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Covalent grafting of chelated othoborate ionic liquid on carbon quantum dot towards high performance additives: Synthesis, characterization and tribological evaluation

Wangji Shang[a,b], Tao Cai[b,*], Yunxiao Zhang[a,b], Dan Liu[b], Liwen Sun[b], Xinyan Su[a], Shenggao Liu[b]

[a] School of Materials Science and Engineering, Shanghai University, NO.99, Shangda Road, Shanghai, 200444, PR China
[b] Ningbo Institute of Industrial Technology, Chinese Academy of Sciences. No. 1219, Zhongguan West Road, Ningbo, Zhejiang 315201, PR China

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ABSTRACT

Ecofriendly carbon quantum dots-ionic liquid hybrid nanomaterial (CQDs-IL) has been synthesized via chemical grafting thus to combine both the friction and wear reducing properties of CQDs and ionic liquid for achieving improved high load performance and shorter function duration with interface. The hybrid nanomaterial with a sphere-in-shell structure exhibit remarkable synergistic effect in improving friction-reducing and anti-wear properties in boundary lubrication than that of CQDs and OHMimBScB alone as well as their blend. It is evident that the synergistic effect contained nano-lubricant of CQDs and inherent polarity of ionic liquid thus to form a stable and protective hybrid tribo-chemical film that composed of chelated orthoborate and CQDs as well as their tribo-chemical products on the steel interfaces for enhanced tribological properties.

1. Introduction

According to statistics, it caused huge economic losses due to friction and wear in every year in all over the world [1,2]. The growing environmental pollution concern and energy shortage problem has encouraged research in energy efficiency in every technological field [3]. This is the reason why research in tribology has focused on the development of low-friction materials and more efficient lubricants. Conventional lubricant additives contained phosphorus, sulphur and chloride element, are being used in lubricating oils as multifunctional additives such as anti-wear and extreme pressure, however, they cannot meet the requirements of environmental protection regulations [4].

The carbon-based nanoparticles as alternative lubricant additives reflect good performance and little pollution to the environment [5–12]. As a new kind of carbon nanomaterials, carbon quantum dots (CQDs) [13] have rapidly attracted great research owing to their unique properties such as outstanding optical properties, good biocompatibility and robust chemical inertness [14–21]. Importantly, according to the lubrication theory and microstructure of CQDs, the concerns of the miscibility, dispersion and long term storage stability could be improved significantly due to the smaller size and controllable functionalized surface of CQDs, it is promising that the CQDs could play as high performance lubricant additive in tribological communities [22–25]. On the other hand, ionic liquid (IL) have been researched due to their unique properties like non-volatility, non-flammability and inherent polarity [26,27]. Imidazolium, phosphonium, ammonium etc. and X^-, $(CF_3SO_2)_2N^-$, PF^{6-} etc. ionic liquids have been studied and exhibited excellent tribological properties [28]. In this context, it is desired to develop IL modified CQDs lubricants and additives which achieved better dispersion stability and tribological properties.

Briefly speaking, there are three methods involved for synthesis of IL modified CQDs, (i) Assembling [29], (ii) One-pot pyrolysis [30], and (iii) Covalent chemical grafting. In previous works, Ma et al. reported a kind of IL/CQDs obtained by grinding mixture solution of choline chloride and ethylene glycol as well as CQDs via assembling, which used as pure lubricant for ultralow friction on Si wafer. Wang et al. reported a kind of ionic liquid capped carbon (CD-NTf_2) dots as a lubricant additive via one-pot pyrolysis. However, IL/CQDs hybrid obtained by covalent chemical grafting method has not been reported, in addition, the reported IL/CQDs hybrid used as pure lubricants made the application costly or contained non environmental atoms would greatly restricted to be used [31,32]. Moreover, the formation of a protective film derived from IL/CQDs processed for a long time of 1 h (3600 s) and exhibited relatively poor friction-reducing under high load (~0.11 at 600 N),

* Corresponding author.
E-mail address: caitao@nimte.ac.cn (T. Cai).

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which cannot protect the engine rapidly and effectively. Thus, there is a great need to develop a facile, low-cost, and work immediately CDs-containing nanomaterial with high effective lubricating properties.

Recently, boron-containing compounds have attracted intense attentions due to their multifunction including friction modifier, low toxicity and anti-oxidation *etc.* In addition, chelated orthoborates IL, which combined boron-containing moiety, have been gradually developed due to their remarkable tribology properties and environmentally friendly features in our previous works [33,34]. In this work, carbon quantum dots-ionic liquid hybrid nanomaterials (CQDs-IL) has been synthesized through covalent grafting of 3-(Hydroxypropyl)-3-methyl imidazolium bis(salicylato)borate (OHMimBScB) onto the surfaces of CQDs (CQDs-OHMimBScB) (Fig. 1 and Figure S1). In addition, the unreported prinsine CQDs as lubricant additive was also explored in this work as reference. The as-synthesized CQDs-OHMimBScB hybrid nanomaterial has wonderful solubility stability in PEG with high concentration over 30% and without any dispersants, thus as-prepared clear solution exhibit a long-term homogeneous phase over 6 months without any noticeable precipitation. The tribological performances of CQDs-OHMimBScB as the lubricant additive was investigated using a four-ball tester by varying concentration and test load. Notably, the CQDs-OHMimBScB hybrid nanomaterials as lubricating oil additives exhibited enhanced friction-reducing and anti-wear properties for steel tribo-pair in boundary lubrication tests than that of CQDs and OHMimBScB alone as well as their blend. Moreover, due to the work mechanism of CQDs in CQDs-IL hybrid nanomaterials as lubricant additives has not been clarified, we try to explore it as well. Therefore, the present work reveals that the potential of CQDs-IL hybrid nanomaterial as a powerful pathway for the development of high performance and environmentally friendly additives.

2. Results and discussion

2.1. Characterization of the as-synthesized CQDs and CQDs-OHMimBScB

Transmission electron microscopy (TEM) and atomic force microscope (AFM) image of the CQDs is shown in Fig. 1a and b and revealing that the CQDs are well-dispersed and uniform with an average diameter of approximately 2.0 nm. The AFM results indicated that topographic average heights of CQDs were approximately 2.0 nm (1.8–2.5 nm), suggesting that the prepared CQDs are spherical with an average particle size of 2.0 nm. There was no lattice structures observed, which is consistent with the XRD pattern (Figure S2). The TEM image in Figure S3 indicated the CQDs-OHMimBScB hybrid nanomaterial had bigger size (approximately 7.5 nm) than CQDs.

Fourier transform infrared (FT-IR) was used to characterize the CA, CQDs, OHMimBScB and CQDs-OHMimBScB (Fig. 1c). The CQDs exhibited bending vibration of $C{=}CH_2$ in the range of 890 cm^{-1} as well as stretching vibrations of C=O in carboxyl at 1766 cm^{-1}, suggesting that the formed CQDs has many -COOH on the surface. After modified by OHMimBScB, the vibration peak of -OH in OHMimBScB and CQDs disappeared obviously, indicating the formation of CQDs-OHMimBScB. The broad peaks range from 1200 to 900 cm^{-1} were assigned to asymmetric stretching vibration of B-O, which also representing the successful introduce of tetrahedral chelated orthoborate in CQDs-OHMimBScB [4]. All these characteristic peaks together conformed the surface of CQDs has been capped by OHMimBScB thus the CQDs-OHMimBScB hybrid has been successfully synthesized. ^{1}H NMR spectra (Figure S4) of CQDs-OHMimBScB reveal that the presence of typical characteristic peaks of OHMimBScB, and CQDs, which providing another support to the proposed structure of hybrid.

The XPS spectrum (Fig. 2 and S5) confirms that CQDs-OHMimBScB is composed of C, O, N and B element. Fine structure spectrum of C1s

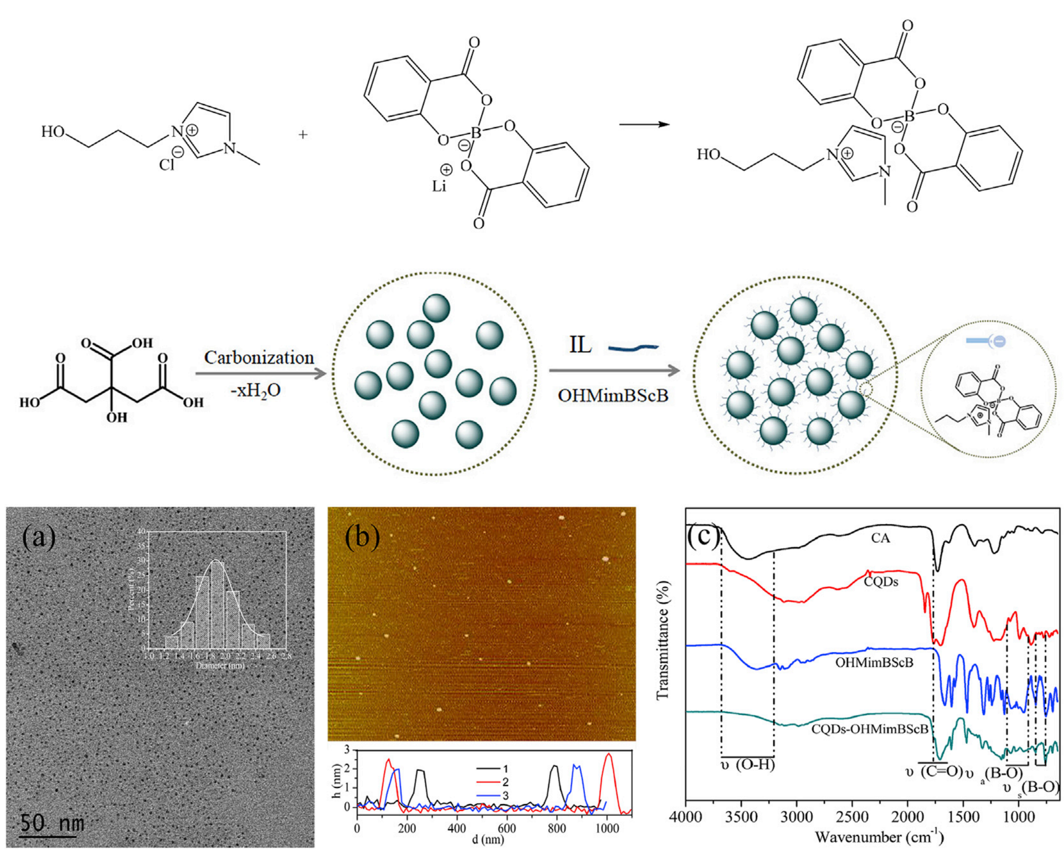

Fig. 1. The schematic diagram of the formed process of CQDs-OHMimBScB. (a) TEM (insert particle size distribution) (b) AFM images and topographic of CQDs (c) FTIR spectra of CA, CQDs, OHMimBScB and CQDs-OHMimBScB.