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Effect of multi walled carbon nanotubes and diamond nanoparticles on the structure and properties of carbon foams

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ABSTRACT

Multi wall carbon nanotubes (MWCNTs) and diamond nanoparticles (DNPs) reinforced carbon foam composites were prepared by the direct pyrolysis of MWCNTs, DNPs and mesophase coal tar pitch mixture. The effect of additive amounts on the microstructure and properties of carbon foams were studied. Significant impacts on the microstructure of carbon foams were observed after the incorporation of additive amounts. Whereas, the additive behavior of MWCNTs and DNPs were further investigated in terms of adsorption, mechanical and thermal properties. The results shows that the nickel (Ni) and cadmium (Cd) metal ions adsorption tendency increases with the increase of MWCNTs and DNPs contents. The maximum adsorption percentage of 84.6 and 86.9% was observed for carbon foam containing 2 wt% MWCNT-DNPs loading for Ni and Cd ions respectively. Furthermore, the compressive strength and thermal conductivity of the carbon foams were enhanced with the increase of additives amounts. Maximum improvement of 19.22 MPa in the compressive strength and 37.46 W/m K at 800 °C of thermal conductivity was revealed by carbon foam composite containing 4 wt% MWCNT-DNPs additive amounts.

1. Introduction

Diamond is considering one of the hardest carbon materials with sp^3 hybridization. It is a well-known material due to its characteristic features, like extreme hardness, good thermal conductivity and excellent biocompatibility. At nano-scale, diamonds are widely distributed and showing unique characteristic properties [1–2]. There are several techniques used for the synthesis of diamond nanoparticles (DNPs), but all have certain limitations. However, the most common is the detonation method which is widely used on commercial scale for the synthesis of DNPs. The present work highlights the performance of DNPs, which has magnificent chemical and physical characteristics especially in nanocomposites [3–4]. Similarly, Carbon foam with porous structure attracts considerable attention due to its unique properties including, large geometric surface area, light weight, high mechanical and thermal stability, low density, hydrophobic surface nature, and good corrosion resistance performance [5–8]. These properties make carbon foam a material of interest for diverse engineering applications such as electrodes, catalyst supports, radiators, heat exchanger, electromagnetic shielding and bone surgery applications [6–7]. Carbon foams can be synthesized from polymers, organic biomass or from mesophase pitch precursors, but polymer, and organic biomass derived carbon foams were not showing so highly satisfying mechanical properties as compared to pitch derived carbon foams [9–10]. The recent development showing that the mechanical and thermal conductivity of the mesophase pitch derived carbon foams (MPCFs) were much improved as compared to carbon foam derived by using other precursors but they still need to be further improved [10]. Different types of additives were used to improve the various properties of carbon foams. Heguang et al. [11] studied the physical and structural properties of coal tar pitch derived carbon foam composites containing different amount of multi walled carbon nanotubes (MWCNTs) as additive. They observed that the compressive strength and electrical conductivity of the carbon foams were significantly improved with the addition of MWCNTs, while the thermal conductivity of the foam is initially increased and then decreased with the addition of MWCNTs. Wang and colleagues [12] reported the mechanical and thermal conductivity of the carbon foams reinforced by clay. They observed that

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clay as additive enhanced the mechanical strength of pitch-based carbon foams, but decreased the thermal conductivity. Wang et al. [7] worked on the mechanical strength of resin derived carbon foam reinforced by hollow ceramic microspheres. They observed that the mechanical properties of carbon foams is initially increased and then decreased with the amount of hollow ceramic microspheres. The highest compressive strength of 7.76 MPa was observed for carbon foam containing 1 wt% hollow ceramic microspheres loading. Some studies were showing the enhancement of carbon foam various properties via reinforcement of pitch fluorides, aluminosilicates, mesocarbon micro beads, $K_2Ti_6O_{13}$ whiskers and zirconium [14–15]. In these reports if one property improves then another property will reduce or not improved effectively.

In the present work, the synergistic incorporation of MWCNTs and DNPs as additives was studied in MPCFs. This novel combination of additives was not studied before. The effect and influences of various additive amounts on the adsorption, mechanical and thermal properties of MPCFs were studied and reported in this work.

2. Experimental

2.1. Materials

The DNPs 99% pure, gray color and about 6 nm in diameter were purchased from Hengqiu Nanotechnology incorporation China. Whereas, the MWCNTs having 95% purity was provided by Tsinghua university China. Coal tar pitch was purchased from Wuhan Steel Corporation limited China for the carbon foam preparation. The physical characteristics of coal tar pitch are given in Table 1. Similarly ammonium bicarbonate 99% pure used for the surface modification of DNPs was provided by Sigma Aldrich, Germany.

2.2. Purification of nanoparticles

MWCNTs and DNPs were first air-oxidized at 650 and 440 °C respectively, for 5 h (h) in electric furnace to remove the metal oxide and non-carbonaceous impurities which were attached during their synthesis process [16]. Metal oxides and other volatile impurities are usually burnt even at less temperature so the provide temperature is enough to burn the impurities during heat treatment.

2.3. Functionalization of DNPs

After the heat purification process, the DNPs were further subjected for ammine group functionalization into ball milling machine. As several literatures reveal that DNPs possess high surface energy due to its large surface to volume ratio and smallest particles size, which tends the DNPs for making aggregates [17]. To de-aggregate the DNPs clusters, ammine functional groups were ideally considering a best option for the surface functionalization of DNPs [18]. Here we used the heat purified DNPs with ammonium bicarbonate in the presence of de-agglomerating media (sodium chloride) in ball milling machine with 1:4:4 mixing ratios respectively. This mixture was set for milling upto 2 h at 500 rpm in the presence of stainless steel balls. After milling, the sample was placed in vacuum furnace at 0.7 MPa for 10 h at 100 °C to remove moisture from the mixture. During this treatment, ammonium bicarbonate is dissociated and amine groups were attached covalently on the DNPs surface to form (aminated) A-DNPs according to the following chemical reaction [17]. The detail description of ammine functionalization on the DNPs surface is also supported by our previous report [17].

$$2DNPs + 2NH_4HCO_3 \rightarrow 2DNPs—NH_2 + 2CO_2 + 3H_2O \quad (i)$$

Table 1
Physical characteristics of the commercial coal tar pitch used for the preparation of carbon foam.

Softening point (°C)	Quinoline insoluble (wt%)	Benzene insoluble (wt %)	C/H (atomic ratio)	Carbon yield (wt%)
82	6.58	20.2	1.74	54.7

2.4. Preparation of carbon foam composites

Pretreatment pitches were prepared from commercial coal tar pitch. Initially 120 g of coal tar pitch was finely grounded to 70 μm and then subjected to heating at 430 °C under the nitrogen atmosphere for 5 h soaking with heating rate of 1.5 °C/min. After heating the pretreatment pitches were again finely grounded and mixed with different ratios of MWCNTs and DNPs for the preparation of carbon foam/MWCNT-DNPs composites. As we know that, the dispersion of nanoparticles into matrix is a crucial step which determines the final properties of a composite, that's why we dispersed the different weight percentages of nanoparticles along with prepared pretreatment pitches in ethanol solution for the uniform mixing of nanoparticles into pretreatment pitches. Then the slurry was heated at 80 °C to remove the ethanol. The obtained mixture was ground to ~70 μm in size. Two series of nanocomposites i.e., carbon foam/MWCNTs and carbon foam/MWCNTs-DNPs were prepared by varied amount of nanoparticles along with blank sample (only carbon foam). In the carbon foam/MWCNTs series 1, 2 and 4 wt% purified MWCNTs were dispersed in pretreatment pitches, while in the carbon foam/MWCNTs-DNPs series of nanocomposites both MWCNTs and DNPs were equally dispersed by wt% in the pretreatment pitches and make their 1, 2 and 4 wt% composites for the comparatively measurements of the various properties. The foaming process of MWCNTs-DNPs/pretreatment pitches was performed in a reaction vessel containing nitrogen atmosphere of 3 MPa [11]. This mixture was initially heated upto 500 °C for two hour soaking with a heating rate of 1.5 °C/min. Finally, the carbon foams containing both nanoparticles as additives was carbonized and graphitized at 850 and 2400 °C under the nitrogen atmosphere for 2 and 1 h of reaction holding times respectively with the heating rate of 2 °C/min. Carbon foam samples containing various amounts of nanoparticles were collected from the reaction vessel after the cooling of vessel temperature and tested for various characterizations.

2.5. Characterization

In this study the microstructure and morphology of the samples were studied by using (Hitachi H-600) transmission electron microscopy (TEM) and (XL30) Scanning electron microscopy (SEM). The crystallite structural information was obtained by using an (D/Max 2500 V PC^{-1}, Cu-Kα radiation) having 2/min scan rate, X-ray diffractometer (XRD). BX Fourier transformed infra-red spectrometer with attenuated total reflectance (ATR) attachment was used to confirm the attachment of functional groups on the surface of DNPs during functionalization process. The thermal analysis was measured using a SDTQ600 thermogravimetric analyzer (TGA) with a heating rate of 10 °C/min. Thermo Escalab 250Xi, X-ray photoelectron spectroscopy (XPS) equipped with a monochromic Al-Ka source was used to determine the chemical composition and chemical bonding of the carbon foam composites. 0.5 mg of the each carbon foam composites was measured and mixed with nickel (Ni) and cadmium (Cd) metal ion solutions. The contaminated solutions containing different wt% of MWCNTs and DNPs were mixed with the help of water bath shaker machine at room temperature for 48 h. After the continuous shaking of solutions their adsorption properties were measured by using atomic absorption spectrophotometer (ZEE nit, 700 P). The compressive strength of the nanocomposites were characterized by using a universal testing machine at room temperature having 50 ± 5% relative