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Hexagonal Boron Nitride Nanosheets as High-performance Binder-Free Fire Resistant Wood Coatings

Juanjuan Liu [1], R Govindan Kutty [1], Qingshen Zheng ,Varla Eswariah, Sivaramapanicker Sreejith and Zheng Liu

Dr. Juanjuan Liu
School of Geography and Environmental Sciences, Guizhou Normal University, Guizhou, China, 550001

R Govindan kutty, Dr. Qingshen Zheng, Dr. Varla Eswariah, Dr. Zheng Liu
Center for Programmable Materials, School of Material Science and Engineering
Nanyang Technological University
Singapore 637798, Singapore

Dr. Sivaramapanicker Sreejith
Division of Chemistry and Biological Chemistry, School of Physical and Mathematical Sciences, Nanyang Technological University,
21-Nanyang Link, 637371, Singapore

Keywords: Hexagonal boron nitride, Nanosheets, Fire resistant coating, Thermal diffusivity, Thermal effusivity

Abstract

Fire resistant coatings with hydrophobicity and oxidation resistance bring a true fire barrier for a wide variety of materials including sheetrock, wood, foam etc. Here, we have demonstrated successfully the use of boron nitride nanosheets for wood coatings for the first time. We have exfoliated hexagonal boron nitride to nanosheets in liquid phase and exploited its use as a binder free fire retardant wood coating. Scanning electron microscopy and Raman spectroscopy were employed to characterize the wood coating. Our binder free h-BN coating is stable against oxidation up to 900°C in air. This BN based high-performance and low-cost materials will shed light on the next generation fire resistance coating.

1. Introduction

Wood is a multifunctional material used in a myriad of applications such as construction, furniture and panels. [1] Fire resistant wood coatings have been a highly sought after research field. Along with fire resistance, an optimum wood coating is judged based on the hydrophobicity, UV protection durability, toughness, oxidation resistance etc. Coatings can be mainly classified into binder free coatings and coating combined with a binder material. [2] Mainly a wood coating material consists of binders, fillers, pigments, flatting agents, solvents and additives. [3] The common wood coatings that are used in the current industry include wax [4], shellac [5], Nitrocellulose lacquer [6], varnish [7], linseed oil [8], poly urethane [9], epoxy resins [10] etc. From the aforementioned coating, polyurethane coatings are distinguished by their high gloss, flexibility and chemical resistance. [11] One type of coating, called a fire retardant coating, uses additives such as borax, boric acid [12], antimony trioxide [13], and chlorinated compounds [14] which do not support combustion. Such fire retardant coatings require additional binding materials which are toxic and as well as not mechanically stable to corrosion, cracking, and other environmental effects.

The hunt for a binder free material which shows an intrinsic fire retardant nature is highly beneficial for the wood coatings. Hexagonal boron nitride (h-BN) is a thermally and chemically resistant compound of boron and nitrogen which is isoelectronic to graphene. [15] h-BN is known for the fire resistant coating for metal and metal oxide surfaces. [16] h-BN/polymer coating shows an efficient corrosion protection with a low corrosion current density of 5.14×10^{-8} A/cm^2 and corrosion rate of 1.19×10^{-3} mm/year and it is associated with the hydrophobic, chemically inert and dielectric nature of h-BN. [17] h-BN is reportedly exhibit oxidation resistance up to 1000°C in air. [18] The use of BN as impermeable coating has been reported in the literature for various substrates. [19,20]But the use of h-BN for wood protection coatings has never been studied before. In this paper, we project the use of binder free exfoliated h-BN nanosheets in fire resistant wood coatings.

2. Results and Discussion

In a typical liquid phase exfoliation experiment, approximately 4g of bulk BN powder was dispersed in already prepared dispersion of SDBS/water suspension of 100 ml volume. We have taken care that all the SDBS is dissolved in water by stirring it in a magnetic stirrer. Here, concentration of SDBS was fixed to 1 mg/ml. The BN/SDBS/water dispersion was probe sonicated for 4 hours with 3 seconds on and 3 seconds off with 50 % amplitude. Ice bath was maintained to suppress the heat generated in the suspension. After 4 hour sonication, the suspension was kept idle for overnight and top 80 % supernatant was collected and centrifuged at 1500 rpm for 90 min. Now, top 60% supernatant was collected and sediment was discarded. The obtained suspension at this stage is purely BN nanosheets but with semi-transparency. In order to achieve high concentration, we have followed high speed centrifugation process. In this typical experiment, the stock BN nanosheets dispersion is subjected to 15000 rpm for 20 min in 2 ml vials and top 90 % supernatant is discarded and sediment 10% is collected and like that whole suspension was performed high speed centrifugation process. Nearly viscous samples obtained at the end of the above approach and used for further analysis. Similarly, BN powder was also exfoliated in IPA solvent but the amplitude was kept at 20% in order not to evaporate the volatile solvent rapidly and the same procedure described above is followed to concentrate the BN nanosheets dispersion.

Wood substrates are of cedar tree, scientifically known as Cunninghamia lanceolate which has being widely used for wood based products. Surface features of pristine wood substrates and coated with BN nanosheets were explored using optical microscope and shown in Figure 1a. A high degree of surface roughness is observed in the optical images of pristine wood substrate as shown in Figure 1b. The magnified image of the wood surface after coating is illustrated in the figure 1c and 1d which clearly depict the disappearance of the surface roughness upon coating with h-BN nanosheets. Elemental composition of the exfoliated h-BN nanosheets were studied using Raman spectroscopy. Figure 2a shows the typical Raman spectra of h-BN nanosheets, where intense peak of the BNNSs appears at 1365.8 cm^{-1}, attributed to the E_{2g} vibration mode of h-BN. [21] The full width at half-maximum (FWHM) of the E_{2g} mode is about 5.21 cm^{-1} for the present BNNSs, which is slightly larger than FWHM of BN powder in the reported literature (4.77 cm^{-1}) [22], suggesting the excellent quality of the as-prepared h-BN nanosheets. Change in intensity of the E_{2g} vibration mode of h-BN may be attributed to the reduced interlayer interaction during the exfoliation process of BN powder. Raman spectra of the BN coated wood substrate after exposing to 1 min and 5 min under fire have been illustrated in the supplementary figure 1. The structural integrity and crystalline ordering of the BN nanosheets were explored employing X-ray diffraction analysis (figure 2b). The characteristic Bragg reflection [002] plane at the 2θ value 26.5^0 confirms the h-BN which is consistent with the reported works in the literature. [23] Elemental composition of BN nanosheets are further explored with XPS spectroscopy and results are compiled in the supplementary figure 2.

Mesoscale surface morphology of the pristine wood substrate and the BN nanosheet coating has been explored using scanning electron microscopy (SEM). SEM results are compiled in the figure 3a-3f. Figure 3a depicts the surface grooves present in the pristine wood substrate. Figure 3b and 3c correspond to the magnified images of the wood substrates which clearly shows the presence of groove structures on the surface of wood. Grooves are not regular in nature and indicate a favorable ground to incorporate the binder free nanosheet coating. Figure 3d illustrates the wood substrate after coated with h-BN nanosheets. It can be seen from the figure 3d that the BN nanosheets have form a complete coating covering all the grooves present in the surface of the wood substrate. The nanosheets got deposited in the grooves and eventually form a strong adhesion to the wood surface. Figure 3e and 3f shows the magnified SEM image of the complete coating formation of BN nanosheets. The average thicknesses of the BN nanosheets coated on the wood substrates were determined using cross-sectional SEM (supplementary figure 3).

Surface morphological of exfoliated BN nanosheets have been further explored employing high-resolution transmission electron microscopy (HRTEM) as shown in figure 4. Figure 4a-4c displays the BN nanosheets at low magnification. The average sizes of the BN nanosheets are in the range of 50 to 300nm. Figure 4d represents typical atomic structure of the BN nanosheets. Figure 4e shows the characteristic moiré patterns of h-BN from the AA' stacking of the h-BN. Figure 4f shows the characteristic honey comb structure of the h-BN in which boron and nitrogen atoms are covalently bonded. The SAED pattern is shown in the inset of figure 4f.

Fire resistant property of the h-BN nanosheet coatings were performed using a fire lighter employing a wood substrate in which half of the portion is coated with BN nanosheets. Fire resistant experiment is depicted in the Figure 5. Figure 5a shows the wood substrate in which white portion is coated with h-BN nanosheets and exhibits an opaque white color and can be easily differentiate with the uncoated portion which possesses the yellowish tint color of the pristine wood substrate. Figure 5b illustrates the pristine wood substrate under fire after 30 seconds and Figure 5c after 1 minute. The uncoated portion of the wood substrate is easily burned under fire and which gets oxidized and turned black (figure 5b and 5c). Considerable damage is visible after 60 seconds when the uncoated portion caught fire. Figure 5d and 5e indicates the fire resistant characteristics of h-BN coating. The experiment is carried out for the same time frame and the h-BN coated portions endured the fire and remained intact after 60 second. Figure 5f shows the wood substrate after fire experiment was carried out for 1 minute with (left) and without h-BN nanosheet coating (right). It can be clearly seen that the h-BN coated portions of the wood substrate remained intact after exposing to fire.

Oxidation resistance studies are compiled in the figure 6a - 6d. Oxidation resistance experiments were carried out at 300^0, 600^0 and 900^0, respectively, with the help of CVD furnace system. CVD furnace is pre-heated in air to the aforementioned temperatures and the h-BN coated wood substrates were introduced to the heated zone. BN coated wood substrates are oxidation resistant up to 900^oC in air. There is no visible damage to the coating upon heating at 200^oC and is evident in the figure 6a. Figure 6b elucidates the evolution of small cracks in the coating when the substrate is exposed at temperature up to 600^oC. Only at 900^oC, considerable morphologies change in the coating. The h-BN coating withered out and comes apart from the wooden substrate, which is evident from the figure 6c due to the thermal induced expansion in the wood under high temperature. Furthermore, a darkish tint color change in the opaque white h-BN coating corroborates the withering process of the coating. However, no significant damage to the wood is observed at 900^oC. This can be seen in figure 6c, as only the coating withers out leaving the wooden material beneath the coating intact and disaffected against oxidation. Above 900^oC, the coating withers out and carbonization commences (Figure 6d). These data suggest that only at very high temperature the coating disintegrated and the wooden material starts to burn upon prolonged exposure. It can be seen in the inset of figure 6d that the visible color change from opaque white to dark, which illustrates mass loss and damage to the wood material. Up on oxidation, there are no visible mass losses observed up to 900^0C. But Carbonization started at temperature beyond 900^0C and considerable mass loss has been observed. These observations suggest that h-BN nanosheet coating with an appropriate thickness has a very good potential to significantly improve oxidation resistance of wood materials at high temperatures and under oxygen-rich atmospheres.

The mechanism of efficient wood protection by BN coating can be explained using thermal conductivity, thermal diffusivity, and thermal effusivity of BN. One of the inherent properties of h-BN is that the in-plane thermal conductivity is higher than the thermal conductivity perpendicular to the plane. [24] Considering BN as the coating, stemming from the poor thermal conductivity perpendicular to the planes will yield a lower thermal diffusivity and effusivity. Thermal diffusivity governs how efficiently the heat is transmitted through the material and defined as in equation (1):

$$\alpha = \frac{K}{\rho C_p} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots . (1)$$

Where, α is the thermal diffusivity, k is the perpendicular thermal conductivity, ρ indicates the density of h-BN and specific heat capacity of BN (C_p). With respect to equation (1), thermal diffusivity of h-BN is low and heat conduction to the wood substrate is largely reduced, which in turn result in the better protection of wood substrate from oxidation. So, the perpendicular thermal diffusivity will be lower when compared with the in-plane thermal diffusivity of the coating. Simultaneously, the lower perpendicular thermal conductivity of h-BN results in a poor thermal effusivity. Thermal effusivity defines the efficiency of heat transfer of a material with its surroundings and can be defined as in equation (2):

$$e = \sqrt{K\rho C_p} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots .. (2)$$

Where, e is the thermal diffusivity, k denotes the perpendicular thermal conductivity of h-BN, ρ denotes the density of h-BN and c_p indicates the specific heat capacity of h-BN. Literature review indicates that the standard experimental basal plane thermal conductivity of h-BN is 390 $Wm^{-1}K^{-1}$ and perpendicular c-axis thermal conductivity is just 2 $Wm^{-1}k^{-1}$. This huge difference in parallel and perpendicular thermal conductivity is because of the anisotropic layered crystal structure of h-BN. [25] Considering the standard values of specific heat capacity and density of boron nitride, the thermal diffusivity and thermal effusivity of h-BN have the values 4.83 x 10^{-2} m^2s^{-1} and 9.1 $Ws^{(1/2)}m^{-2}k^{-1}$, respectively. These low values of thermal effusivity and diffusivity indicate that heat is poorly conducted perpendicular to the planes in h-BN. Such anisotropic in thermal conductivity is the main reason why BN coating protects the wood at high temperatures and makes it difficult for oxygen to penetrate through the coating to support combustion or oxidation. Further, the coating strength of BN on the wood substrates have been studied using ASTM D3363standards and results are compiled in supplementary information figure 4 and 5. Stress- strain behavior of wood substrates before and after coating with BN was studied and results are explained in the supplementary information figure 6.

3. Conclusion

We have demonstrated the use of exfoliated h-BN nanosheets as a high-performance binder free fire resistant coating for wood. The surface of the wood substrate remained intact after exposing to fire. The anisotropic thermal conductivity and low thermal diffusivity and effusivity of h-BN make it an excellent wood protection coating. We have successfully demonstrated the oxidation resistance property of h-BN wood coating up to 900^0C in air. So far to our knowledge; this is the first time reporting the use of exfoliated boron nitride nanosheets as fire resisting oxidation resistant wood coatings.

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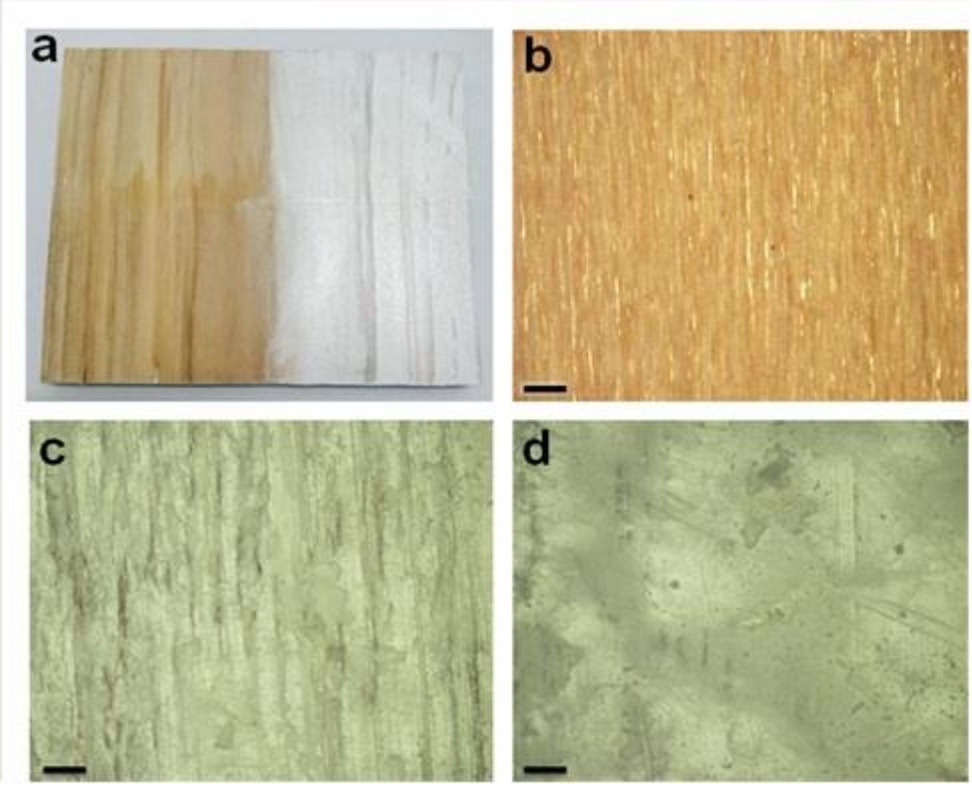

Figure 1. a) Shows the image of a wood substrate. Left portion is uncoated wood surface and coated with BN nanosheets on the right. b) Illustrates an optical image of the pristine wood substrate. c) And d) shows the optical image of the wood substrates coated with h-BN nanosheets. Scale bar is 200µm.

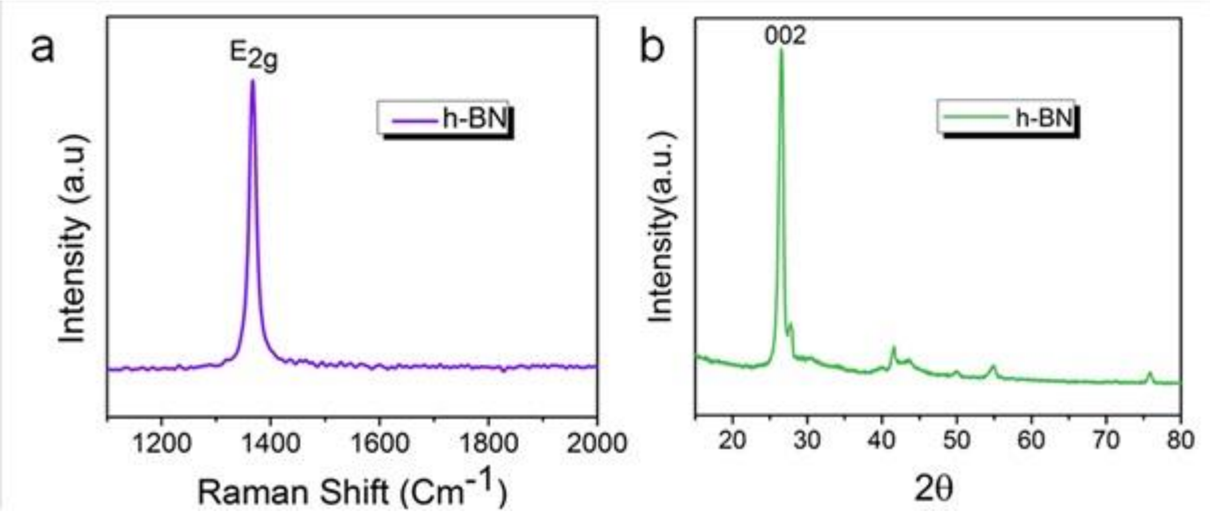

Figure 2. a) Shows the Raman spectra of wood substrate after coating with BN and b) shows the XRD spectra of BN nanosheets used for coating.

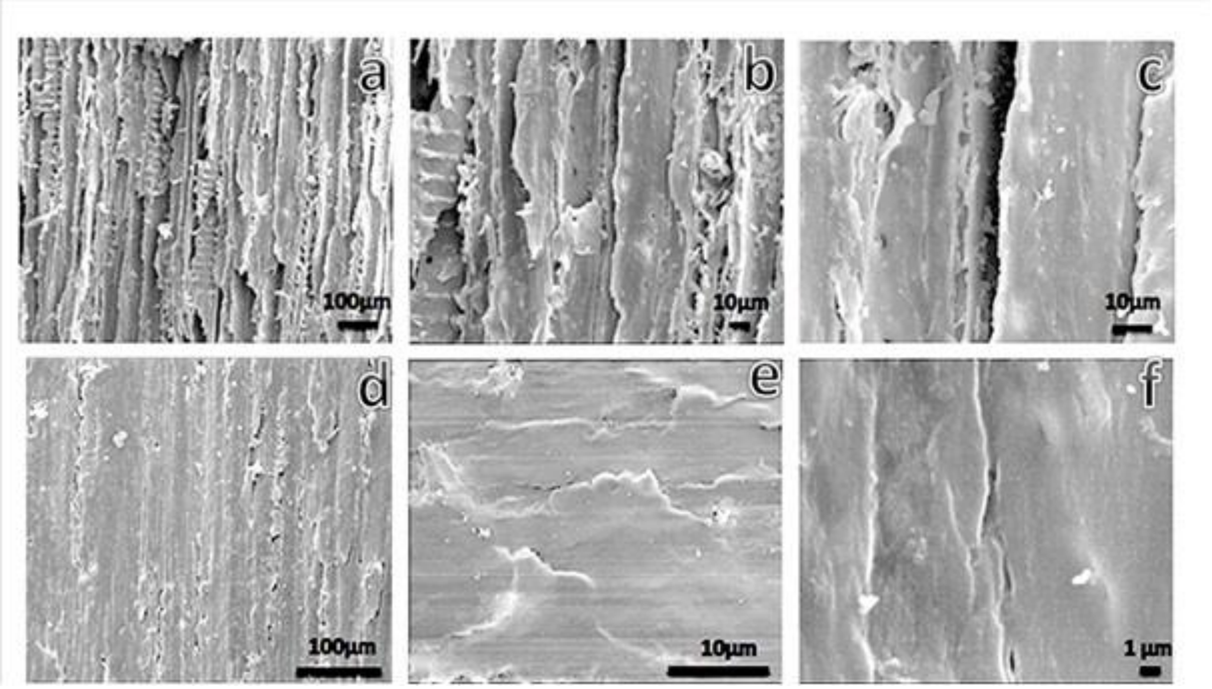

Figure 3. a, b, c) shows the SEM images of pristine wood substrate and d, e, f) wood substrate coated with exfoliated BN sheets.

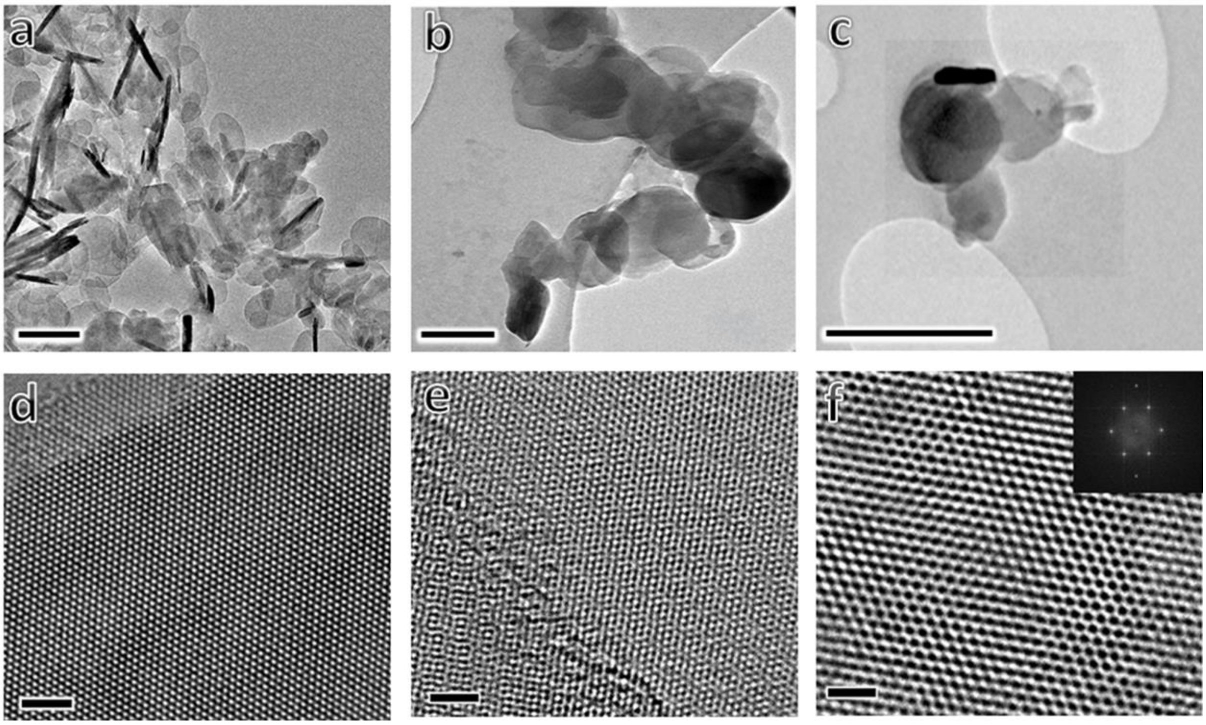

Figure 4. a,b,c) represents the exfoliated BN nanosheets. d,e,f) shows the atomic scale HRTEM images of BN nanosheets. e) Indicates the characteristic moire pattern of BN

nanosheets. f (inset) shows the SAED pattern of the exfoliated BN nanosheets. Scale bar: a) 200nm, b) 100nm, c) 500nm. Scale bar d) is 5nm. Scale bar for e, f is 2 nm.

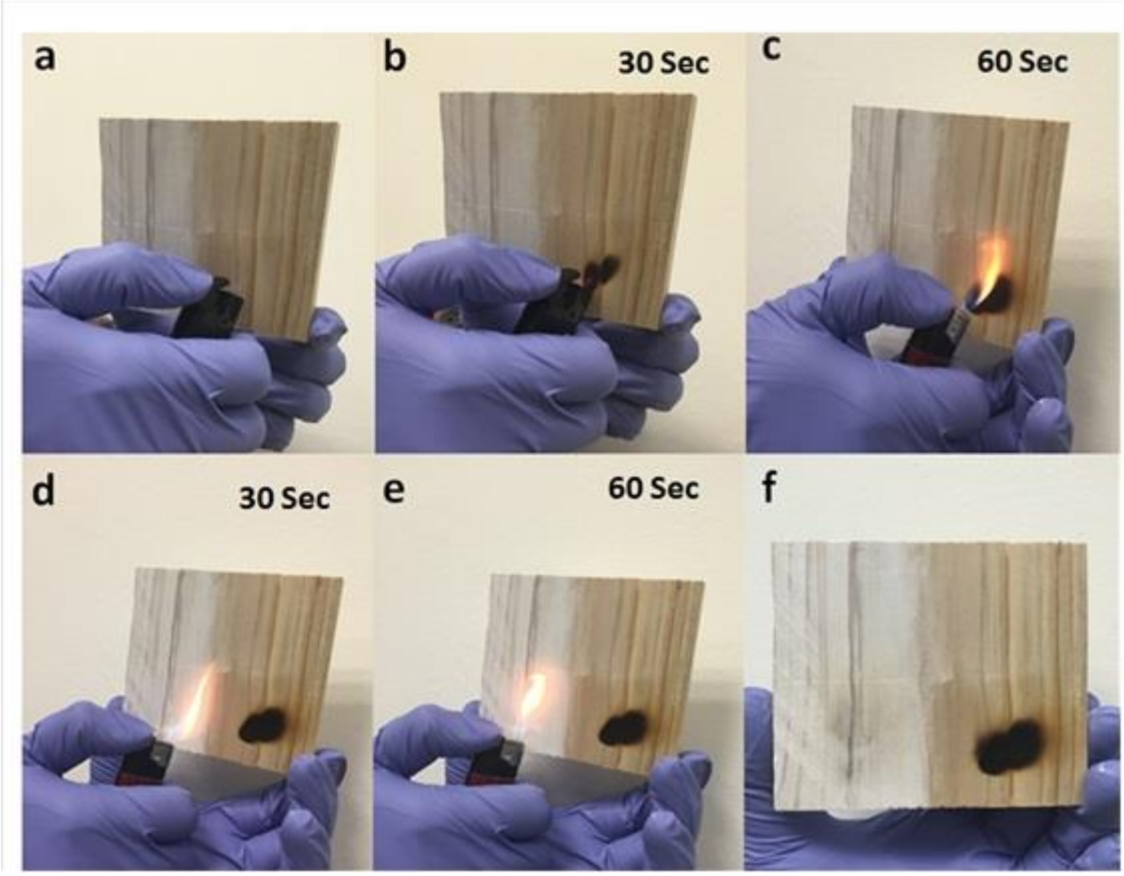

Figure 5. (a-f) displays the fire resistant property of BN coated wood substrates. a) Shows the coated and uncoated surface of the wood substrate. b) And c) shows the carbonization of pristine uncoated wood substrate surface exposed to fire after 30 seconds and 60 seconds. d) And e) demonstrates the fire resistance of h-BN nanosheet coating on exposure to fire following the same time. f) Shows the aftermath of the fire resistant experiments.

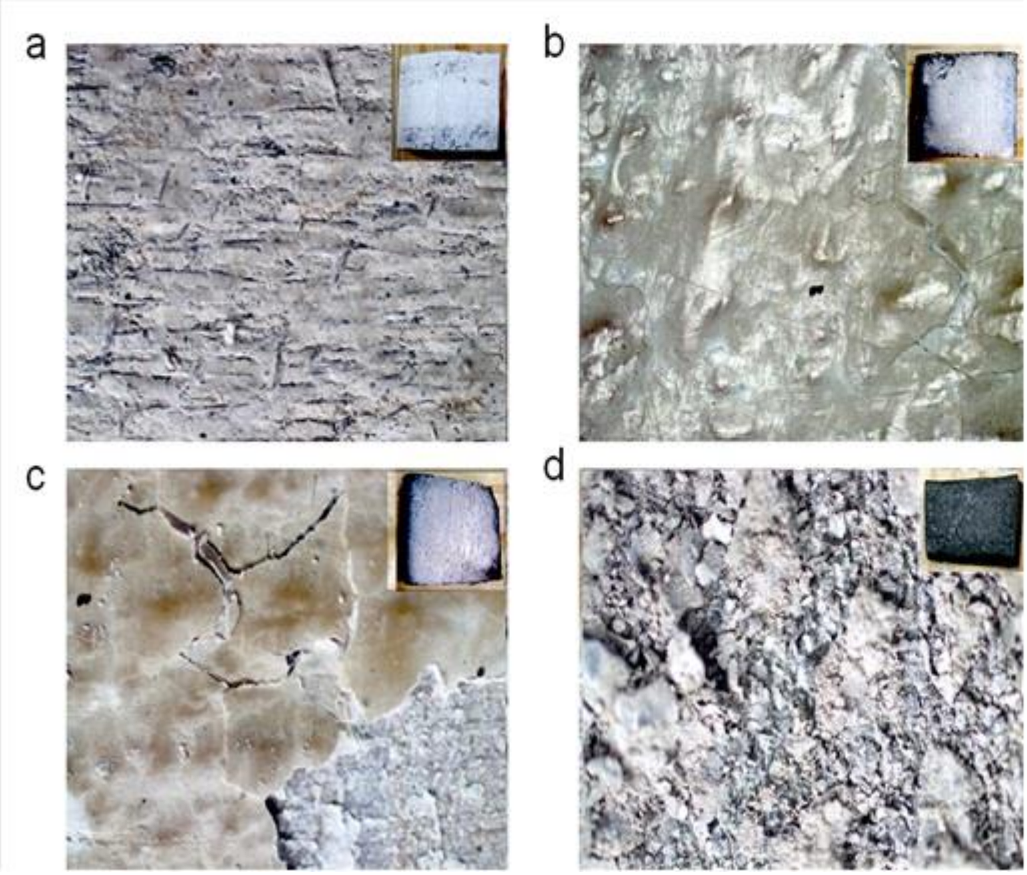

Figure 6. a) ,b) and c) show the oxidation resistance of h-BN coated wood substrate at temperatures 300^{0}C, 600^{0}C and 900^{0}C respectively. d) Shows the surface of the wood substrate subjected to carbonization up on heating above 900^{0}C. Corresponding normal pictures of the wood substrates subjected to oxidation are shown in the inset. Scale bar: 200µm.

TOC

Hexagonal boron nitride (h-BN) nanosheets are synthesized through a facile shear force liquid phase exfoliation method and demonstrated its use as a binder free oxidation and fire resistant wood coating. Characterized by intrinsic low thermal diffusivity and thermal effusivity, h-BN nanosheet coatings show an excellent fire resistance and oxidation resistance up to 900^{0}C in air.

Keyword: Hexagonal boron nitride, Nanosheets, Fire resistant coating, Thermal diffusivity, Thermal effusivity

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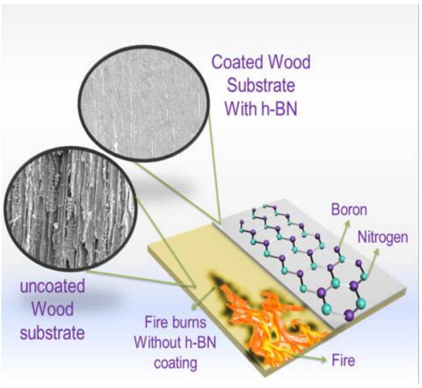
TOC figure



Supporting Information

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