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Full Length Article

Improved tribological properties of the synthesized copper/carbon nanotube nanocomposites for rapeseed oil-based additives

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ABSTRACT

Carbon nanotubes (CNTs) decorated with uniform copper nanoparticles (Cu NPs) were successfully prepared via a facile approach towards surface modification of CNTs with spontaneous polydopamine (PDA). The structures and morphologies of the nanocomposites were investigated by different kinds of techniques, including X-ray diffraction (XRD), transmission electron microscopy (TEM), and X-ray photoelectron spectroscopy (XPS). Cu/PDA/CNTs nanocomposites were fabricated by growing the Cu NPs with an average diameter of 5 nm on the surfaces of PDA-modified CNTs. The CNTs functionalized with PDA layer not only provide an anchoring platform for the Cu NPs immobilization, but also endow Cu/PDA/CNTs with good dispersion stability when Cu/PDA/CNTs nanocomposites were used as lubricant additive. The tribological performance of the nanocomposites as the rapeseed oil lubricant additive, as well as Cu NPs, CNTs, and Cu/CNTs, was also investigated using a MS-T3000 ball-on-disk tribometer. Results show that the 0.2 wt% Cu/PDA/CNTs nanoadditive simultaneously reduce the friction and wear by 33.5% and 23.7%, respectively, outperformed the tribological performance of Cu NPs, CNTs, and Cu/CNTs nanoadditives. In addition, the presence of active sites in Cu/PDA/CNTs was beneficial to reduce the time of running-in period, give rise to the fastest speed to be stable of the friction coefficient curve as compared to the other nanoadditives. X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy of the worn surfaces lubricated by the soybean oil with Cu/PDA/CNTs nanocomposites showed that formation of low shear strength tribofilms containing Cu/PDA/CNTs nanocomposites and its self-lubricating property was key factor in reduction of the friction and protection against wear and deformation.

1. Introduction

Advances in lubricants have been continuously sought by modern society for energy efficiency and environmental protection. In the tribological field, although good tribology performance for varieties of current solid oil additives (such as ZnS, Fe_3O_4, SnO_2, CuO, $CeVO_4$, and so on) had been clearly revealed, several problems about the complicated synthesis procedures to produce them and their toxicity and high cost still exsist. In addition, performance degradation on long-term usage of these solid oil additives is another issue. However, carbon nanomaterials such as grapheme, and carbon nanotubes are performance steady, easy producing and environmental friendly lubricating additives. This aroused wide interest in the tribological investigation of carbon nanomaterials [1–5].

Carbon nanotubes (CNTs), one kind of the most studied carbon nanomaterials, have gained intensive research interest from all over the world since their first discovery in 1991. Because of their unique structures and remarkable physicochemical properties, CNTs have been extensively explored for a variety of applications, such as energy storage and conversion [6], catalysis [7], and drug delivery [8]. Owing to their excellent thermal and mechanical performance, as well as self-lubricating effect, CNTs have been extensively employed in tribological areas used as water/oil base lubricant additives or reinforcements for metals or polymers [9–12]. Addition of CNTs leads to considerable reduction of friction and wear as compared to the base lubricant or substrate. Chen et al. [13] reported that tribological performance was improved when stearic acid modified CNTs were added in the lubricant base oil. Pei et al. [14] demonstrated the tribological properties of polyacrylamide (PAM)-grafted CNTs as water base lubricant additives. They considered that good anti-wear and friction reduction prop-

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erties as well as load-carrying capacity attribute to the nanometer sized tiny bearings role of modified CNTs during lubrication. Meng et al. [15] investigated the friction and wear behavior of CNTs reinforced polyamide 6 (PA6/CNTs) composites, results showed that CNTs could improve the wear resistance and reduce the friction coefficient of PA6 considerably.

On the other hand, metal nanoparticles (NPs) have attracted great attention in tribology area due to their unique properties compared to their corresponding bulk materials [16–18]. Cu NPs, a kind of soft metal with low cost, environmental friendly and high lubricating efficiency performance have attracted considerable attention as lubricating additives. Unlike some nanoparticles such as Fe NPs, Ag NPs, or Ni NPs, Cu NPs are easily produced in a facile and inexpensive way [19–21]. It is reported that Cu NPs usually display good friction-reducing and anti-wear behavior by the effect of tiny-bearings and the formation of tribofilms with low shearing strength on rubbing surfaces. For instance, Choi et al. [22] studied the friction and wear behavior of Cu NPs used as lubricant additive by a disc-on-disc tribotester, and results show that the average friction coefficient for 25 nm and 60 nm Cu NPs suspended oil is decreased by 44% and 39%, respectively, under a load of 3000 N. Especially, in our previous work, Song et al. [23] prepared Cu/PDA/GO composites and found that the addition of a low content of fillers can greatly improve tribological performances of soybean oil. Because the both CNTs and GO have the similar structure, it is believed that Cu NPs decorating on CNTs would promise exhibiting better tribological performance compared to the individual CNTs or Cu NPs because of the synergistic effect of the two components. However, due to the chemical inertness of the pristine CNTs and their poor dispersion in both aqueous and organic solvents, it is difficult for Cu NPs to be deposited directly onto the surface of CNTs. Previously, attempts have been devoted to aiming at functionalizing the surface of CNTs and followed by the decorating of Cu NPs. Xu et al. [23] reported a electroless plating method to deposit densely distributed Cu NPs on the acids pretreated CNTs. However, the surface modification procedure suffered from many limitations such as structural damage, hazardous chemical agents and harshness and complexity of reaction process. Up to date, few of previous studies have been reported focusing on the successfully decorating of uniform Cu NPs on CNTs. Therefore, it is still challengeable to develop a facile and versatile strategy for the deposition of homodispersed Cu NPs on CNTs surfaces.

Mussel inspired chemistry has been an efficient and universal surface functionalization strategy in recent years [24–28]. Dopamine, a fascinating molecule, can be polymerized spontaneously onto any surfaces without surface pre-treatment in alkaline solutions with the dissolving of O_2 and form a tight nano thick polydopamine (PDA) films. More importantly, the adhered PDA layer provided plenty of functional groups such as catechols and amines, which had a strong affinity for binding metal irons. Hao et al. [29] reported a novel strategy for the preparation of CNTs decorated with silver NPs through PDA surface functionalization. This novel strategy also provides an effective methodology for the surface modification of many other materials. Therefore, mussel inspired dopamine would be useful for the fabrication of CNTs based nanocomposites.

In this study, a green and effective biomimetic strategy was developed for uniform Cu NPs decorating on PDA-modified CNTs. The Cu NPs with diameters of 4–7 nm were evenly immobilized on the surface of CNTs. The formation mechanism of Cu/PDA/CNTs nanocomposites was proposed in detail. Tribological tests were performed using a MS-T3000 ball-on-plate apparatus. The results displayed that the nanocomposites delivered better friction and anti-wear properties contrast to Cu NPs, CNTs, and Cu/CNTs additives. This study provides a universal strategy for decorating Cu NPs on the external surface of CNTs, which simultaneously aims at improving the dispersion stability of the Cu/PDA/CNTs nanocomposites in the base oil.

2. Experimental

2.1. Materials

Multiwalled CNTs (length: 10–30 μm, diameters: 20–30 nm) were purchased from Nanjing XFNANO Materials Tech Co., Ltd. China. Tris was purchased from Meryer Chemical Technology Co., Ltd. (Shanghai, China). Dopamine hydrochloride was supplied from Sigma Aldrich. The precursor of Cu NPs ($Cu(CH_3COO)_2{\cdot}H_2O$), and reducing agent ($NaH_2PO_2{\cdot}H_2O$) was commercially obtained from East Instrument Chemical Glass Co., Ltd, China. The rapeseed oil was purchased from the COFCO Corporation in China. All chemical reagents were directly used without further purification.

2.2. Preparation of PDA-functionalized CNTs (PDA/CNTs)

In a typical procedure: CNTs (0.1 g) were dispersed in 200 mL Tris–HCl (pH = 8.5) buffer solution through ultrasonic vibration to form a homogeneous suspension. Then, dopamine hydrochloride (0.4 g) was dissolved in the solution via magnetic stirring and sustained vigorous stirring for 10 h. The resulting black dispersion was washed with distilled water repeatedly via centrifugation at 13,000 rpm for 5 min until the supernatant was transparent. Ultimately, the PDA/CNTs composites were obtained after drying with vacuum freeze dryer.

2.3. Synthesis of Cu/PDA/CNTs nanocomposites

To synthesize Cu/PDA/CNTs nanocomposites, PDA/CNTs nanocomposites (0.02 g) were dispersed in 100 mL of ethanol via ultrasonication to form homogeneous solution. $Cu(CH_3COO)_2{\cdot}H_2O$ (0.15 g), used as the precursor for the synthesis of Cu NPs, was dissolved in the solution with drastic magnetic stirring. PDA/CNTs composites were completely precipitated with obvious bluish supernatant after placed for 12 h. Ethanol was re-added into the precipitation again to prepare 100 mL homogeneously dispersed solution after the bluish supernatant was decanted. $NaH_2PO_2{\cdot}H_2O$, used as reducing agent, was dissolved in 40 mL ethanol via magnetic stirring. The re-prepared PDA/CNTs suspended solution mixed with the $NaH_2PO_2{\cdot}H_2O$ solution was then long-drawn reflux condensed in a thermostatic simethicone bath kept the temperature of 80 °C, the mixture was vigorously magnetically stirred for 20 min until the perfectly reaction of the hydrothermal reduction for evenly Cu NPs decorating on PDA/CNTs surfaces. The products were cooled to room temperature and washed with ethanol several times via centrifugation to remove the remaining impurities. Then Cu/PDA/CNTs nanocomposites were obtained after drying. The Cu NPs were prepared by the same reduction method using $Cu(CH_3COO)_2{\cdot}H_2O$ and $NaH_2PO_2{\cdot}H_2O$. For comparison, Cu/CNTs were synthesized under the same procedure. The reaction procedure can be depicted as follows:

$$Cu^{2+} + 2H_2PO_2^- + 2H_2O \rightarrow Cu + 2H_2PO_3^- + 2H^+ + H_2$$

2.4. Chemical and structural characterization

The morphologies of CNTs, PDA/CNTs and Cu/PDA/CNTs composites were investigated by transmission electron microscopy (TEM, JEOL JEM 2100). The phase structure of CNTs, PDA/CNTs and Cu/PDA/CNTs composites was characterized by X-ray diffraction (XRD, Philips X'pert X-ray diffractometer) with Cu-Kα radiation at 40 kV and 30 mA over the 2θ range 5–80° (λ = 1.5406 Å).The