

Fabrication and Characterization of Carbonized Rice Husk/Barium Titanate Nanocomposites

G J H Melvin^{1,*}, Z Wang², Q-Q Ni³, N J Siambun¹ and M M Rahman¹

¹ Faculty of Engineering, Universiti Malaysia Sabah, Jalan UMS,
88400 Kota Kinabalu, Sabah, Malaysia.

² Institute of Carbon Science and Technology, Shinshu University,
4-17-1 Wakasato, Nagano 380-8553, Japan.

³ Department of Functional Machinery and Mechanics, Shinshu University,
3-15-1 Tokida, Ueda 386-8576, Japan.

*melvin.gan@ums.edu.my

Abstract. Carbon materials were prepared by carbonizing rice husk (RHs) at 2500 °C. Few- and multi-layer graphene were obtained from this carbonization process. Barium titanate (BTO) nanoparticles were fabricated by using sol-gel method. Then, the BTO nanoparticles were grafted onto the surface of carbonized rice husk (CRH) to fabricate CRH/BTO nanocomposites. The nanocomposites were characterized using scanning transmission electron microscopy (STEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), Raman measurement, and X-ray photoelectron spectroscopy (XPS). Based on the broadening of (1 1 0) peak from XRD result, the average crystalline size of BTO nanoparticles were calculated to be 16.5 nm. Coexistence of cubic and tetragonal phase of BTO nanoparticles is expected, based on the XRD and Raman results. From XPS result, carbon, barium, titanium, and oxygen peaks were also observed. The combination of CRH with BTO can integrate the properties of these two components to form nanocomposites for broad applications.

1. Introduction

Since the discovery of fullerene in 1985 [1]; the first synthesis in 1976 [2] and the structural characterization in 1991 [3] of carbon nanotubes (CNTs); and the extraction of graphene from bulk graphite in 2004 [4], the interest in carbon materials has rapidly increased. Furthermore, carbon materials possess outstanding properties that allow them to be exploited for various applications and research studies. Not limited to chemical process or reaction to obtain carbon materials, they also can be derived from agricultural waste materials, such as rice husks (RHs), through carbonizing them using heat [5-7]. Moreover, unique structure and morphology of carbon materials derived from waste materials also can be obtained at high temperature [8, 9]. The utilization of waste materials to obtain valuable carbon materials can promotes greener and low cost synthesis process.

Barium titanate (BTO) is one of the widely used materials for electric ceramics and has been applied for wide range of applications [10-12]. Various methods can be carried out to fabricate BTO particles. For instance, Bi et al [13] and Huang et al. [14] used solvent-thermal method to fabricate BTO/CNT compound. Meanwhile, Wang et al. [15] fabricated BTO and carbon black compound by using sol-gel method. Sol-gel method is a broadly used and common fabrication approach, which offer



a lot of advantages such as high purity, better homogeneity, lower temperature of preparation, and low manufacturing cost [16, 17].

In this study, the RHs were carbonized at high temperature of 2500 °C (CRH). Then, the BTO nanoparticles (sol-gel method) were grafted onto the surface of CRH to fabricate CRH/BTO nanocomposites. Their structure, morphology, elemental composition and crystallization were evaluated and discussed. This type of material can be exploited for various applications, such as electromagnetic wave absorber [10-12], dielectric materials or microelectronic applications [18], energy storage [19], and so on.

2. Experimental

The carbonization of RHs was carried out in two steps. First, the raw RHs were pre-carbonized at 800 °C, under the presence of argon gas, for 1 h using furnace. Then, the pre-carbonized RHs were loaded into graphite box, further heated at 2500 °C, 0.5 h using graphite resistance furnace operating in a high purity argon gas atmosphere at 760 Torr. The samples in both steps were cooled down naturally and then grounded into powder. RHs carbonized at 2500 °C will be denoted as CRH, hereafter.

BTO nanoparticles were prepared by using sol-gel method based on Refs. [10-12], with some modifications, and then CRH were mixed together to fabricate CRH/BTO nanocomposites. Barium acetate $\text{Ba}(\text{CH}_3\text{COO})_2$, titanium tetraisopropoxide $\text{Ti}[(\text{CH}_3)_2\text{CHO}]_4$, acetic acid, ethanol, and pure water were used as the chemical reagents. $\text{Ba}(\text{CH}_3\text{COO})_2$ was dissolved in mixed solution of 20 ml ethanol and 3 ml acetic acid (solution 1), stirred in water bath at 60 °C for 0.5 h. Simultaneously, $\text{Ti}[(\text{CH}_3)_2\text{CHO}]_4$ was mixed in 10 ml ethanol (solution 2). Solution 1 and 2 were combined and 1 ml pure water was added to perform hydrolysis. Then these two solutions were stirred at 60 °C for 1.0 h to form a sol, which contained Ba/Ti molar ratio 1:1. Next 0.2 g CRH were added to the final solution, sonicated for 0.5 h, and stirred furthermore for about 0.5 h, 90 °C until gel was formed. The black color gel was then dried at 100 °C for 12 h to make an xerogel. Finally, the product was calcined at 800 °C for 2 h under the presence of argon gas. Samples for BTO nanoparticles were prepared using similar process excluding the addition of CRH.

The samples were observed using scanning transmission electron microscopy (STEM; Hitachi HD-2300A) and transmission electron microscopy (TEM; JEM-2100F, JEOL) operated at 200 kV. X-ray diffraction (XRD; Rigaku SmartLab) was conducted to characterize the crystal structure. Raman spectroscopy measurement was conducted on a Raman spectrometer (Renishaw inVia Raman spectroscope) with 532 nm laser excitation. X-ray photoelectron spectroscopy (XPS; PHI Quantera II) was performed to characterize the elemental composition.

3. Results and discussions

STEM image is shown in figure 1(a). BTO nanoparticles can be observed to be grafted onto the surface of CRH. Noticeably, the BTO nanoparticles partially bundled up to form a bigger agglomerate. The BTO nanoparticles were dispersed throughout the CRH surface. Magnified TEM images were depicted in figure 1(b) and (c), for clearer observation. The BTO nanoparticles are in spherical shape and also grafted onto the surface of CRH. Figure 1(c) further reveals that the BTO nanoparticle form a single crystal with crystal spacing of ~ 0.28 nm corresponds to (1 1 0) crystal plane [10-12]. RHs carbonized at 2500 °C produced clean surface, clear edges, and relatively high crystallinity of few- and multi-layer graphene. Furthermore, from figure 1(a)~(c), mixture of flattened graphene, corrugated graphene, and partially carbon cage can be observed. Moreover, no amorphous carbon was observed on the graphene surface. This can be attributed to realignment or restructure of vapor carbon at high temperature [9].

XRD patterns of the CRH/BTO are shown in figure 2(a). All peaks of the CRH/BTO can be assigned to the cubic perovskite structure (JCPDS no. 31-0174) [10-12]. Strong intensity of (110) peak can be observed from CRH/BTO at $2\theta = 31.6^\circ$. The typical (002) peak of carbon materials, which in our case CRH, can be detected at $2\theta = 26.2^\circ$. Using the Scherrer's equation as shown below

$$D = \frac{0.9\lambda}{\beta \cos \theta} \quad (1)$$

where, D is the particle size, λ is the wavelength of the Cu K α radiation (0.15406 nm), θ is the diffraction angle, and β is the full width at half maximum of the peak, average crystalline size of BTO nanoparticles were calculated to be 16.5 nm from the broadening of BTO/CNT (110) peak. From the TEM images, the diameter of BTO nanoparticles are about 10~15 nm, and this shows high similarity with the calculation using equation 1.

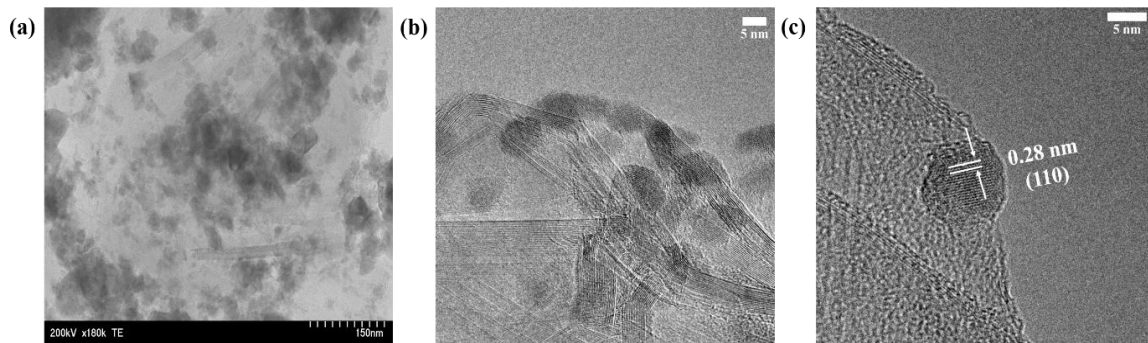


Figure 1. (a) STEM, (b) and (c) TEM images of CRH/BTO nanocomposites.

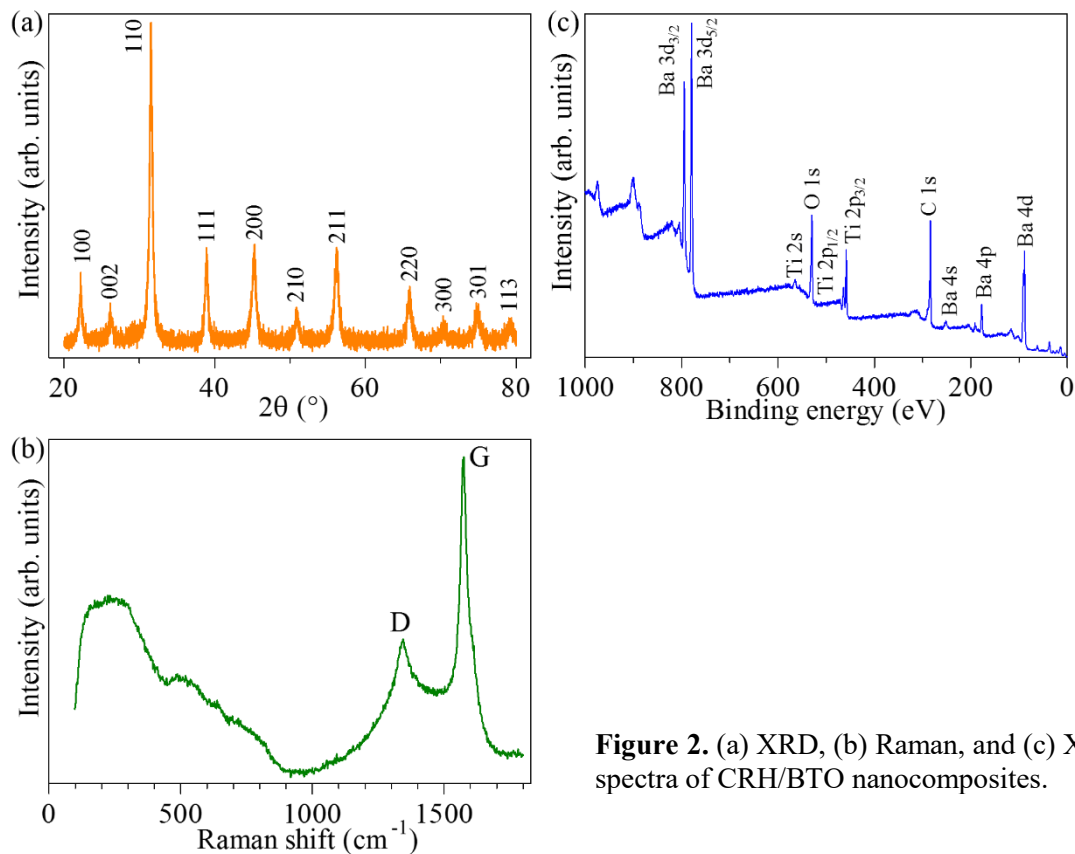


Figure 2. (a) XRD, (b) Raman, and (c) XPS spectra of CRH/BTO nanocomposites.

Raman spectroscopy is a nondestructive and an effective tool to probe structure at the atomic scale on the basis of vibrational symmetry. Generally, cubic BTO has no Raman active modes, but such modes are expected for the noncentrosymmetric tetragonal structure [12, 20]. The Raman spectra of CRH/BTO is depicted in figure 2(b). The Raman peaks at low wavenumber (100~1000 cm⁻¹) can be

assigned to more than one phonon mode, which are suggestive of a tetragonal phase [12, 20]. Although XRD patterns reveal a cubic perovskite structure (figure 2(a)), a certain degree of tetragonal phase mixed with cubic phase on the atomic scale is expected [12, 20]. From the XRD and Raman results, coexistence of cubic and tetragonal phase is thinkable. The typical characteristic bands of carbon materials were also observed from CRH/BTO nanocomposites, D band (defect) at $\sim 1345\text{ cm}^{-1}$ and G band (graphite band) at $\sim 1575\text{ cm}^{-1}$. The relative intensity of the D and G bands (I_D/I_G) obtained from the Raman spectra can be associated to the amount of structural defects. Based on Ref. [12], the I_D/I_G for pristine CNT ($d = 20\text{-}30\text{ nm}$) and BTO/CNT is 1.02 and 1.09, respectively. The I_D/I_G for CRH/BTO is 0.6, and relatively lower than those mentioned before. This might be attributed to the high crystallinity of CRH.

XPS evaluation was conducted to determine the elemental composition of CRH/BTO nanocomposites, and the results are illustrated in figure 2(c). The XPS wide survey spectra of the CRH/BTO confirmed the presence of carbon (C 1s) at 284 eV, oxygen (O 1s) at 530 eV, barium (Ba 3d, Ba 4d, Ba 4p, Ba 4s), and titanium (Ti 2p, Ti 2s). The presence of Ba 3d, Ti 2p, and O 1s peaks further proves the success formation of BTO nanoparticles. The Ba 3d_{5/2} and Ti 2p_{3/2} appeared at 779.2 eV and 458.4 eV, respectively, and are in good agreement with those reported [10, 12, 20]. The atomic percentage ratios for the CRH/BTO are 27.6% for C 1s, 11.7% for Ba 3d, 10.6% for Ti 2p, and 50.1% for O 1s. The atomic percentage ratio of Ba 3d and Ti 2p is about 1:1, similar to the molar ratio of Ba/Ti in the fabrication process. Notably, no other elemental compositions are detected, proving the high purity of CRH/BTO nanocomposites.

4. Conclusions

BTO nanoparticles were fabricated by using sol-gel method and then immobilized onto the surface of RHs carbonized at 2500 °C, which consist of few- and multi-layer graphene. Their structure, morphology, elemental composition and crystallization evaluations were carried out through STEM and TEM observation, XRD and Raman measurement, and XPS evaluation. The BTO nanoparticles exist in spherical shape and successfully grafted onto the surface of CRH. The average crystalline size of BTO nanoparticles were calculated to be 16.5 nm, and is in good agreement with the TEM observation. Mixture of cubic and tetragonal phase is expected from the BTO nanoparticles. CRH/BTO nanocomposites can be exploited by utilizing both properties from separate material for various applications.

Acknowledgements

This work was supported by grant (SLB0120-SG-2016) from Universiti Malaysia Sabah (UMS), Malaysia. The authors also would like to acknowledge members of Institute of Carbon Science and Technology, Japan for their technical supports.

References

- [1] Kroto H W, Heath J R, O'Brien S C, Curl R F and Smalley R E 1985 *Nature* **318** 162-3
- [2] Oberlin A, Endo M, Koyama T 1976 *J. Cryst. Growth* **32** 335-49
- [3] Iijima S 1991 *Nature* **354** 56-8
- [4] Novoselov K S, Geim A K, Morozov S V, Jiang D, Zhang Y, Dubonos S V, Grigorieva I V and Firsov A A 2004 *Science* **306** 666-9
- [5] Guo Y, Yu K, Wang Z and Xu H 2000 *Carbon* **41** 1645-87
- [6] Wang L, Wang X, Zou B, Ma X, Qu Y, Rong C, Li Y, Su Y and Wang Z 2011 *Bioresour. Technol.* **102** 8220-4
- [7] Kumagai S, Sato M and Tashima D 2013 *Electrochim. Acta* **114** 617-26
- [8] Saito Y and Arima T 2007 *Carbon* **45** 248-55
- [9] Wang Z, Ogata H, Morimoto S, Fujishige M, Takeuchi K, Hashimoto Y and Endo M 2015 *Carbon* **90** 154-9
- [10] Melvin G J H, Ni Q-Q and Wang Z 2016 *Phys. Status Solidi A* DOI: 10.1002/pssa.201600541

- [11] Ni Q-Q, Melvin G J H and Natsuki T 2015 *Ceram. Int.* **41** 9885-92
- [12] Melvin G J H, Ni Q-Q and Natsuki T 2014 *J. Alloy. Comp.* **615** 84-90
- [13] Bi C, Zhu M, Zhang Q, Li Y and Wang H 2011 *J. Nanosci. Nanotechnol.* **11** 1030-6
- [14] Huang X, Chen Z, Tong L, Feng M, Pu Z and Liu X 2013 *Mater. Lett.* **111** 24-7
- [15] Wang G, Chen X, Duan Y and Liu S 2008 *J. Alloy. Compd.* **454** 340-6
- [16] Kaviani R and Saidi A 2009 *J. Alloy. Comp.* **468** 528-32
- [17] Li W, Xu Z, Chu R, Fu P and Hao J 2009 *J. Alloy. Comp.* **482** 137-40
- [18] Wan Y-J, Zhu P-L, Yu S-H, Yang W-H, Sun R, Wong C-P and Liao W-H 2017 *Compos. Sci. Technol.* **141** 48-55
- [19] Wang G, Huang X and Jiang P 2017 *ACS Appl. Mater. Interfaces* DOI: 10.1021/acsami.6b14454
- [20] Brutchey R L and Morse D E 2006 *Angew. Chem.* **118** 6714-6