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Structure and surface characterization of co-adsorbed layer of oleic acid and octadecylamine on detonation nanodiamond

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ABSTRACT

Aiming to form an alkyl-functionalized surface and to realize the particle dispersibility in apolar solvents, oleic acid (OA) and octadecylamine (ODA) were introduced to modify detonation nanodiamond (DND). Compared with their single addition, the combined use of OA and ODA resulted in better particle dispersion and suspension stability. The co-adsorbed layer containing both OA and ODA is of a crystal structure, while the single-added OA and ODA form only amorphous structures on DND. The acid–base interaction originated from the electrostatic attraction between the amino groups on ODA and the carboxyl groups on OA may contribute to the assembly of both surfactants. With the significant increase of adsorption concentration and layer thickness, the steric repulsion of DND particles can be strengthened. By taking this approach, the alkyl-functionalization effect and the dispersion of DND particles in organic solvents or in polymer composites can be improved.

1. Introduction

Possessing excellent properties of superhardness, biocompatibility, thermal conductivity and chemical stability, nanoscaled diamond powder is one of the hot topics in the field of superhard materials [1–3]. Nanodiamond powders synthesized by different commercial approaches, such as milled HPHT monocrystal diamond, dynamic high-pressure shock-compacted polycrystalline diamond and detonation nanodiamond (DND), have varied morphology, size and surface properties, and can be employed for different applications. Among them, DND has the smallest crystalline size (around 2–6 nm), and the morphology and diameter of DND crystallines are quite homogeneous [4]. As DND monocrystallines always form aggregates of micron scale or submicron scale because of the high surface free energy for nanoparticles, it is crucial to actualize particle dispersion for better utilization [5].

Over the past decade, many encouraging achievements have been made in disaggregation and surface modification technique of DND, especially for its application in aqueous systems [6–8]. Thereafter, a lot of progresses have been made in its application trials in CVD seeding and nucleation [9,10], drug/gene transfection [11–14], and as a biomaterial to accelerate osteogenesis [15].

The diamond structure in DND was encircled by a large quantity of functional groups, among which, the majority groups for the well-oxidized DND are of high polarity [16–18]. The polar surface ensures the active property as it provides abundant anchoring points for surface functionalization. Meanwhile, its hydrophilic property makes it difficult to attain a good dispersion and distribution in oil-based matrixes [19]. Unlike in aqueous system, where the electrostatic repulsion mechanism can be utilized to realize the dispersion of particles and the surface electrical potential (ζ-potential) can be modified by introducing some electrolytes or ionic surfactants, the steric hindrance turns to be the main effect to ensure the dispersion of DND in organic systems, especially in apolar matrixes. As the effect of surface charge is not so prominent, it is usually essential to introduce some polymer dispersants to achieve steric repulsion of particles [20].

Researches on the application of DND particle in polymers as filler have started for decades, and the results show that DND can bring excellent advantage by improving the performance of composites [21]. DND ensures uniform thermal stability and excellent compatibility between polyurethane (PU) and epoxy (EP), and it can thus be used as a reinforcing additive in PU/EP interpenetrating nanocomposites [22]. With small content of DND particles, the tribological and mechanical properties of epoxy-based nanocomposites can be obviously reinforced [23]. Significant increase in scratch resistance and thermal conductivity for the composites of epoxy polymer-binded DND can be observed [24]. When DND was introduced to form composite with the polyvinyl alcohol (PVA) matrix, the thermal conductivity can be increased drastically and it is superior to other carbon-based nanofillers as the high optical transparency of PVA can be guaranteed [25]. Composites prepared by DND particles and PVA aqueous solutions can benefit the seeding in chemical vapor deposition diamond growth [26]. Owing to the enhanced intrinsic photoluminescence (PL) within DND particles due to ion-implantation generated defects and by PL originating from

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structural transformations produced by protons at the DND/matrix interface, prominent PL enhancement was observed for the proton-irradiated poly(dimethylsiloxane) (PDMS) incorporated with DND [27]. Containing DND functionalized by poly L-lactic acid (PLLA) and octadecylamine (ODA), fluorescent composite bone scaffold material shows properties close to that of the human cortical bone [28].

To enhance adhesive interactions with polymer matrix, a common measure is to introduce long-chain alkyl groups to modify particle surface [29]. Aiming to intensify alkyl groups on DND which can improve the thermo-mechanical properties of nanocomposites, an alkyl-functionalization approach was introduced through which alkylated DND compounds can be generated after an esterification of a dried DND-COOH sample prepared by surface oxidation in aqueous solution with excess alcohol [30]. To increase alkyl groups on DND, this esterification approach has as well be conducted by DND hydroxylation with carboxylic acid chlorides, and the modified particles exhibit a significantly improved dispersibility in organic solvents such as tetrahydrofuran (THF) and dichloromethane [31]. Oleic acid (OA) was used by Peng et al. to modify diamond and SiO_2 nanoparticles in liquid paraffin, and the tribological property for liquid paraffin containing modified particles is better than that of pure liquid paraffin [32]. Before dispersed in mineral oil, the deagglomeration of DND can be actualized in OA/octane system, and after the evaporative removal of octane, the thermal conductivity enhancement of the remaining fluids exceeds 11% [33]. ODA was as well be introduced to modify DND in dichloromethane, and blue fluorescent DND particles can be obtained in hydrophobic solvent [34]. Oleylamine (OLA) can be used to disperse DND in THF and these as-received suspensions can enhance the diamond nucleation [35]. Long chain fatty acids can adsorb onto DND coated by a water nanolayer, and organo-modification of DND can be actualized, resulting in DND dispersion in general organic solvents as a mimic of solvency [36]. Similarly, in order to create well-dispersed DND suspensions in apolar solvents, it is always a primary solution to introduce surfactants with long carbon chain. As the adsorption mechanism and behavior for different surfactants varies, and there may form interaction between different types of reagents amid surface modification, it is occasionally more efficient when surfactants are used combinedly. In this case, it is necessary to study the interrelationship between the introduced dispersants.

Fatty acids and amines, including stearic acid (SA), OA, ODA and OLA, are commonly used surfactants for modification and dispersion of particles and the synthesis of particles including nano-gold particles, magnetic Fe_3O_4 nanoparticles, ZnO nanorod arrays, and so forth [37–42]. When used as dispersant, OA can improve the fluidity of the delivery system of magnetic lipid nanoparticles [43] and the dispersibility and hydrophobicity of magnetic strontium hexaferrite particles [44]. Using OA as a modifier for surface coating, Cu nanoparticles smaller than 15 nm can be prepared from Cu wire by electrical explosion in n-hexane, an apolar solvent [45]. ODA can be used to stabilize gold colloidal particles in toluene and ODA-capped particles can be readily dissolved in different organic solvents [46]. By the Langmuir–Blodgett method, well-ordered multilayer structure of ODA-coated nanogolds with the mean diameter of 6.8 nm was created [47]. ODA has been introduced to improve the dispersion of thermal oxidized DND in THF, methyl ethyl ketone or acetone, organic solvents of medium polarity, and its performance is better than OA, yet, both dispersants are inferior to OLA, as colloidal solutions can be prepared after bead-milling in the presence of OLA [48]. Combinations of OA and OLA play an important role for magnetic iron oxide nanoparticles synthesizing, as a perfect fit can be created between the particle surface charge, free proton concentration in the dispersion medium, and ζ-potential [49].

With the aim to attain an alkyl-functionalization of DND surface in apolar solvents, OA and ODA were introduced to evaluate the dispersion behavior of DND in petroleum ether, and the mechanisms for the reagents-DND interaction and the synergy effect of reagents were studied.

2. Experimental

2.1. Materials

Raw DND powder was supplied by Chengdu Fortune Myriad Diamond Nano-Tech Co., Ltd. This gray DND powder is synthesized with 2, 4, 6-trinitrotoluene as the carbon source and with other explosives such as cyclotrimethylenetrinitramine to increase the detonation pressure. After the detonation process in the combustion container, the black detonation soot was collected and purified with chlorine acid, sulfuric acid and potassium permanganate.

OA (Analytical reagent, AR) was purchased from Tianjin Kemiou Chemical Reagent Co., Ltd. and ODA of AR-grade was synthesized by Tianjin Guangfu Fine Chemical Research Institute. An apolar solvent, petroleum ether (AR) with the boiling range of 60–90 °C, was purchased from Tianjin Hengxing Chemical Reagent Co. Ltd. It was used as the reaction media for dispersion, adsorption and milling processes, and for sample cleaning in the infrared sample preparation.

2.2. Sample preparation

To enhance the surface modification in the presence of adsorbates, sonication approach was introduced to treat DND powder in apolar solvent. Two ultrasonic apparatuses with the same frequency of 53 kHz, SK5200HP and SK2200HP, were purchased from Shanghai Kudos Ultrasonic Instrument Co., Ltd. The output powers for these two apparatuses are 200 W and 100 W respectively. The liquid–solid separation was accomplished by centrifuge produced by Changsha Xiangzhi Centrifuge Instrument Co. Ltd.

DND suspensions in petroleum ether were prepared by adding solvent, DND sample and reagent(s) to each dried glass beaker in sequence as 200 mL petroleum ether, 1 g DND sample and 2 g OA (2 g ODA, or, 1 g OA and 1 g ODA simultaneously), then the beakers were put into the ultrasonic apparatus and sonicated for 30 min. Then, samples were collected individually and transferred into glass cuvettes for size measurement, and 40 mL solution for each sample was transferred to the glass bottle and numbered for further observation of DND suspension stability.

Using solvent, powder and reagents with correspondingly doubled quantities, samples for structure and surface properties study were prepared following a similar procedure. To remove the unadsorbed reagents, the suspensions were transferred into centrifugal bottles and centrifuged 7 times at a speed of 2000 r/min for the initial 2 times and 4000 r/min for the following 5 times. The supernatants were removed and pure petroleum ether was replenished for each washing. The washed samples were air-dried for further characterization.

The milling process was conducted with a planetary ball milling apparatus QM-3SP4 from Nanjing NanDa Instrument Plant, the rotation speed was 350 r/min, and the revolution speed of 175 r/min, 304 stainless steel jar of 1 L each was used and stainless steel beads of 1 mm was used as milling media. In each stainless steel jar, 1400 g stainless steel beads of 1 mm were added in advance. Mixed with 150 mL of petroleum ether, 2 g DND, 1 g OA and 1 g ODA were added to the jar and were milled for 8 h. The milled sample was washed with pure petroleum ether while the solid phase was separated out by centrifuge and air-dried, and the structure, surface properties and thermal behavior were investigated. The impurities are not removed by sedimentation or magnetic separation approaches in this study.

2.3. Characterization

The particle size distribution (PSD) for DND aggregates modified by OA, ODA and their combination was measured with photon correlation spectrum (PCS) method with Zetasizer 3000HS from Malvern Instruments Ltd. The analyzer contains a power source of 633 nm He–Ne laser and the scattering angle is fixed at 90°. After sonication treatments,