sure, there is no metal impurity responsible for this catalytic application. In addition to this catalyzed MCR of phenyl hydrazine, ethyl acetoacetate, benzaldehyde and 4-hydroxycoumarin, the research results on the use of MWCNT/Silica aerogel and modified MWCNT/Silica aerogel as heterogeneous catalyst is underway and will be published in full elsewhere.

3.2 Decolorization of aqueous dye solutions by MWCNT/Silica aerogel

Dyes appear colored because these aromatic compounds absorb some particular wavelengths of light more than others. Most dyes are resistant to aerobic digestion (biological wastewater treatment) and are therefore very difficult to degrade and decolorise (owing to their structural features). The activated carbon has drawn widespread attention because it is able to adsorb various types of coloring contaminants with ease but high operation cost and regeneration complexity are the major limiting factors in setting-up an activated carbon unit in a wastewater treatment plant. It would be good if one could employ green chemistry approach or technique to remove water coloration by using functional materials other than the prevalent metal containing semiconductors (Sharma, 2015). In addition to adsorption, chemical treatment through destructing the chromophoric group of dye is yet another useful methodology. The authors expect that though the chemical destruction of chromophore does not offer the complete mineralization, this method can be applied to the treatment of colored water in combination with adsorption or absorbance techniques (Figure 5).

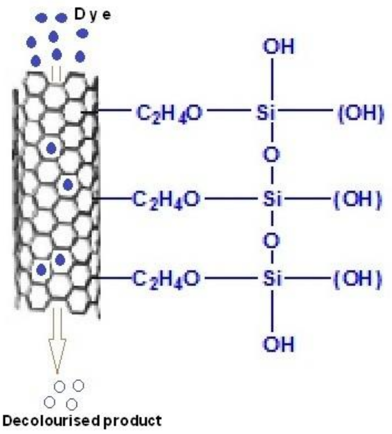

Figure 5. Schematic representation of the MWCNT/Silica aerogel. Silanol groups capped on a single layer of functionalized MWCNT are shown here.

The major advantages the authors have herein is of using ultra-light metal-free aerogel, which at its face value, allows us to apply different physical and chemical techniques at once with easy decolorization of the selected dye solutions. This is evident from the UV absorbance and % absorbance data noted down from the UV spectrophotometer at the respective lambda max of the chromophoric groups. A comparison has also been made with decolorizing activities of silica gel and activated charcoal. In case of the decolorization of aqueous MB dye solution, the activated charcoal showed the best performance followed by silica and then this MWCNT/Silica aerogel. In separate experiments with respect to the decolorization of EBT from its aqueous solution [Table 1 and the observations written and remarks given therein], the MWCNT/Silica aerogel showed the best efficiency followed by silica and then the activated charcoal. The best results were also confirmed after 2 hours' time-on-experiment using UV spectrophotometer.

4. Conclusions

Herein, sol-gel method followed by ambient pressure drying was employed to prepare 2.3 x 10^{-3} wt% multi-walled carbon nanotube incorporated silica aerogel. The as-synthesized material was appropriately characterized. This metal-free aerogel nanocomposite was found to be active towards the synthesis of benzylpyrazolyl coumarin via a four-component reaction of 4-hydroxy coumarin, benzaldehyde, phenyl hydrazine, and ethyl acetoacetate at room temperature. The MWCNT/Silica aerogel is also found efficient in decolorizing aqueous solutions of EBT and MB dyes.

Acknowledgements

I.R.S. is grateful to his father for funding the Ph.D. at SRTMU. I.R.S is thankful to N.N. Maldar (Solapur University), P.K. Zubaidha (Host Lab Supervisor - School of Chemical Sciences, SRTMU) and A.B. Bhosle (School of Earth Sciences, SRTMU) for providing laboratory facilities. U.K.H.B. is very grateful to Department of Science and Technology for Young Scientist Fellowship under fast-track scheme. The synthesis of aerogel catalyst was supported by a major research project on ‘aerogels’ (Grant No. SB/FTP/PS-030/2014). I.S. is the lead author (and writer) of this original article.

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