Preparation of black phosphorus coatings with photo-thermal conversion properties

Hehuan Liu, Yunbo Shi, Bolun Tang, Tian Wang and Huanhuan Zhang

The Higher Educational Key Laboratory for Measuring & Control Technology and Instrumentations of Heilongjiang Province, School of Measurement-Control Technology & Communications Engineering, Harbin University of Science and Technology, Harbin 150080, People’s Republic of China

E-mail: shiyunbo@hrbust.edu.cn

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Abstract
Black phosphorus (BP) is a semiconductor material with excellent optical properties. To explore a more convenient method for preparation bulk BP and facilitate new applications of BP in engineering field, we used a single-zone tube furnace to fabricate bulk BP using tin and iodine as mineralisers. Further, a BP slurry with a uniform particle size was prepared by cutting the bulk BP in a solvent. BP coatings with different thicknesses were prepared, and their photo-thermal conversion properties were evaluated. The characterisation and test results showed that the BP coating was superimposed by BP flakes with an estimated plane size of \( \sim 10 \mu m \). The infrared absorptivity of the BP coatings was 87.83\%–92.48\%. The results clearly indicated that the BP coatings exhibit photo-thermal conversion properties that can be exploited for various applications.

1. Introduction

Black phosphorus (BP) is a direct bandgap semiconductor with a bandgap between 0.3 eV (bulk) and 2 eV (monolayer) [1–3]. BP above eight atomic layers shows the band gap properties of bulk BP. The structure and properties of BP indicate its potential application to various fields such as photoelectric devices [4–8], medicine [9, 10], infrared (IR) detection [11–13], gas sensors [14] and humidity sensors [15, 16]. Bulk BP can be converted into few-layer or monolayer BP by mechanical [8] or liquid-phase exfoliation [17]. Bulk BP can be fabricated using the high-pressure catalytic method [18, 19], bismuth solution catalytic method [20] and low-pressure mineralisation method [21–25]. The low-pressure mineralisation method offers the advantages of a high conversion rate and safe operation. However, some low-pressure mineralisation experiments, employ Au and other expensive catalysts are used, which increases the production cost of bulk BP. The bandgap characteristics of BP determine its photo-thermal conversion potential. Some photo-thermal conversion materials such as carbon nanotubes have various application prospects, photo-thermal conversion coating being one of them. The photo-thermal conversion coatings are commonly used in IR detectors. The change in the intensity of the IR light irradiated on the IR detector chip will change the output voltage of the chip by changing the temperature. The metal electrode on the IR detector surface can reflect the IR light and reduce the temperature change induced by the IR light. Therefore, the IR photo-thermal conversion absorption layer is an indispensable part of IR detectors. The existing photo-thermal conversion coatings include goldblack coatings [26], carbon nanotube coatings [27], and carbon black coatings [28, 29]. The development of photo-thermal material using a low-cost and simple fabrication method for synthesising photo-thermal conversion coatings is crucial for the future advancement of IR detectors. In this study, we focused on optimising the low-pressure mineralisation method for BP production. The optimised method requires a tubular furnace with a single temperature zone and tin and iodine as catalysts. This method is characterised by simple equipment, cheap catalysts and low toxicity. We prepared a BP slurry with a uniform particle size by cutting the bulk BP in a solvent, and we used the slurry to prepare BP coatings. We performed tests to characterise the BP coatings and explore their applicability to photo-thermal conversion.
2. Material and methods

2.1. Preparation of bulk black phosphorus

Bulk BP was fabricated and used to prepare BP coatings for photo-thermal conversion. The raw materials for the bulk BP were 500 mg of red phosphorus, 100 mg of tin powder, and 50 mg of iodine granules. A tube furnace with a single temperature zone was used to prepare the bulk BP. The raw materials were packed in a 150 mm long quartz tube with an inner diameter of 15 mm. The quartz tube was placed in the furnace, and the raw materials were placed at the end of the tube at the centre of the furnace. The temperature of the tube furnace was set as follows: heating to 620 °C in 1800 min, holding at 620 °C for 120 min, cooling to 485 °C for 600 min, holding at 485 °C for 120 min, cooling to 120 °C for 1200 min and then naturally cooling to room temperature. The experimental parameter settings for preparing the bulk BP are shown in figure 1. Consequently, bulk BP with a diameter of more than 10 mm was obtained at the cold end of the quartz tube.
Figure 2 shows the preparation process of BP coatings. First, the bulk BP was ground to powder in an agate mortar. Next, 100 mg of BP powder and 25 ml of terpineol were mixed in a beaker. The mixture was ground using a high-speed cutter at $12,000 \text{ r min}^{-1}$ for 30 min to obtain a BP suspension. The BP suspension was allowed to stand for 48 h; then, its supernatant was removed. Finally, a BP slurry was obtained at the bottom of the beaker. The BP slurry was coated on the test substrate to obtain BP coatings, and tests were performed to evaluate their photo-thermal conversion performance. Scanning electron microscopy (SEM), Raman spectroscopy and x-ray diffraction (XRD) were used to characterise the bulk BP and BP coatings.

2.2. Test platform for evaluation the photo-thermal conversion performance of BP coating
Monolayer or few-layer BP cannot exist stably in air; hence there was no need for excessive stripping of BP in this work. Thick BP flakes meet the requirements for photo-thermal conversion in the IR wavelength range as well as ensure that the BP coating does not oxidise too quickly. We used a high-speed disperser to grind the BP powder

Figure 3. (a) Image and (b) structure of the test substrate.

Figure 4. Simulation diagram of the test platform.

Figure 5. Test substrates: (a) blank, (b) coated with black phosphorus coating 1, (c) coated with BP coating 2, and (d) coated with BP coating 3.

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in the solvent to ensure uniform-sized BP flakes in the BP slurry. The BP slurry was then coated on the test substrates to form BP coatings, and the photo-thermal properties of these coatings were evaluated. The image and structural diagram of the test substrate are shown in figures 3(a) and (b), respectively. The uppermost interdigital electrode can simulate the electrode layer of the infrared detector chip. The resistance of the thermometric electrode changes with the detected temperature of the upper material. Therefore, the test substrate can detect the temperature change in the photothermal conversion layer passing through the metal electrode layer.

Figure 4 shows the platform we established to test the photo-thermal conversion performance of the BP coatings. The test platform comprises IR source, heat insulation film and test board. The IR source was an ENIR715 scattering IR light source that emits light in the wavelength range of 0–5 μm and has a radiation range that can cover the test plate. The heat insulation film was composed of a polyimide film, which offers good heat insulation and light transmittance. The influence of the thermal radiation of the light source on the platinum resistance of the test substrate was eliminated by the polyimide film.

To evaluate the performance of the BP coatings more accurately, a hood was three-dimensionally printed. The IR source was installed at the centre of the hood top to ensure that the four test substrates were in the same test environment. Then, the temperature data of the BP coatings were collected under light. Figure 5 shows the test board on which the four test substrates were placed. Figure 5(a) shows the blank substrate, and figures 5(b)–(d) show the test substrates coated with BP coatings 1–3. The output resistance data of the test board were collected using a data acquisition card, and the 6½ digits multimeter in the data acquisition card can realize the resistance value acquisition of 0.00001 Ω.

3. Results and discussion

According to the literature and formation experiments, the raw materials were heated to form a mixture, which then gradually formed bulk BP as it cooled (figure 1). During the heating process, the packaged raw materials created a mixture that attached to the quartz tube wall. During the cooling process, the mixture gradually produced bulk BP at the cold end of the quartz tube. Finally, we obtained bulk BP crystals with a diameter of more than 10 mm in the quartz tube [23]. The bulk BP structure was observed using an electron microscope and
SEM. As shown in figure 6(a), the bulk BP appeared as black crystals exhibiting a metallic lustre. Figure 6(b) demonstrates that the bulk BP showed an obvious lamellar structure. Figure 6(c) shows that the bulk BP exhibited three typical Raman peaks at 359, 436 and 463 cm$^{-1}$, corresponding to $A_{2g}^1$, $B_{2g}$ and $A_{2g}^2$, respectively. Figure 6(d) demonstrates that the bulk BP showed good crystallinity.

The surface and cross-section of the BP coatings were observed using an SEM (Zeiss Sopra 55). The figure 7 presents the SEM images of the BP coatings. The plane size of the BP flakes was approximately 10 μm, and the particle size was relatively uniform. Three BP coatings with different thicknesses were prepared. Figures 7(b)–(d) present the SEM images of the cross-sections of BP coatings 1, 2 and 3, respectively. BP coating 1 was the
thinnest, while BP coating 3 was the thickest. The coatings were superimposed with BP flakes, which is consistent with the plane characteristics.

The BP coatings were subjected to Raman scattering. Fourier-transform infrared spectroscopy (FTIR) was used to detect the IR absorptivity of the coating. Figure 8(a) shows the Raman spectra of the BP coatings. The BP coatings exhibited three typical Raman peaks at 363.5, 438 and 466.3 cm$^{-1}$, corresponding to $A_1^g$, $B_2^g$ and $A_2^g$, respectively. To test their IR absorptivity, the BP coatings were coated on a 0.2-mm-thick polished copper sheet. Because the copper sheet showed a transmissivity of 0%, the absorptivity of the BP coatings could be calculated by measuring its reflectivity. The IR absorptivity of BP in the range of 2.5 μm (limited by detection) to 5 μm (limited by light source) is presented in figure 8(b). The IR absorptivity of the BP coatings was 87.83%–92.48%.

Figure 9 shows the test results of the BP coatings. The deviation caused by the basic resistance of the substrates could be eliminated by calibration. First, the test data without illumination were collected for 105 s. During this process, the four substrates showed good consistency, indicating that all the substrates were in the same stable test environment. When the IR light was switched on at 105 s, the temperatures of the four substrates increased at different speeds. The temperature of the substrate coated with BP coating 3 increased at the fastest rate, while that of the blank substrate was the slowest for the first 100 s of illumination. After 100 s, the IR light was switched off, and the decrease in the temperature curves of the four substrates was mostly coincident.

Figure 10 shows a comparison between the temperatures of the substrates coated with BP coatings 1–3 and that of the blank substrate. The heating rate and maximum temperature of the BP coatings increased with the thickness. The maximum heating temperatures of BP coating 1, 2, 3 were 0.11348 °C, 0.19676 °C and 0.33988 °C, respectively. After the IR light was switched off, the temperatures of all three BP coatings decreased rapidly.
and eventually reached the initial temperature without. The test results clearly demonstrated that the BP coatings exhibit photo-thermal conversion properties. The photo-thermal conversion efficiency of the BP coatings increased with the thickness.

According to the aforementioned test results, the BP coatings composed of BP flakes showed excellent infrared absorption and photo-thermal conversion performance. In the existing literature, BP quantum dots have been used in tumor photo-thermal ablation owing to the photo-thermal properties of BP [9, 30]. However, no research has focussed on the photo-thermal conversion performance of BP coatings. The BP coating prepared in this study confirmed its photo-thermal conversion performance and facilitated the expansion of BP applications in engineering fields.

4. Conclusion

In summary, we introduced a simple method for preparing BP bulk. BP slurry was prepared with a uniform particle size using the solvent cutting method, and BP coatings were synthesised using the BP slurry. The structure and absorption properties of the BP coatings were characterised using SEM, Raman and FTIR. To evaluate and the photo-thermal conversion performance of the BP coatings, a test platform was established. The characterisation and test results showed that the BP coating exhibited a uniform structure, obvious infrared absorption and photo-thermal conversion performance. This research proves the applicability of BP in the field of photo-thermal conversion, which expands the applications of BP.

Data availability statement

ORCID iDs

Yunbo Shi © https://orcid.org/0000-0003-4605-9721

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