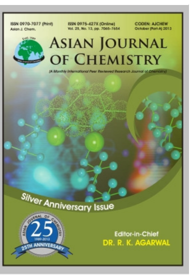
Asian Journal of Chemistry; Vol. 25, No. 17 (2013), 9840-9844

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2013.15488



Modification of Diamond Particles for Improved Dispersion in Liquid Phase

MIRZA NADEEM AHMAD[1,2,*], KHALID MAHMOOD ZIA[2], SOHAIL NADEEM[3], TAHIR FAROOQ[2], MUHAMMAD NAVEED ANJUM[2], ASMA TUFAIL SHAH[4], SHAZIA KHURSHID[3], KHURRAM SHEHZAD[5], MOHAMMAD ZUBER[2] and WANTAI YANG[1]

[1]State Key Laboratory of Chemical Resource Engineering and College of Materials Science and Engineering, Beijing University of Chemical Technology, Beijing 100029, P.R. China
[2]Department of Applied Chemistry, Government College University, Faisalabad 38000, Pakistan
[3]Department of Chemistry, Government College University, Lahore 54000, Pakistan
[4]Interdisciplinary Research Centre in Biomedical Materials, COMSATS Institute of Information Technology, Lahore 54000, Pakistan
[5]Center for Nano & Micro Mechanics, Tsinghua University, Beijing 100084, P.R. China

*Corresponding author: Fax: +86 10 64416338; Tel: +86 10 64432262; E-mail: pioneerravian@yahoo.com

(*Received*: 15 March 2013; *Accepted*: 25 October 2013) AJC-14286

Photochemical modification of diamond was carried out by covalently bonding the radicals of 2-propanol-2-yl $[(CH_3)_2C^*OH]$ on the surface of diamond, which were produced by the photochemical disintegration of 2-hydroxy-2-methyl-1-phenyl-1-propanone irradiated by ultraviolet rays. A dispersion of diamond was prepared in acetone with the subsequent addition of 2-hydroxy-2-methyl-1-phenyl-1-propanone which acted as photoinitiator. This mixture was put under irradiation with UV light for the generation of free radicals from 2-hydroxy-2-methyl-1-phenyl-1-propanone. These free radicals were introduced onto the surface of diamond and improved the dispersion in liquid phase. The modified diamond was characterized by Fourier transform infrared spectroscopy, nuclear magnetic resonance spectroscopy, thermogravimetric analysis, thermogravimetric analysis-mass spectrometry and scanning electron microscopy. The scanning electron microscopy and dispersibility data demonstrated that the surface modification of diamond helped to improve its dispersibility in common organic solvents as well as the functional behaviour of its surface which may be useful in diagnosis/treatment of various diseases.

Key Words: Diamond, Surface modification, Facile dispersion, Photoinitiator.

INTRODUCTION

Diamond has been found to be a potentially useful material due to its unique characteristics including hardness, large gap in bands and stability against chemical reagents. More over it has high transparency over a wide wavelength region and high thermal conductivity[1,2]. Therefore, many researchers have regarded diamond as one of the most promising material in various fields[3,4]. Although, diamond is composed of only sp^3 carbon atoms, but still its surface can be modified by bonding with elements other than carbon which impart new properties.

Actually, the utilization of diamond needs the development of proper technologies for its surface modification to make it useful in various applications. These applications may include precision polishing, conducting resins, high thermal conductive fluid dispersing diamond particles, *etc*.[5,6]. Furthermore, the diamond surface modified under optimized conditions, the attached organic functional groups, would provide a route for the synthesis of new families of materials having organic-inorganic character that possesses the physical properties of diamond and the chemical properties of functional group[1].

Several researchers have been working on modification of the diamond surface. The work on the modification of diamond surface can be classified into two main groups *i.e.* vapour phase modifications[7-13] and liquid phase modifications[14-20]. The surface modification of diamond in the liquid phase has been found more suitable for industrial applications. Another advantage of liquid phase is that organic substances with organic functional groups can be easily attached on a diamond surface and in this way new organic-inorganic functionalities would be developed. Recent researches included the diamond surface modification by using silane coupling reagents[21] and carboxylic acids[22].

Although a variety of oxidative, thermal or atomic beam chemical modification of hydrogenated diamond have been reported by different research groups[23,24]. However, a few studies have been targeted towards photochemical surface modification of diamond by the introduction of free radicals[25]. In addition, many of such experiments have been performed in the vapour phase, causing the requirement of expensive equipment, high vacuum apparatuses and ultra pure materials. This made it impractical for broad spectrum industrial applications of these materials.

The previous studies showed that the development of a facile and optimized modification technique for diamond surface was not a trivial task. Therefore, the current investigation has been pursued keeping in view that photochemical reactions could be exploited to develop some suitable inexpensive modification techniques which do not harm the surface of diamond during the modification process. The use of 2-hydroxy-2-methyl-1-phenyl-1-propanone (HMPP) photoinitiator expanded the photoreactivity of diamond surface, especially; the generality of the process has been proved to be widely applicable in many types of modifications to the diamond structure.

EXPERIMENTAL

Diamond (purity 99.99 %, particle diameter 500 nm) were obtained from Tomei Diamond Ind. Co., Ltd., Japan. 2-Hydroxy-2-methyl-1-phenyl-1-propanone (HMPP) has been procured from Ciba Inc., Ltd., Jiangsu, China. Carbon disulfide, THF, 2-propanol, toluene, DMF and Acetone were used as received from Beijing Chemical Co., Ltd., Beijing, China.

Functionalization of diamond particles by photochemical reaction: In a typical reaction, diamond (5.0 mg, particles diameter 500 nm) and acetone (30 mL) were mixed in a quartz round bottom flask, the dispersion was carried out by sonicating the reaction mixture for 0.5 h. After the addition of 2-hydroxy-2-methyl-1-phenyl-1-propanone (3 mg) the contents of the flask were purged with argon at a constant stirring to degas the reaction contents. After 0.5 h, the irradiation of the reaction mixture was carried out with ultraviolet radiations. The reaction flask was placed at a distance of 10 cm from the lamp. At this distance the intensity of the radiations was 7000 μW/cm^2 at 254 nm wavelength. The solvent was removed by centrifugation at 5000 rpm. After 0.5 h, the washing of the residual particles was carried out first with acetone in 10 mL portion and then with toluene in three portions of 10 mL each. The product was dried under at 50 °C for 12 h. The analytical characterization was accomplished using various analytical techniques.

Characterization: Thermo Nicolet Nexus 670 FTIR spectrometer was used using KBr pellet method at a range of 4000-400 cm^{-1}. Nuclear magnetic resonance (NMR) measurements were recorded on a Bruker AV 600 MHz spectrometer by dispersing the modified diamond in $CDCl_3$ at room temperature. Thermal analysis (TGA) was recorded on a NETZSCH TG 209 system under nitrogen atmosphere. The scanning rate was 10 °C/min. Perkin Elmer Pyris Diamond TGA-MS was used for TGA-MS analysis using electron impact ionization mode. Scanning electron microscopy (SEM) was used to determine the morphology of diamond particles on a Hitachi S-4700 microscope operating at 30 kV.

RESULTS AND DISCUSSION

Fourier transform infrared studies: The modification of diamond was evidenced through the FT-IR spectra. Fig. 1 presents the FT-IR spectral changes before and after the modification of diamond samples. There was no obvious band in the spectrum [Fig. 1(a)] of diamond which indicates that the diamond contains no functional group.

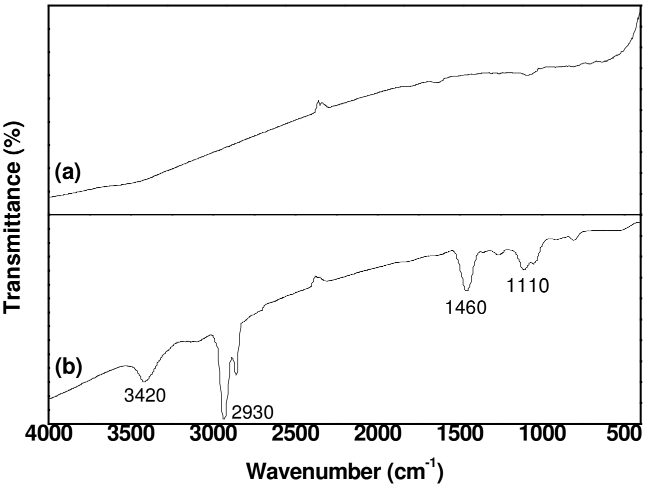


Fig. 1. Fourier transform infrared spectra of diamond in potassium bromide: (a) diamond, (b) modified diamond

While Fig. 1(b) clearly showed the characteristic stretching vibration of O-H at 3420 cm^{-1} and corresponding band at 1110 cm^{-1} indicating the presence of C-O-H bond for hydroxyl functionality. The peak value for OH group revealed its tertiary nature. Actually, the OH group present in $(CH_3)_2C^*OH$ was secondary in nature has been transformed to tertiary considering the bond formation between $(CH_3)_2C^*OH$ and carbon atom present on the surface of diamond[18,26]. Furthermore, the bands at 2930 and 2860 cm^{-1} represented the antisymmetric and symmetric stretching vibrations of sp^3-hybridized C-H bond respectively. The C-H bond asymmetric and symmetric bending frequencies occurred as deformation band at 1460-1250 cm^{-1}, respectively. These results confirmed the modification of diamond surface and explained the changes in the nature of functional groups as well before and after modification.

Nuclear magnetic resonance studies: The confirmation of modification of diamond surface was also supported by ^{1}H NMR (600 MHz, $CDCl_3$) as indicated in Fig. 2. It was found that the characteristic resonance of 2-propanol-2-yl group occurred for methylic protons at $\delta = 1.2$ ppm while the proton present in tertiary hydroxyl group resonated at $\delta = 3.9$ ppm. The ratio of protons in methyl group and hydroxyl group is 6:1 exactly, which indicated the presence of two methyl groups in the vicinity of –OH group. This showed that ^{1}H NMR results are in good agreement with FT-IR.

Thermal gravimetric studies: The information obtained from thermal analysis provided important information about modification of diamond, as the functional groups present on diamond were organic in nature so, at high temperatures those became unstable *i.e.* most of the organic functional groups were decomposed before the onset of diamond decomposition.

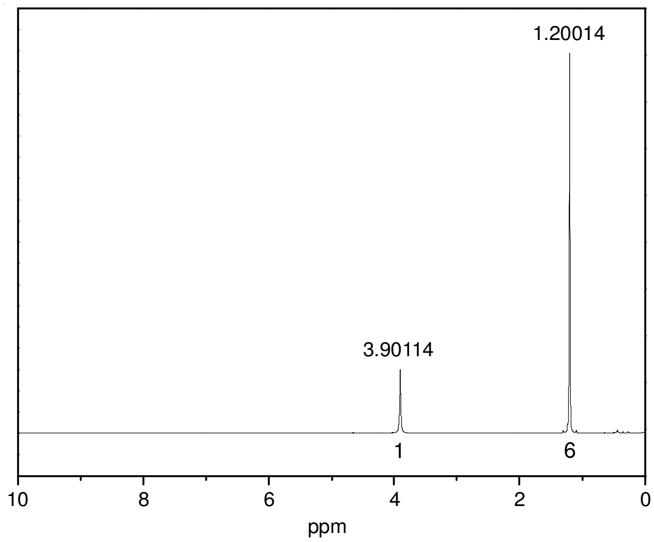


Fig. 2. Proton nuclear magnetic resonance chemical shifts of modified diamond in deuterated chloroform ($CDCl_3$)

Fig. 3 represents two data sets labeled as (a) & (b) which corresponds to the diamond before modification and after modification respectively. The percentage weight loss curves represented that the overall weight loss, during the process, was 0.52 % for diamond and about 5.91 % for modified diamond. The percentage weight loss of diamond apparently originated from volatilization of moisture and amorphous carbon particles, which presumably decomposed by oxidation mechanism at higher temperature. Excluding this part, the net weight loss of 5.39 % for modified diamond at 400 ºC, revealed the decomposition of functional groups on the diamond surface. This percentage weight loss was substantially suggestive that the appreciable number of functional groups was introduced despite the known low reactivity of diamond. Thus, the method proves to be efficient for introduction of functional groups onto the surface of diamond.

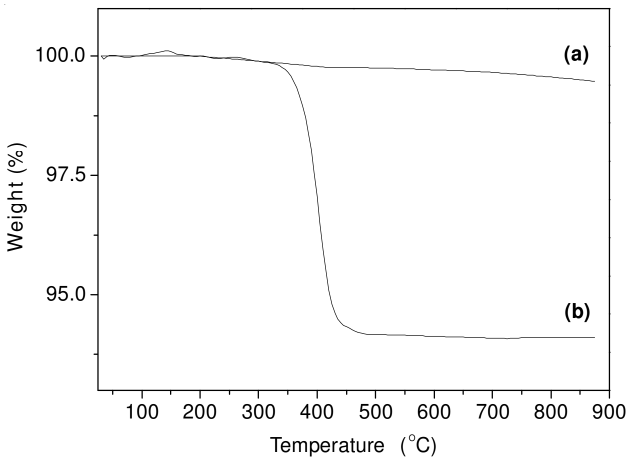


Fig. 3. Thermal analysis of diamond in N_2 atmosphere: (a) diamond, (b) modified diamond

Thermal gravimetric analysis-mass spectrometric studies: Thermal analysis coupled with mass spectrometry (TGA-MS) provided useful information about modification of diamond surface. The fragmentation of attached substituents was monitored with TGA temperature range of 20-900 ºC along with online monitoring of volatile products through mass spectrometer.

In Fig. 4, the TGA-MS spectrogram illustrated the evolution of detached 2-propanol-2-yl groups at 400 ºC as shown by a major peak (a) at *m/z* 59 despite of two shoulder peaks due to atmospheric effect. The decomposition of functional groups, at relatively high temperature (400 ºC), is remarkably related to the stability of functional moieties and consistent with TGA results. Fig. 4(b) resulted in a base line at *m/z* 105 which means that there was no $C_6H_5C^+O$ ion detection by mass spectrometer during the thermal decomposition of modified diamond. Then, it is evident that the benzoyl radicals $C_6H_5C^*O$ had no contribution in functionalization. Hence, the modification was solely due to 2-propanol-2-yl radicals, which were originated from the surface of modified diamond and detected by mass spectrometer.

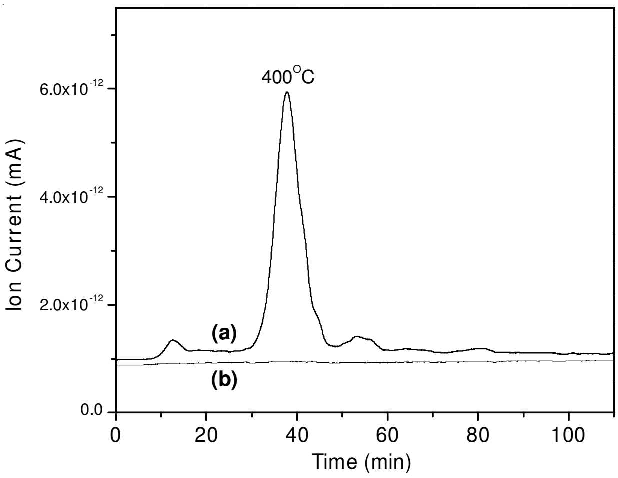


Fig. 4. TGA-MS spectrogram of modified diamond: time *vs.* ion current

Scanning electron microscopic studies: Scanning electron microscopic images of diamond and modified diamond are compared in Fig. 5. The diamond seemed to be a cluster of diamond particles. On the other hand, the modified diamond appeared to be more dissociated and this phenomenon directs it to disperse and behave individually. Because, the modification has prevented diamond to aggregate and enhanced their discreteness, therefore, when compared to pristine diamond, modified diamond have shown high and facile dispersion in different solvents.

Fig. 5. (a) SEM image of diamond: for diamond at 5 µm resolution

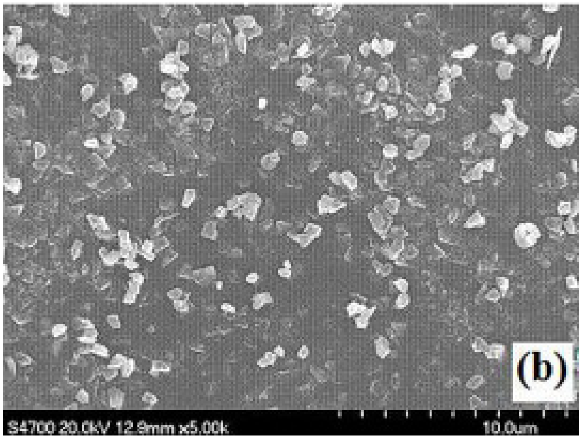


Fig. 5. (b) SEM image of diamond: for modified diamond at 10 μm resolution

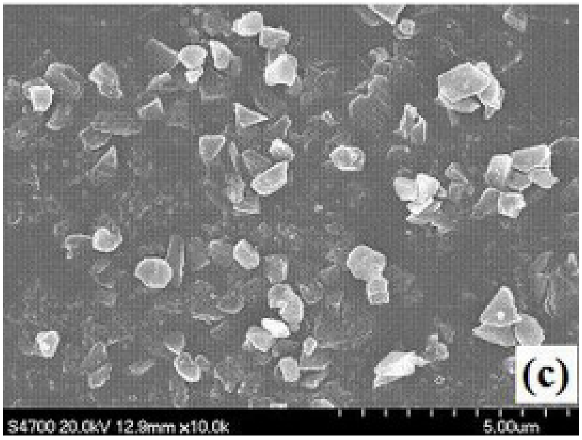


Fig. 5. (c) SEM image of diamond: for modified diamond at 5 μm resolution

The SEM images were taken by placing a drop of dispersion on a grid and air dried. These images provided important information about the surface modification with HMPP. It neither damaged nor created the defects on the surface of diamond during its modification. These images proved that the method described here for the modification of diamond surface is mild enough to create covalent bonds of organic groups with diamond surface without damaging it.

Dispersibility: The dispersibility of diamond after modification has been improved significantly and their dispersion in various solvents can be easily prepared (Table-1).The quantitative estimation of dispersibility was carried out according to reported method[19,27]. The dispersibility of modified diamond in *N,N*-dimethyl formamide was about 9.8 mg/L, about 7 times better than that of diamond (1.4 mg/L). Fig. 6 represented the visual judgment of enhanced dispersibility of unmodified diamond (a) in comparison to modified diamond (b).

As, the data showed that modified diamond is more dispersible in common organic solvents such as isopropanol, tetrahydrofuran and carbon disulphide than diamond. It is very interesting that the dispersibility of modified diamond increased nearly 7 times that of diamond in THF. It can be concluded that modification improved the dispersibility of diamond by decreasing the surface interactions due to the hindrance of surface functional groups of modified diamond. Moreover, the interactions, between the functional groups and solvent, are responsible for facile dispersion. The hydroxyl groups facilitate the dispersibility in polar and semi-polar solvents while methyl groups facilitate in non polar which is more valuable than simply -OH functionalized diamond. 2-Propanol-2-yl groups are relatively bulky than -OH groups and reduce the surface interaction to facilitate the dispersibility while -OH functionalized diamond possess much force of interaction due to polarity of hydroxyl groups. Therefore, this process of modification is more worthy and expected to facilitate their chemical manipulation, characterization, properties investigation and wide applications.

TABLE-1
ROOM-TEMPERATURE DISPERSIBILITY DATA (mg/L)
FOR DIAMOND AND MODIFIED DIAMOND
IN DIFFERENT SOLVENTS

Solvent	Diamond (mg/L)	Modified-diamond (mg/L)
N,N-Dimethyl formamide	1.4	9.8
Isopropyl alcohol	Not dispersed	2.1
Tetrahydrofuran	0.6	4.2
Carbon disulfide	0.5	3.5

Note: Dispersibility was checked at room temperature after 24 h.

Fig. 6. Diamond dispersions in *N,N*-dimethyl formamide (9.8 mg/L) after 24 h: (a) diamond; (b) modified diamond

Based on experimental data, the route for the modification of diamond can be proposed as shown in Fig. 7. 2-Propanol-2-yl and benzoyl radicals were generated by the photolysis of 2-hydroxy-2-methyl-1-phenyl-1-propanone in the presence of diamond particles in acetone. Mechanistically, 2-propanol-2-yl radicals with high reactivity than benzoyl radical attacked on the surface of diamond, which was activated by the absorption of photoelectrons emitted by UV light source to form modified diamond.

TGA-MS results, indicated that no benzoyl radical was attached to the surface of the diamond which may be attributed to relative stable benzoyl radicals which may have joined together to give benzil. In the meanwhile, the 2-propanol-2-yl radicals were introduced onto the surface of diamond with relatively higher rate constant than benzoyl radicals[28] and modified the diamond surface.

Conclusion

A simple and facile method for chemical modification of diamond like inert materials has been described here. This method provided the incorporation of organic functional groups like 2-propanol-2-yl [$(CH_3)_2CH\text{-}OH$] to the diamond surface. As a result of modification the diamond particles dissociated which caused the enhancement of its dispersion in organic solvents like DMF. Moreover, the attachment of such organic functional groups has opened a new way for the attachment of diamond with other materials for important

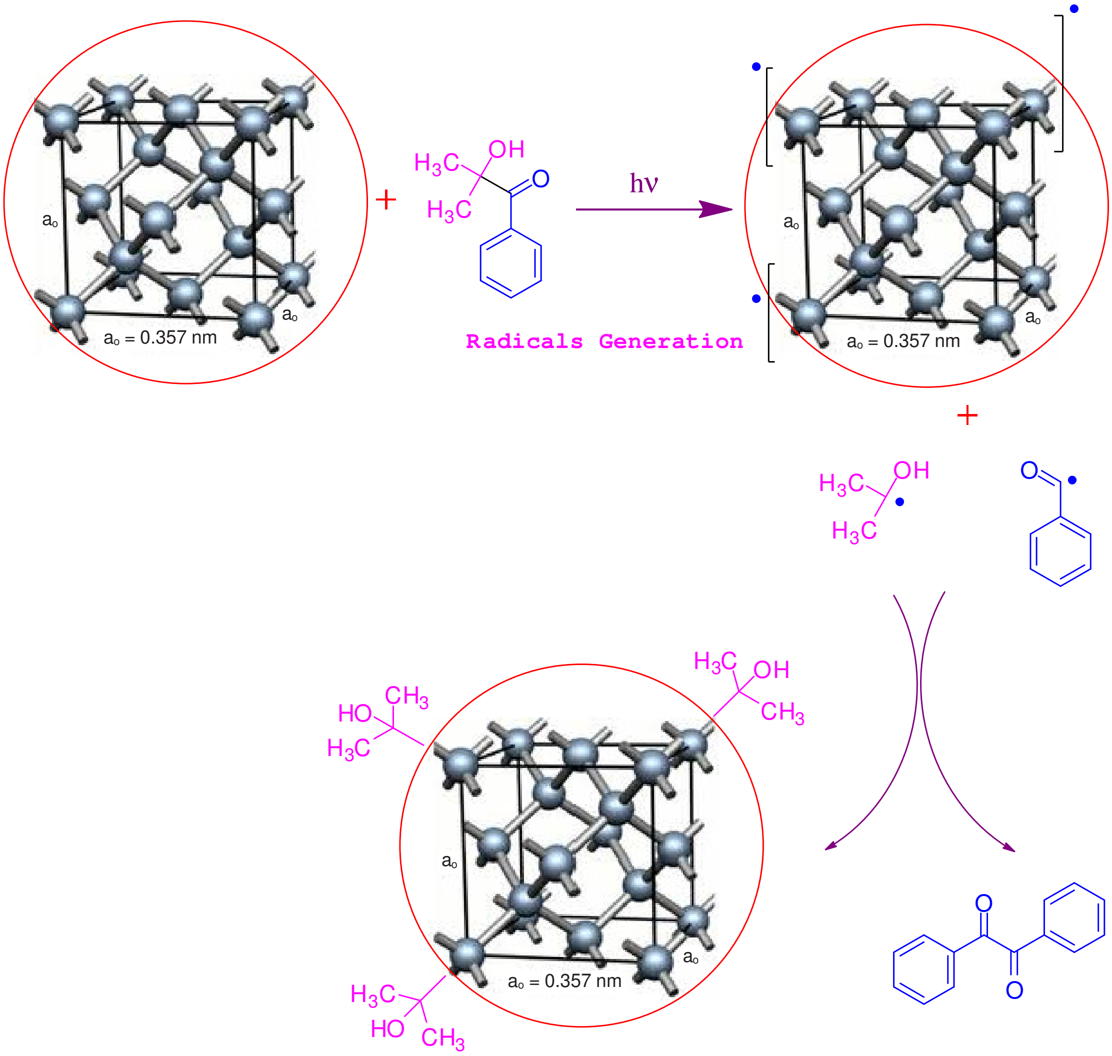


Fig. 7. Schematic illustration of chemical modification of diamond by HMPP photoinitiator

applications. This method also provides a new route for the use of photoinitiators in chemical modification of such inert materials.

REFERENCES

1. A. Shatskiy, D. Yamazaki and G. Morard, *Rev. Sci. Instrum.*, **80**, 23907 (2009).
2. V.I. Konov, *Laser Photon. Rev.*, **6**, 739 (2012).
3. T. Irifune and R.J. Hemley, *Eos Trans. Am. Geophys. Union*, **93**, 65 (2012).
4. Z.J. Lin, J.Z. Zhang and B.S. Li, *Appl. Phys. Lett.*, **98**, 121914 (2011).
5. X. Wang, X. Li and C. Yi, *Mater. Lett.*, **73**, 83 (2012).
6. T. Tsubota, T. Ohno and H. Yoshida, *Diamond Rel. Mater.*, **15**, 668 (2006).
7. T. Ando, M. Ishii, M. Kamo and Y. Sato, *J. Chem. Soc. Faraday Trans.*, **89**, 1783 (1993).
8. T. Jiang, K. Xu and S. Ji, *J. Chem. Soc. Faraday Trans.*, **92**, 3401 (1996).
9. T. Ando, K. Yamamoto, O. Fukunaga, M. Kamo, K. Kobayashi and M. Yoshikawa, Advances in New Diamond Science and Technology, MYU, Tokyo, p. 431 (1993).
10. T. Ando, K. Yamamoto, M. Ishii, M. Kamo and Y. Sato, *J. Chem. Soc. Faraday Trans.*, **89**, 3635 (1993).
11. T. Jiang, K. Yamamoto, M. Matsuzawa, Y. Takamatsu, S. Kawasaki, F. Okino, H. Touhara, M. Kamo and Y. Sato, *Diamond Rel. Mater.*, **5**, 1021 (1996).
12. T. Ando, M. Nishitani-Gamo, R.E. Rawles, K. Yamamoto, M. Kamo and Y. Sato, *Diamond Rel. Mater.*, **5**, 1136 (1996).
13. T. Ando, S. Inoue, M. Ishii, M. Kamo and Y. Sato, *J. Chem. Soc. Faraday Trans.*, **89**, 749 (1993).
14. T. Tsubota, O. Hirabayashi, S. Iida, S. Nagaoka, M. Nagata and Y. Matsumoto, *Diamond Rel. Mater.*, **11**, 1374 (2002).
15. T. Tsubota, S. Tanii, S. Iida, M. Nagata and Y. Matsumoto, *Phys. Chem. Chem. Phys.*, **5**, 1474 (2003).
16. T. Tsubota, S. Iida, O. Hibarashi, S. Nagaoka, S. Nagayama, M. Nagata and Y. Matsumoto, *J. Ceram. Soc. Japan*, **110**, 904 (2002).
17. T. Tsubota, S. Tanii, S. Ida, M. Nagata and Y. Matsumoto, *Phys. Chem. Chem. Phys.*, 5, 1474 (2003).
18. T. Uchida, T. Takatera, T. Sato and S. Takeuchi, *Proc. IEEE Ultrason. Symp.*, **1**, 431(2001).
19. H. Visbal, S. Sugita, C. Ishizaki and K. Ishizaki, *Adv. Tech. Mater. Proces. J. (ATM)*, **6**, 77 (2004).
20. H. Visbal, C. Ishizaki and K. Ishizaki, *J. Ceram. Soc. Japan*, **113**, 344 (2005).
21. T. Tsubota, S. Iida, O. Hibarashi, S. Nagaoka, S. Nagayama, M. Nagata and Y. Matsumoto, *J. Ceram. Soc. Japan*, **110**, 904 (2002).
22. T. Tsubota, S. Tanii, S. Ida, M. Nagata and Y. Matsumoto, *Phys. Chem. Chem. Phys.*, **5**, 1474 (2003).
23. R. Hoffmann, H. Obloh and N. Tokuda, *Langmuir*, **28**, 47 (2012).
24. A. Krueger and D. Lang, *Adv. Funct. Mater.*, **22**, 890 (2012).
25. B. John and D. Miller, U.S. Patent5593783 (1997).
26. D.L. Pavia, G.M. Lampman, G.S. Kriz and J.R. Vyvyan, Introduction to Spectroscopy, Cole Pub. Co. Ltd, Belmont, USA, p. 124 (2009).
27. H. Peng, L. Alemany and J. Margrave, *J. Am. Chem. Soc.*, **125**, 15174 (2003).
28. K. Vacek and J. Geimer, *J. Chem. Soc. Perkin Trans. II*, 2469 (1999).