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RESEARCH ARTICLE - CHEMISTRY

Surface Reforming of Diamond Particles by the Dispersion Enhancement in Common Liquids

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Abstract The dispersibility of diamond has been improved by reforming its surface with 2-propanol-2-yl [$(CH_3)_2C^{\cdot}OH$] radicals. These radicals were produced by the photochemical breakdown of 1-[4-(2-hydroxyethoxy)-phenyl]-2-hydroxy-2-methyl-1-propane-1-one (HPHMP) under ultraviolet (UV) radiations. The diamond particles were mixed with HPHMP in acetone and were placed under UV rays for the generation of required free radicals which were in situ reformed the diamond surface. Fourier transform infrared, nuclear magnetic resonance spectroscopy and scanning electron microscopy (SEM) confirmed the structural and surface reforming of diamond. The thermogravimetric analysis, thermogravimetric analysis–mass spectrometry spectrogram confirmed the surface reforming of diamond with 2-propanol-2-yl radicals. The dispersion behavior of the diamond after reforming was observed by SEM analysis and revealed an improvement in dispersibility in common solvents.

Keywords Diamond particles · Surface properties · Photochemical reforming · Enhanced dispersion

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1 Introduction

Surface modification using advanced techniques of polymer thin films for single wall carbon nanotube-based nanofluids and fabricated glass-filled polyamide have been reported in the established literature [1–3]. Reforming and characterization of graphite flakes and thermal, electrical, microstructure and microhardness properties of the eutectic magnesium–tin have been comprehensively reported [4,5]. The work on carbon fiber reinforced polymer cables and polymer–fullerene bulk heterojunction-based strain-sensitive flexible organic field-effect transistor has also been conducted by some of the researchers [6,7].

Diamond is considered to be an important material in chemistry because of its tremendous properties which include stability, hardness, wide-range wavelength transparency, high thermal conduction and large band gap [8,9]. This is the reason that a number of researchers regarded diamond as industrially important material, which plays an important role in various fields [10].

The structure of diamond consists on a network of carbon atoms bonded to each other through sp^3 hybridization. It is true that structurally diamond consists of carbon atoms only; in addition to that its surface is further stabilized by bonding with other elements. The diamond surfaces terminated with hydrogen have been found to be hydrophobic in nature and p-type conducting. The composition-diamond lemma for free differential algebras has also been established [11]. But surface termination with oxygen turned it into hydrophilic and insulating in nature. It is evident that the chemical properties of diamond depend mainly on the species present on its surface. The diamond surface modified with organo-metal complexes, simple organic functionalities and even enzymes have opened new horizons of novel applications in diversified fields of science [12,13].

For such applications, surface reforming of diamond has become an interesting area of today's research. Diamond with modified surface has been proposed for many applications by various researchers: electrode in electrochemistry [14], field-effect transistors in biosensor [15], and as substrate for the immobilization of DNA [16], high dispersive diamond slurry for precision polishing, high thermal conductive fluid dispersing diamond particles and high conductive resin containing diamond fillers [17]. The main point for the materialization of such applications is the establishment of the technology for the reforming of diamond surface. The controlled modification of diamond surface with different functionalities would provide a new organic–inorganic functional material, which possesses the physical functions of diamond and the chemical functions of the organic functional group [8].

Although a little research related to the reforming of diamond surface have been performed yet, and a very little attention has been devoted to the photochemical reforming of the diamond, rather than hydrogen-terminated diamond. In past, a variety of oxidative [18,19], thermal [20,21] or atomic beam [22,23] modification reactions have been performed by using hydrogenated diamond, but the few studies [20–23] have largely been targeted toward photochemical reforming using diamond [24]. The diamond surface can also be modified with different radicals such as benzoyl or perfluoroalkyl radicals. These reagents are able to react with all kinds of diamond surfaces, not only oxygen-containing ones, and are therefore applicable to hydrogenated diamond particles as well [25]. Because of this, the reactivity and reforming of the diamond surface have been expected to lead improvement of its functional behaviors and dispersion in organic solvents [26,27]. There have been few publications focused on the reforming techniques of the diamond surface. For the photochemical generation of radicals, different precursors have been used, e.g., perfluoroazooctane [28], chlorine gas [26], 2-hydroxy-2-methyl-1-phenyl-1- propanone (HMPP) [29], 1-[4-(2-hydroxyethoxy)-phenyl]-2-hydroxy-2-methyl-1-propane-1-one (HPHMP) [30] and so on. A few articles have been found in the literature which described a direct method for the surface reforming of diamond in the liquid phase. That is why the surface reforming with new functionality under controlled and mild conditions is not a trivial task. However, most of the experiments in the literature have been concerned with the chemical modification of diamond in the vapor phase. Moreover, highly expensive equipment, high vacuum apparatuses and high purity materials have been used in these studies. Therefore, these highly expensive experimental arrangements are not economical for further applications.

The current investigation has expanded the range of photoreactivity of diamond surface by using HMPP/HPHMP photoinitiators using acetone as solvents. Actually, diamond powder shows stable dispersion in acetone due to its polarity. Moreover, HPHMP has shown relatively high solubility in acetone (15 g/100 g solution at 20 °C) than many other organic solvents. For photochemical reforming of diamond surface, the low-pressure mercury lamp is operated at wavelength of 254 nm that is the λ_{max} of HPHMP. At this wavelength, acetone absorbs a little ultraviolet radiation which only activates the surface of diamond for reforming reaction in spite of decomposing itself into free radicals [29]. That is why it is favorable for the photo-assisted reforming carrying out at room temperature. In this way, the generality and applicability of photochemically reformed diamond (R-diamond) surface have been achieved. This work was pursued with the motivation that the photochemical approach could be exploited to develop the kind of reforming technique.

2 Experimental

2.1 Materials

Diamond particles, with zero percent surface containing groups, were procured from Tomei Diamond Ind. Co., Ltd., Japan, with purity 99.99 % and 500 nm diameter and used without any pre-treatment to save time and chemicals. The Irgacure 2959 (1-[4-(2-Hydroxyethoxy)-phenyl]-2-hydroxy-2-methyl-1-propane-1-one (HPHMP)) was obtained from Ciba Inc., Ltd., Jiangsu, China. Common solvents such as acetone, tetrahydrofuran (THF), 2-propanol, toluene, *N*, *N*-dimethylformamide (DMF) and carbon disulfide were used as received from Beijing Chemical Co., Ltd., Beijing, China.

2.2 Photochemical Reaction for the Reforming of Diamond Surface

Diamond particles (5 mg, 500 nm of diameter) were placed into a three-neck flat bottom quartz flask containing 30 mL acetone and were sonicated for 30 min. After the complete dispersion of the diamond particles, 3 mg of HPHMP was added and the contents of the flask were degassed by passing argon gas and continuous stirring for 30 min. Then the contents were irradiated for 2 h with ultraviolet radiation obtained from a low-pressure mercury lamp for 2 h at room temperature under argon atmosphere and stirring. The reaction mixture was irradiated 10 cm away from ultra-violet lamp with intensity of 7000 μW/cm2 at 254 nm wavelength. The solvent was removed from the reaction mixture by centrifuging at the rate of 5000 rpm for 30 min. The residual powder was first washed with acetone (10 mL) and then with 30 mL toluene in three fractions (10 mL each time). The product was dried in vacuum oven at 50 °C for 12 h and characterized by corresponding analytical techniques.

2.3 Instruments and Measurements

Fourier transform infrared (FT-IR) spectra were recorded on a Thermo Nicolet Nexus 670 spectrometer using KBr pellet method over the range of 4000 to 400 cm^{-1}. Nuclear magnetic resonance (NMR) measurements were carried out on a Bruker AV 600 NMR spectrometer by dispersing the R-diamond in deuterated chloroform ($CDCl_3$) at room temperature. Thermogravimetric analysis (TGA) was obtained using NETZSCH TG 209 thermal analysis system under a flowing nitrogen atmosphere at a scan rate of 10 °C/min.

Thermogravimetric analysis–mass spectrometry (TGA-MS) analysis was performed on a Perkin Elmer Pyris Diamond TGA-MS equipped with a ThermoStar mass spectrometer operating in electron impact ionization (EI) mode. Scanning electron microscopy (SEM) was used to determine the morphology of diamond using a Hitachi S-4700 microscope operating at 30 kV. The samples were cast in the form of a thin film onto SEM grid and dried in air at room temperature.

3 Results and Discussion

The literature has reported that FT-IR spectrum shows the surface functionalities of the diamond powder before and after the reforming [28]. Figure 1 provided the evidence for the surface reforming of diamond due to the changes in FT-IR signals. There were no obvious bands in the spectrum of diamond (Fig. 1a) except atmospheric one, indicating that the diamond contains no functional groups.

The spectrum of R-diamond (Fig. 1b) clearly showed the characteristic stretching vibration of O–H at 3410 cm^{-1}, and the band at 1100 cm^{-1} was appeared due to the bending vibration of C–OH bond of hydroxyl group. The value at 1100 cm^{-1} can be attributed to the OH group present on the carbon, tertiary in nature. As the secondary nature of OH group, in the free radical from HPHMP, has converted to tertiary by making the bond between $(CH_3)_2C^{\cdot}OH$ and carbon atom present on the surface of diamond [31]. Furthermore, the peaks at 2930 and 2851 cm^{-1} were assigned to the asymmetric and symmetric stretching modes of sp^3-hybridized C–H bond, respectively. The deformation band (1250–1450 cm^{-1}) is assigned to asymmetric and symmetric bending frequencies of C–H bond. These results indicated the reforming of diamond surface and the nature of functional groups as well.

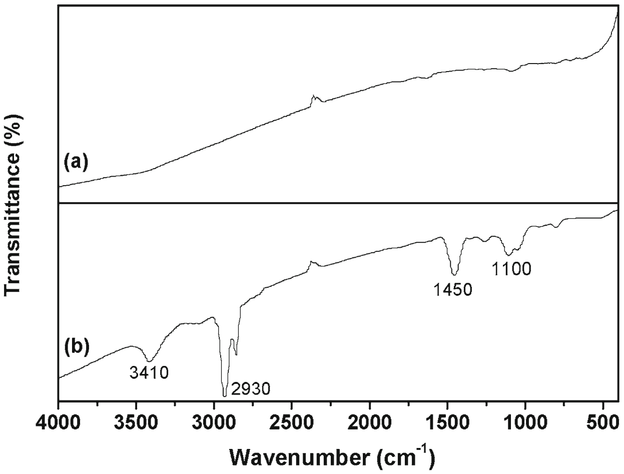


Fig. 1 FT-IR spectra of diamond in KBr: **a** diamond, **b** R-diamond

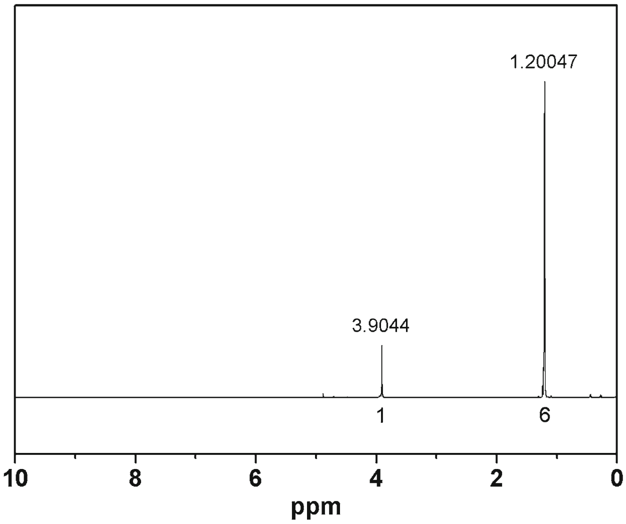


Fig. 2 ^{1}H NMR spectrum of R-diamond recorded in $CDCl_3$

The ^{1}H NMR results also provided further evidence for the reforming of diamond surface as indicated by the spectrum of R-diamond (Fig. 2).

Figure 2 represented the characteristic resonance band for protons corresponding to two methyl groups appeared at $\delta = 1.2$ ppm. The proton of hydroxyl group present on tertiary carbon resonated at $\delta = 3.9$ ppm. Moreover, the ratio of methylic to hydroxylic protons is exactly 6:1 which revealed the arrangement of protons in the functional group. These characteristic values explained the chemical structure of the functional group. The ^{1}H NMR studies have been found in good agreement with FT-IR studies about the nature of functional groups.

Thermogravimetric analysis provided important information about reforming of diamond surface. Most of the organic functional groups were decomposed before the onset of diamond; therefore, the functional groups present on diamond surface were thermally unstable.

During the process, the percentage weight loss curves indicated that the overall weight loss was 0.52 % for diamond and about 6.05 % for R-diamond (Fig. 3a, b). The weight loss during the heating of the diamond was apparently due to

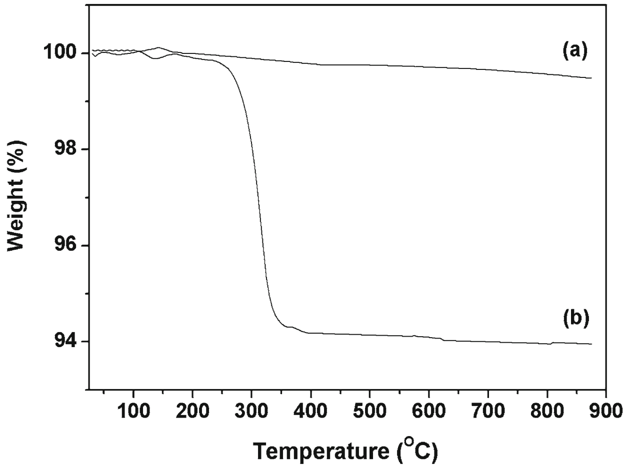


Fig. 3 TGA graph of diamond: **a** diamond, **b** R-diamond

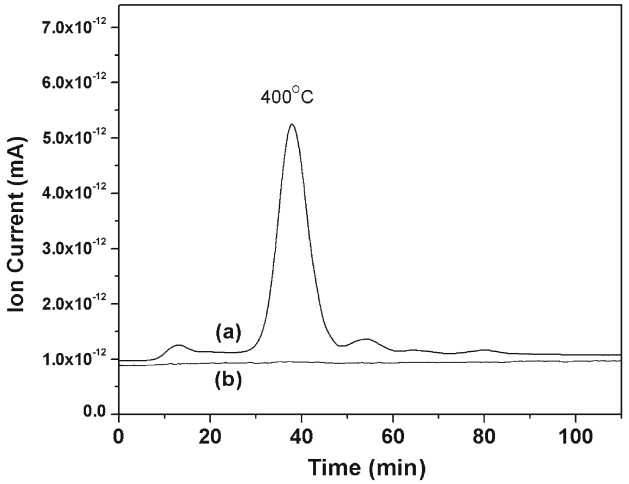


Fig. 4 TGA-MS spectrogram of R-diamond: Ion current vs. time plot for m/z values **a** 59 $(CH_3)_2C^+OH$, **b** 165 $HOCH_2CH_2OC_6H_4C^+O$

volatilization of water as moisture and some amorphous carbon particles, which presumably oxidized at higher range of temperature. This part of weight loss was excluded for the exact calculations. The net weight loss of 5.53 % for R-diamond revealed the decomposition of the functional groups present on the diamond surface. The percentage of weight loss was considerable which meant that the appreciable number of functional groups was responsible for the reforming of diamond surface despite of its low reactivity. Thus, the method described here is found to be very efficient for the reforming of diamond surface.

Thermogravimetric analysis–mass spectrometry provided substantial information for the reforming of diamond surface with functional groups. The temperature range used for this purpose was 20–900 °C with online monitoring of volatile products by mass spectrometer operating in an electron impact ionization mode.

TGA-MS data presented in Fig. 4 clearly indicated a peak for $(CH_3)_2C^+OH$ group at about 400 °C at m/z 59. The high-temperature (400 °C) decomposition of functional groups was notable and represented the stability of functional moieties. The curve (Fig. 4b) resulted only in a base line at m/z 165 which meant that there was no ion detected by the instrument corresponding to $HOCH_2CH_2OC_6H_4C^+O$, during the course of thermal decomposition of R-diamond. From these results, it is clearly indicated that $HOCH_2CH_2OC_6H_4C^*O$ radicals had no contribution to the reforming of diamond surface. Therefore, it may be concluded that the diamond surface was reformed solely with 2-propanol-2-yl radicals, and during the TGA-MS analysis, only these radicals were originated from the surface of R-diamond and detected by mass spectrometer.

The images from scanning electron microscope for diamond and R-diamond have been presented in Fig. 5a. By comparing these images, it can be seen that diamond seemed to be a cluster of diamond particles. On the other hand, the R-diamond appeared to be more dissociated that directs it to disperse and behave individually. Because, the reforming has prevented diamond to aggregate and enhanced their discreteness. Therefore, the R-diamond also showed high and facile dispersion in solvents than diamond.

The SEM images were recorded by loading the sample dispersions on a grid and dried in air. These images provided useful information about the surface morphology of the R-diamond particles. It has been observed that reforming with HPHMP neither damaged nor created the defects on the surface of diamond. So, it may be inferred that the reforming technique was mild rather than harsh, which could itch the diamond surface texture.

Significant improvement in the dispersibility of R-diamond has been observed as indicated in Fig. 5b, c. The improvement in dispersibility was verified quantitatively using the method described by Peng et al. [32]. The dispersibility data revealed that the reforming enhanced the dispersibility of diamond up to 11.5 mg/L in *N*, *N*-dimethyl formamide (DMF) at room temperature, which has been eight times larger than that of diamond (1.4 mg/L). The dispersions of diamond and R-diamond in various solvents have been indicated in Table 1.

The dispersibility data presented in Table 1 clearly indicated the enhanced dispersibility of the R-diamond in some common solvents, i.e., DMF, THF, 2-Propanol, CS_2 as compared to the diamond without reforming. It has been found to be interesting that R-diamond dispersed in THF about 13 times more as compared to diamond. The enhancement in the dispersibility may be attributed to the reforming of the diamond surface which changed the surface behavior of diamond. The functional groups present on its surface created some steric effects which made R-diamond to dis-

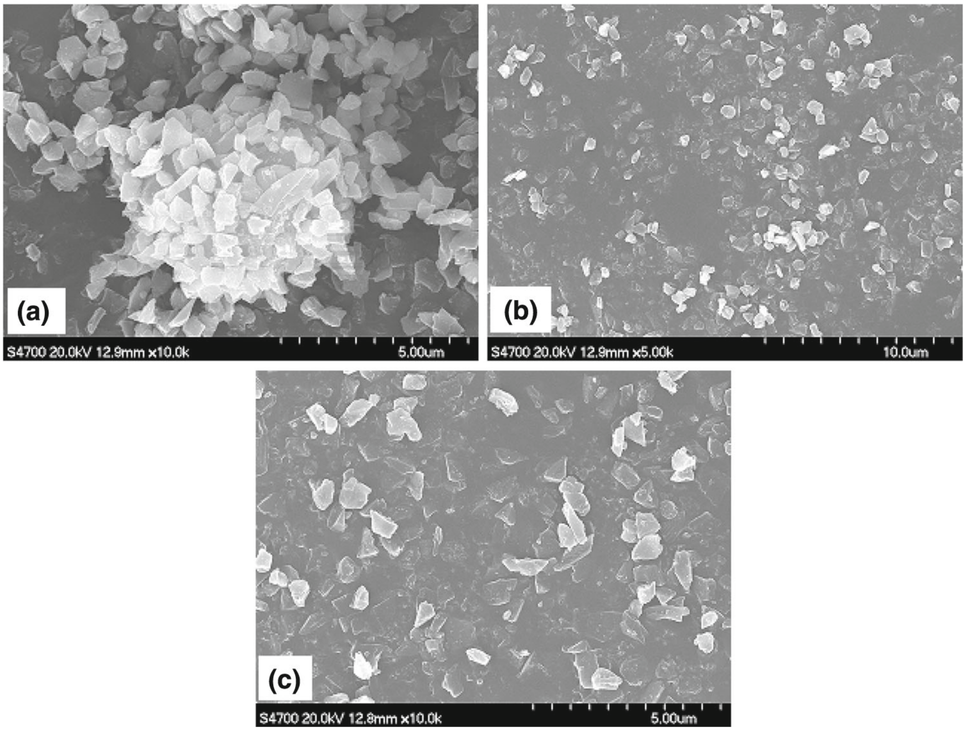


Fig. 5 SEM image for **a** diamond; **b**, **c** R-diamond

Table 1 Diamond and R-modified diamond dispersions in different solvents (mg/L)

Solvent	Diamond	M-diamond
N, *N*-Dimethyl formamide (DMF)	1.4	11.5
Isopropyl alcohol (2-propanol)	Not dispersed	2.2
Tetrahydrofuran (THF)	0.6	7.8
Carbon disulfide (CS_2)	0.5	4.1

Data for dispersibility was taken at room temperature after 24 h

perse more as compared to diamond. Moreover, the –OH group facilitated the dispersibility in polar and semi-polar solvents and on the other hand methyl groups helped the dispersibility in non-polar solvents. It is worth to mention that 2-propanol-2-yl groups have been relatively bulky as compared to hydroxyl groups and caused the surface interactions to facilitate the enhanced dispersion. Therefore, the method of surface reforming presented here in this article has found to be more worthy and expected to facilitate their chemical manipulation, characterization, properties and wide application.

Based on the data from above experiments, the route for the reforming of diamond as indicated in Fig. 6 has been proposed which shows the radical breakdown of HPHMP under the effect of UV radiations resulting the generation of 2-propanol-2-yl and derivative benzoyl radicals. Mechanistically, highly reactive 2-propanol-2-yl radicals are responsible for the reforming of diamond surface, which was activated by the UV light for the formation of R-diamond (Scheme 1). The surface reforming of diamond with 2-propanol-2-yl functional group has been reported and supported by FT-IR, NMR, TGA and TGA-MS [29].

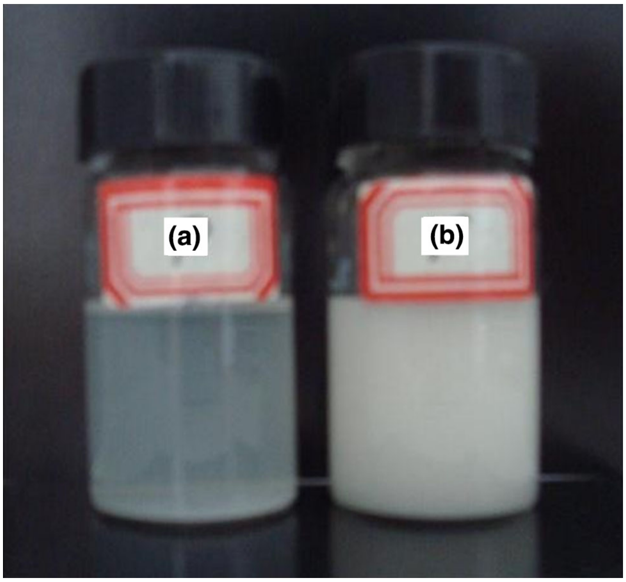
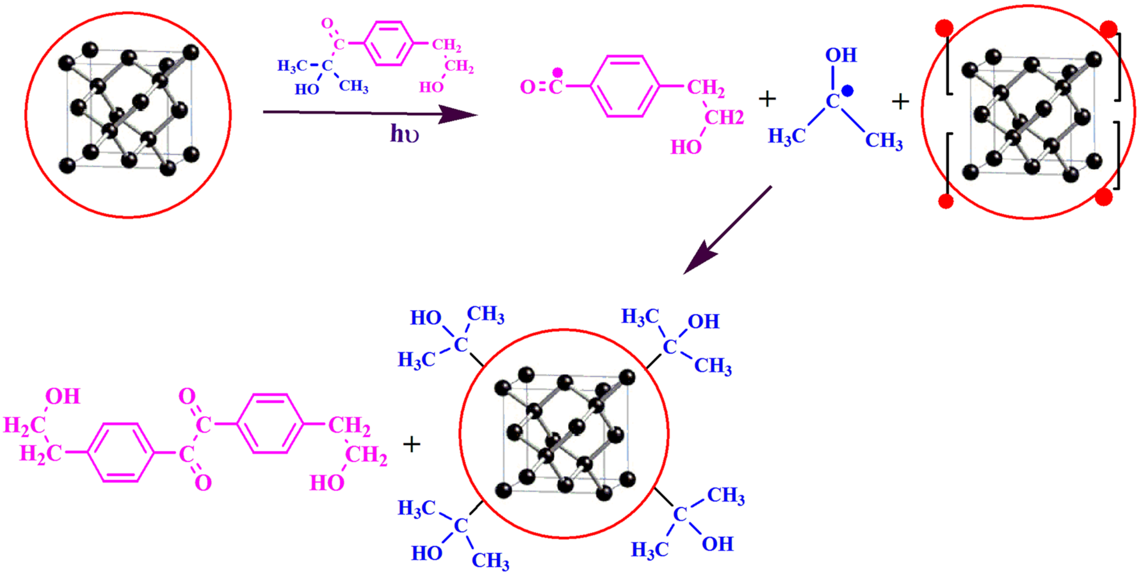


Fig. 6 Dispersions in DMF (11.5 mg/L) after 24 h: **a** diamond, **b** R-diamond

According to TGA-MS results, it can be inferred that the relatively stable derivative benzoyl radicals may have joined together to form benzyl derivative. In the meanwhile, the 2-propanol-2-yl radicals reformed the surface of diamond with relatively higher rate constant than derivative benzoyl radicals [33] and reformed the diamond surface as illustrated above.



Scheme 1 Photochemical reforming of diamond surface using HPHMP initiator

4 Conclusions

The new, simple and facile method for the reforming of diamond with HPHMP was described. The 2-propanol-2-yl functional groups were responsible for the reforming of diamond surface. The reforming of the diamond enhanced the dispersion in organic solvents as well. So, the ease in dispersion makes R-diamond useful in wide range of application to improve the physical and chemical properties of materials. Moreover, the R-diamond could be used to prepare polymer composites. This new way of modification has successfully helped to reform the diamond surface by using different kinds of photoinitiators. We envision this new approach can assist to modify further the already present functional moieties into several interesting derivatives.

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