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PMMA-BN composites incorporated with Au nanoparticle fabricated by laser ablation

Atsushi Yamaguchi, Pankaj Koinkar*, Akihiro Furube

Graduate School of Technology, Industrial and Social Sciences, Tokushima, University, Tokushima 770-8506, Japan

Email: koinkar@tokushima-u.ac.jp

Abstract. As a class of layered materials, two dimensional (2D) materials have attracted great attention all around the world due to their inherent use for next generation nano technology devices. We can see 2D materials including carbon in our daily life and at many places, for instance, graphite, diamond and so on. New study is also being conducted to produce new functional materials by combining 2D material and polymer. Hexagonal boron nitride (h-BN) which is one kind of 2D material is dispersed in Poly methyl methacrylate (PMMA) or poly styrene (PS). The composite material of h-BN coated with polymer shows an improvement in the properties such as the higher thermal conductivity and higher mechanical strength. In this study, the composite material of PMMA, h-BN and gold nanoparticles has been synthesized. Boron nitride nano-structures were prepared by nanosecond laser ablation in acetone and was carried out at room temperature with laser ablation time of 120 min. The PMMA films were made by PMMA granules dissolved in acetone solvent and then mix with h-BN and gold colloid solution. The prepared composite films were characterized by scanning electron microscopy (SEM), and UV-vis spectroscopy. Such type of unique 2D nano-composite materials make their mark for the future exploitation in electronics and nanocomposite-related applications.

1. Introduction

In current era, novel 2D materials that have been studied extensively in the world includes graphene, fullerene, carbon-nanotube (CNT), and boron nitride (BN) and others [1-6]. Many researchers have shown great interest in a binary material that has been similar structure that of graphene and shows complementary properties with graphene. A few examples of these materials are molybdenum sulfide (MoS_2) and tungsten disulfide (WS_2), BN and few semiconductor transition metal compounds which are insulators. In recent years, these materials are attractive for their unique properties and their use in next generation nanotechnology devices because they are relatively easy to fabricate complex structures as compared to primary materials. Among these materials, BN has many polymorphs because B and N atoms can bind together by sp^2 and sp^3 hybridizations. The well known polymorphs of BN are hexagonal boron nitride (h-BN) and cubic boron nitride (c-BN). The h-BN has a similar kind of structure as that of graphite whereas c-BN has a structure near to that of diamond as well as

has hardness similar the order of diamond. h-BN is the most widely used polymorph among other boron nitrides due to its isoelectronic structure in which boron and nitrogen atoms are positioned alternatively to form planar conjugated layers [1-2]. the boron nitride nanostructure is considered as a promising candidate for various potential applications in high performance electron devices, gas absorbents, reinforcing agents. As a material property of BN, it is a white colored powder with a melting point of approximately 3000 ^{o}C, high band gap is 5.5 eV [7]. As a feature, it is difficult to oxidize up to around 900 ^{o}C while it is structurally stable up to around 900 ^{o}C. It has high thermal conductivity and electrical insulation properties and it has the possibility to make a composite material with new high strength. h-BN can change to c-BN by employing high pressure and high temperature. At typical high pressure about from 7 to 10 GPa and high temperature of 2000 to 3000 K, h-BN can be transformed into c-BN. In addition, it has been reported that the h-BN can change to boron nitride nanotubes and c-BN by using laser ablation [7-8]. When more laser power increased, high concentration of c-BN could be produced [2]. The BN nanostructure obtained through laser ablation process showed that there were variations in length and thickness of boron nanotube. When comparing boron nitride nanotube and carbon nanotube, boron nitride nanotube superior to carbon nanotubes in transparency. It is also the most preferable materials for strengthening polymers, ceramics and metals because of its high rigidity and excellent chemical stability. It is superior to antioxidant power and heat resistance. Recently, we have reports a simple approach for production of BN nanostructures using nanosecond laser ablation (Nd:YAG, 532 nm) in acetone at room temperature and atmospheric pressure [9]. Nowadays, studies have also been made to combine processed boron nitride nanomaterials with polymer materials to produce new functional materials. When BN is used, it has been reported that a polymer material such as poly-methyl methacrylate (PMMA) or polystyrene (PS) can be coated on the surface of boron nitride to improve the interfacial adhesion in the composite material. This polymer based BN nanocomposite exhibit the improvement in thermal conductivity and mechanical properties which is required for the applications ranging from optoelectronics to energy devices [1,10]. In addition, few research reports described that the BN, which is an insulator, is decorated with gold nanoparticle make new composite materials. These novel 2D nano-composite materials make their mark for the future exploitation in electronics and nanocomposite-related applications [11-12]. In this study, we have reported the preparation of PMMA-BN composites film incorporated with Au nanoparticle using laser ablation in acetone.

2. Experimental

2.1 Chemicals and Materials

Chemicals and materials used were purchased and were used as received; BN powder (Wako Chemical Japan), $HAuCl_4$ $4H_2O$ (0.1 ml 2.5×10^{-5} mol) (Kishida Chemical, Japan, 99.0 %), $Na_3C_6H_5O_7$ (Kanto Chemical, Japan : 0.100 g /10 ml, 294.1 g /mol), Poly-metylmetaclyl-acid (PMMA), and Acetone (Kishida Chemical, Japan : 99.5%).

2.2 Preparation of 40 nm diameter gold nanoparticles

Gold nanoparticles are synthesized by the chemical method. An aqueous solution of $HAuCl_4$ (0.1 ml : 2.5×10^{-5} mol) was added into deionized water (100 ml). The mixture was heated and stirred at 100 ^{o}C. Then, the $Na_3C_6H_5O_7$ (1 ml) solution was added into the mixture. After this, the mixture was stirred at heating for 5 minutes and then kept for cooling at room temperature. Finally, deionized water was added for total volume 100 ml. Au nanoparticle size was determined by the experimentally observed peak position of UV-vis spectra.

2.3 Laser Ablation

The BN nanostructure was prepared by nanosecond laser ablation using acetone as a solvent. We used analytical grade h-BN powder about 100 mg mixed with 30 mL acetone into a glass bottle. Before the laser ablation, the solution was kept for magnetic stirring for 30 min. The laser ablation was performed

using Nd:YAG laser (wavelength 532 nm, pulse duration 10 ns, pulse repetition frequency 10 Hz, beam size 5 mm and laser power 56 mJ). The solution was rotated by magnetic stirrer during the laser ablation process, and laser ablation time was 120 min. After laser ablation, BN colloidal suspension was heated in air to obtain dry BN nanoparticle in the form of powder. The laser ablated BN sample was characterized by and scanning electron microscopy (SEM) and to confirm the formation of nanostructure, surface morphological changes as well as optical features.

2.4 Preparation of PMMA-Au-BN nanocomposite

About 0.33 ml of Au nanoparticle colloid was dissolved into 5 ml of Acetone. After this, 2.8 mg and 14.2 mg laser ablated BN powder was added into Au nanoparticle colloid and acetone mixture. This mixture was kept on magnetic stirring for the duration of 30 minutes to prepare Au-BN solution. Finally, 1.34 g of PMMA was dissolved into Au-BN solution. PMMA-Au-BN solution into the glass bottle at room temperature for 3 hours. At the same time, sample also without BN content was also prepared which is refereed as sample S1. The PMMA-Au-BN composite film with 2.8 g of BN and 14.2 g of BN hereafter referred as sample S2 and S3 respectively. The preparation details of sample 1, 2 and 3 is shown in Table 1.

Table 1. Synthesis details of PMMA-BN-Au nanocomposite.

Sample	Acetone (ml)	PMMA (g)	BN (mg)	Au colloid (ml)	BN : Au (Weight ratio)
S1	5	1.34	0	0.33	0:1
S2	5	1.34	2.8	0.33	100:1
S3	5	1.34	14.2	0.33	500:1

3. Results and Discussion

Figure 1 shows that the photographs of three different samples S1, S2 and S3. Figure 1 (a) shows the image of sample S1 that PMMA and Au nanoparticle only whereas Figure 1 (b) displayed the image of sample S2 that is PMMA and Au nanoparticle with BN of 2.8 mg. Figure 1 (c) shows the photograph of sample S3 that PMMA and Au nanoparticle with BN 14.2 mg. It is obvious that there was no bubble in the sample except a part.

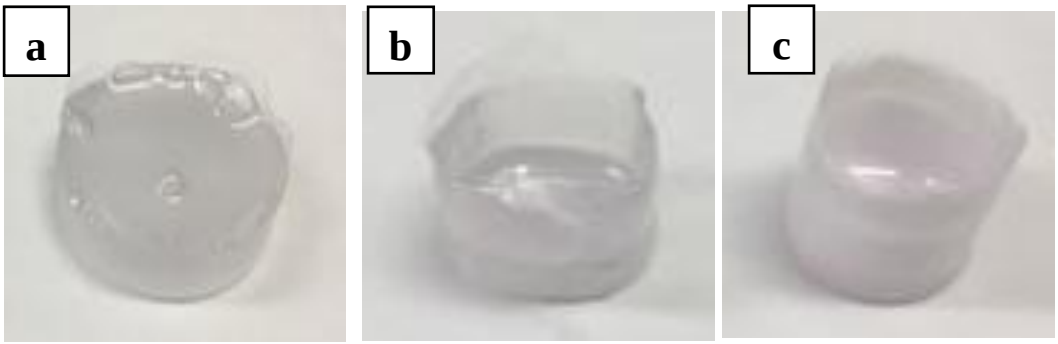


Figure 1. Photographs of 3 different types of PMMA-BN-Au film (a) S1 (PMMA-Au without BN, (b) S2 (PMMA-Au with 2.8 mg BN), (c) S3 (PMMA- Au with 14.2 mg BN).

As the amount of boron nitride increases, the color of the film produced is purplish because of Au nanoparticles contained in the film are influenced by boron nitride to scatter the incident light. Whether Au nanoparticles contained in these samples are aggregated or not is examined by using

reflection spectra or SEM images.

The polymer nanocomposite material prepared by combining PMMA, BN and Au nanoparticles was characterized using reflection spectra. Figure 2 shows the reflection spectra of samples S1, S2, and S3. For comparison, the reflection spectrum of PMMA is also included. In the case samples S2 and S3, Au nanoparticles are considered to form aggregation because plasmon absorption of Au was seen between 500 nm and 700 nm and grows steadily stronger. Non-aggregated Au would give absorption only between 500 nm and 550 nm. Plasmon absorption was observed when boron nitride was contained in the sample. It is due to the influence of gold nanoparticle scattering by with BN.

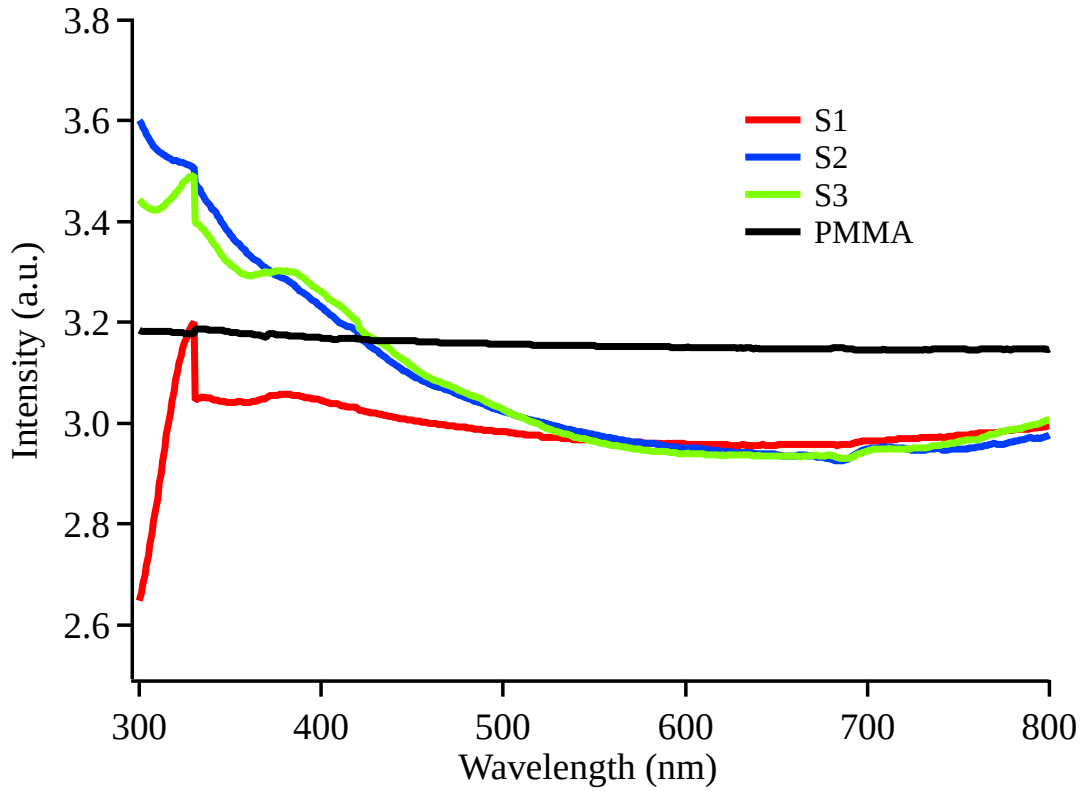


Figure 2. Reflection spectra of PMMA, S1, S2, and S3 sample.

Figure 3 shows that SEM images of (a) laser ablated BN, (b) Au nanoparticle on PMMA (sample S1, (c) Au nanoparticle on PMMA-BN (Sample S2). Figure 3 (a) reveals the images of the laser ablated BN for 120 min which confirmed the formation of micro and few hundred nano order sheets. Figure 3 (b) illustrates SEM images of laser ablated BN for 120 min. The image shows the formation of BN nanostructures upon laser ablation. Figure 3 (b) shows image of sample S1 which clearly indicates the uniformly dispersed Au nanoparticle on PMMA films. Figure 3 (b) depicts the image of sample S2 which shows the coverage of Au nanoparticle and PMMA-BN composite film. It is observed that the diameter of Au nanoparticle is about 40 nm. Furthermore, back scattered electron (BSE) image provides a sharp composition contrast between element having high atomic number and element having low atomic number. Figure 4 shows a conventional BSE image of sample 3 at on scale 1 μm and 500 nm. Figure 4 (a) to (b) are images taken with black and white change depending on the size of the atomic number. The material with the lower atomic number becomes black, and the material with the higher atomic number becomes whiter. Figure 4 (a) shows that it was confirmed that Au nanoparticles and boron nitride spreads on the PMMA surface. Figure 4 (b) is an enlarged image of

Figure 4 (a). Figure 4 (b) shows that PMMA and BN are represented by black color while gold nanoparticles by white color. It is found that the highly dense gold nanoparticles are distributed on the surface of PMMA-BN as compared to sample 2 and this may be attributed to high concentration of BN in sample S3.

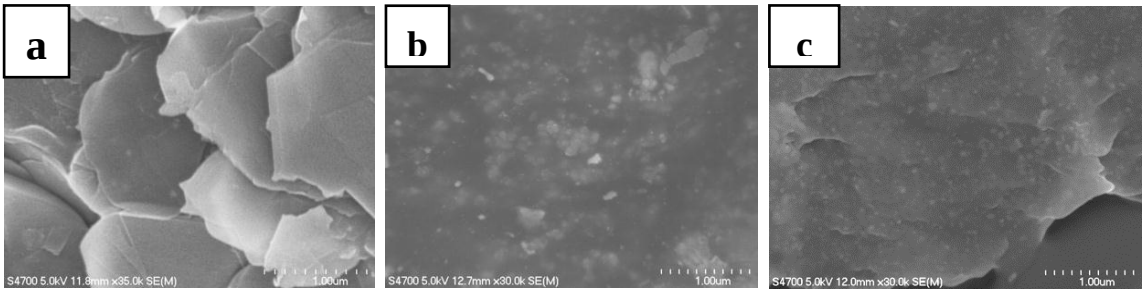
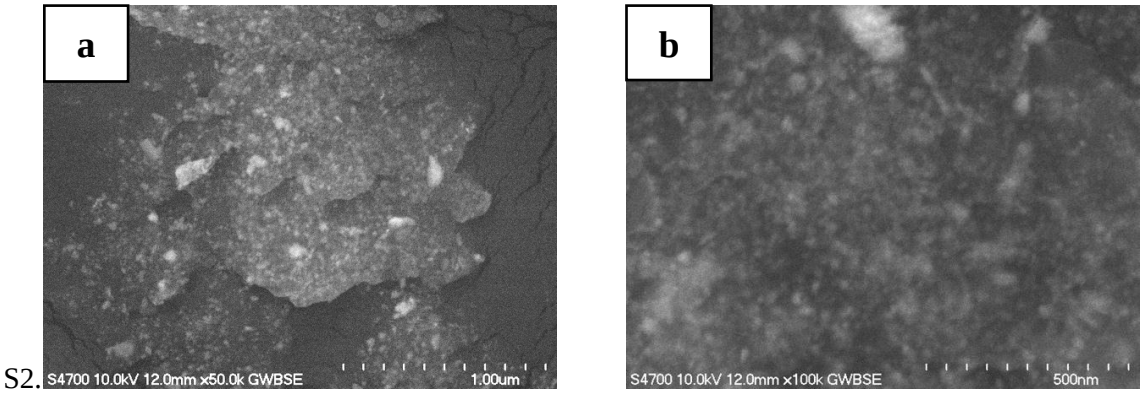


Figure 3. SEM images of (a) laser ablated BN, (b) sample S1 (c) Sample.



S2.

Figure 4. Back scattered electron (BSE) image sample S3.

4. Conclusion

We have successfully fabricated the BN composite material using PMMA and Au nanoparticle. The formation of composite material is confirmed by SEM images and UV-vis spectra. In addition, it is clearly seen from the BSE image that the elements of composite material can be distinguished according to their atomic number. These nanocomposite materials might be prime candidate for future optoelectronics devices.

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