

# Deposition of YBCO Nanoparticles on Graphene Using Matrix-assisted Pulsed Laser Evaporation

Songlin Yang<sup>1</sup>, Longyi Chen<sup>1</sup>, Paul Ogilvie<sup>2</sup>, and Jin Zhang<sup>1</sup>

<sup>1</sup>Department of Chemical and Biochemical Engineering, University of Western Ontario  
London, Ontario, Canada, N6A 5B9

<sup>2</sup>Saint Jean Carbon Inc.  
86 Wilson Street, Oakville, ON L6K 3G5

**Abstract** - Matrix-assisted pulsed laser evaporation (MAPLE) process has demonstrated to deposit polymers with a contamination-free fashion. Here, MAPLE process is applied to deposit yttrium barium copper oxide (YBCO) superconductor particles on graphene sheets. The microstructures and elemental composition of YBCO nanoparticle deposited on graphene sheet by the MAPLE process were studied as a function of the irradiation time ( $t$ ). The amount of YBCO nanoparticles deposited on graphene is increased with increasing  $t$ . The average particle size of the spherical YBCO nanoparticles deposited on graphene sheets is decreased from  $70 \pm 25$  nm to  $50 \pm 15$  nm when  $t$  increases from 0.5 hr to 2.0 hr. This study demonstrates that MAPLE is a suitable process for depositing superconductor nanoparticles on graphene sheets.

**Keywords:** Laser processing; graphene hybrid nanosheets; superconductive materials

## 1. Introduction

Yttrium barium copper oxide (YBCO), a large series of crystalline chemical compounds with molecular formula,  $\text{YBa}_2\text{Cu}_3\text{O}_7$ , displays superconductivity properties at temperature around 77 K. High-temperature superconductivity has been utilized in magnetic resonance imaging, electrical devices, and magnetic field sensors, *etc.* [1]. Long-term efforts have been attempted to develop thin/ultra-thin superconductivities at high temperature. For instance, YBCO thin film coated on electrically conductive materials can overcome the low current density, the grain boundary angle, and, therefore, they could be used in different areas, including transformers and cables.[2]

Graphene is a two-dimensional carbon nanomaterial. It offers remarkable mechanic and electrical properties, and find various applications in energy-storage device, polymer composite materials, mechanical resonators and sensors *etc.*[3]. To date, attempts have been made to develop graphene-nanoparticles nanocomposites with enhanced performance and novel chemical, physical properties for the applications in supercapacitor, photovoltaic, electrodes, sensors *etc.* [4, 5] Conventional method to deposit nanoparticles on graphene sheets chemical vapor deposition (CVD) and physical vapor deposition (PVD) can be applied to deposit nanostructured materials on graphene sheets.[6-7] However, conventional vapor deposition process may cause decomposition of the substrate materials.[8] In addition, very few studies have been reported on incorporating YBCO nanoparticles onto graphene sheets. The major challenges lie in producing stable YBCO nanoparticles, and maintaining strong interaction between YBCO nanoparticles and graphene sheet.

Here, we report a new way of fabricating the graphene/YBCO hybrid nanosheets by matrix-assisted pulsed laser evaporation (MAPLE). MAPLE provides a more gentle and protective method to deposit nanoparticles, biomaterial and polymer on the substrate.[9] The target material is normally dissolved or suspended in a volatile solvent, which is then frozen by liquid nitrogen. The frozen solution (target) is irradiated by a pulsed laser. Under ultra-high vacuum, solvent molecules are pumped away, and the target molecules can be deposited on the substrate surface. In this paper, the size and size distribution of YBCO nanoparticles deposited on graphene sheets were characterized as a function of laser irradiation time ( $t$ ). This research work demonstrates a simple and contamination-free method to produce graphene-nanoparticles hybrid nanosheets.

## 2. Results and Discussions

All the measures were performed in triplicate. Figure 1 shows the UV-Vis spectra of graphene oxide and graphene, and the small inset is the TEM micrograph of graphene sheets. The absorbance of graphene oxide in aqueous medium is observed at 231 nm. After hydrazine reduction, the absorbance peak has a red shift to 270 nm, which suggested that the electronic conjugation within graphene basal plane is restored.[2-3] The graphene nanosheets can be clearly seen in the TEM micrograph, wrinkles or folds on the nanosheets may be attributed to graphene's large aspect ratio.

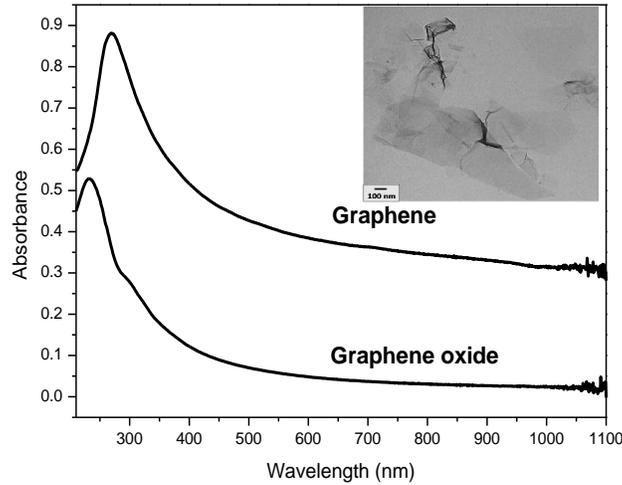


Fig. 1: UV-Vis spectra of graphene oxide and graphene. The small inset is the TEM micrograph of the graphene sheets.

YBCO powder used as the precursor for producing nanoparticles in MAPLE were characterized. Figure 2a shows the TEM micrograph of YBCO powder which shows irregular particle shape with  $3.5 \pm 2 \mu\text{m}$  of average particle size. The

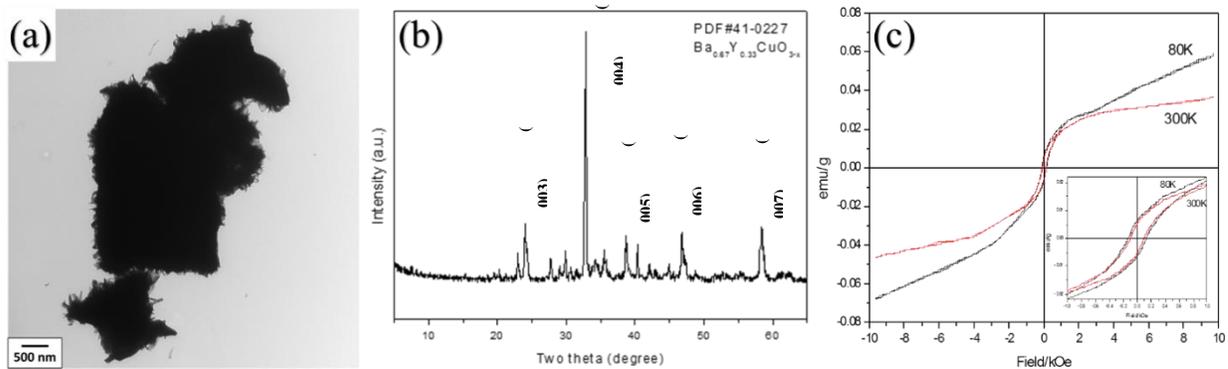


Fig. 2: (a) TEM micrograph of YBCO particles used as the precursor of YBCO nanoparticles produced by MAPLE. (b) XRD profile of the YBCO powder, similar with the XRD proles of  $\text{Ba}_{0.68}\text{Y}_{0.33}\text{CuO}_{3-x}$  (PDF#41-0227). (c) Hysteresis loops of YBCO powder at 300 K and 80K.

XRD profile of the YBCO powder fits well with the structure of  $\text{Ba}_{0.68}\text{Y}_{0.33}\text{CuO}_{3-x}$  (the card number PDF#41-0227) as shown in Figure 2b. The magnetic properties of YBCO powder was investigated by VSM under 10 kOe. The hysteresis loops of YBCO were measured at 80 K and 300 K respectively, as shown in Figure 2c. The YBCO powder shows ferromagnetic at room temperature, and typical superparamagnetic properties at low temperature. When temperature decreased from 300K to 80K, the saturation magnetisation ( $M_s$ ) at 10 KOe increases from 0.03 to 0.05 emu/g, while the coercivity ( $H_c$ ) increases slightly from 120.6 to 123.0 Oe. As the particle size is much smaller than the bulk YBCO, the critical superconductor temperature for the YBCO powder may be even lower than 80 K.

In the MAPLE process, the YBCO powder is ablated by the laser irradiation due to the photon-electron interaction. Under the high vacuum, the ablated nanoparticles transported with the evaporated solvent to the graphene sheets used as

the substrate. Here, laser irradiation time ( $t$ ) = 0.5 hr, 1.0 hr, 1.5 hr, 2.0 hr. The microstructure and particle size distribution of the hybrid nanosheets were studied by TEM as function of the laser irradiation time,  $t$ . The spherical nanoparticles of the YBCO are observed on graphene; and the amount of YBCO nanoparticles increases with the laser irradiation time,  $t$ . In Figure 3a, the average particles size of YBCO nanoparticle is  $70 \pm 25$  nm when  $t = 0.5$  hr, compared to  $3.5 \pm 2$   $\mu\text{m}$  of the precursor, YBCO powder. When  $t$  increases to 1.0 hr, the YBCO nanoparticles with smaller particles size (diameter  $< 20$  nm) are increasing (Figure 3b). When  $t = 1.5$  hr and 2.0 hr (Figure 3c and 3d), the average particle size is reduced to  $50 \pm$

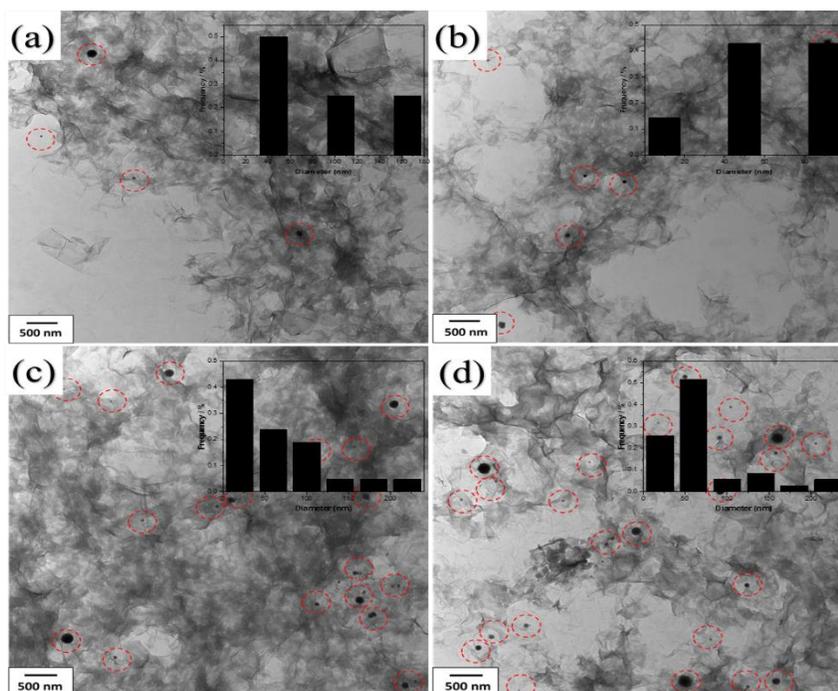


Fig. 3: TEM micrograph of the YBCO particles on the surface of the substrate under different deposition time ( $t$ ) (a)  $t = 0.5$  hr; (b)  $t = 1.0$  hr; (c)  $t = 1.5$  hr; (d)  $t = 2.0$  hr; (e) TEM-EDX spectrum of the graphene/YBCO hybrid nanosheets ( $t = 2.0$  hr).

15 nm with a broad size distribution. While more small nanoparticles (diameter  $< 20$  nm) can be observed when  $t = 2.0$  hr compared to the size of YBCO nanoparticles deposited with  $t < 1.0$  hr. In addition, the result of TEM-EDX spectrum of hybrid graphene/YBCO nanosheets with  $t = 2.0$  hr, which is same as the bulk YBCO.[11] In MAPLE process, large YBCO particles could be ablated along with the evaporation of the solvent.[12]

#### 4. Conclusions

The hybrid graphene nanosheet was successfully synthesized by a modified Hummers method following a laser process. YBCO nanoparticles were deposited on graphene sheets by MAPLE with a pulsed Nd:YAG laser at 532 nm, a contamination-free process. The results of TEM clearly indicate that the particle size and size distribution of YBCO nanoparticles deposited on the surface of graphene sheets by MAPLE depend on the irradiation time,  $t$ . The amount of YBCO nanoparticles with smaller particles size (diameter  $< 20$  nm) increases with increasing  $t$  in the MAPLE process. Consequently, MAPLE is able to produce graphene/YBCO hybrid nanosheets without additional chemical reagents.

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#### References

- [1] R. Hott, Application Fields of High-Temperature Superconductors, in: A.V. Narlikar (Ed.) High Temperature Superconductivity 2. Springer Berlin Heidelberg, Berlin, Heidelberg, pp. 35-48, 2004.

- [2] V. Narayanan, I. Van Driessche, "Aqueous chemical solution deposition of lanthanum zirconate and related lattice-matched single buffer layers suitable for YBCO coated conductors: A review," *Prog. Solid State Chem.*, vol. 40, pp. 57-77, 2012.
- [3] S. Park, R. S. Ruoff, "Chemical methods for the production of graphenes," *Nat Nano*, vol. 4, pp. 217-224, 2009.
- [4] D. Wang, R. Kou, D. Choi, Z. Yang, Z. Nie, J. Li, L.V. Saraf, D. Hu, J. Zhang, G. L. Graff, J. Liu, M. A. Pope, I. A. Aksay, "Ternary Self-Assembly of Ordered Metal Oxide-Graphene Nanocomposites for Electrochemical Energy Storage," *ACS Nano*, vol. 4, pp. 1587-1595, 2010.
- [5] X. Huang, Z. Yin, S. Wu, X. Qi, Q. He, Q. Zhang, Q. Yan, F. Boey, H. Zhang, "Graphene-Based Materials: Synthesis, Characterization, Properties, and Applications," *Small*, vol. 7, pp. 1876-1902, 2011.
- [6] L. Montero, G. Gabriel, A. Guimerà, R. Villa, K.K. Gleason, S. Borrós, "Increasing biosensor response through hydrogel thin film deposition: Influence of hydrogel thickness," *Vacuum*, vol. 86, pp. 2102-2104, 2012.
- [7] S. R. Foltyn, P. Tiwari, R.C. Dye, M.Q. Le, X.D. Wu, "Pulsed laser deposition of thick YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7- $\delta$</sub>  films with J<sub>c</sub>  $\geq$  1 MA/cm<sup>2</sup>," *Appl. Phys. Lett.*, vol. 63, pp. 1848-1850, 1993.
- [8] K. L. Choy, "Chemical vapour deposition of coatings," *Prog. Mater Sci.*, vol. 48, pp. 57-170, 2003.
- [9] F. Stokker-Cheregi, A. Matei, M. Dinescu, C.E. Secu, M. Secu, "Photoluminescence of Eu-doped LiYF<sub>4</sub> thin films grown by pulsed laser deposition and matrix-assisted pulsed laser evaporation," *J. Phys. D: Appl. Phys.*, vol. 47, pp. 045304-09, 2014.
- [10] D. Li, M.B. Muller, S. Gilje, R.B. Kaner, G.G. Wallace, "Processable aqueous dispersions of graphene nanosheets," *Nat Nano*, vol. 3, pp. 101-105, 2008.
- [11] C. S. Lim, L. Wang, C.K. Chua, Z. Sofer, O. Jankovsky, M. Pumera, "High temperature superconducting materials as bi-functional catalysts for hydrogen evolution and oxygen reduction," *J. Mater. Chem. A*, vol. 3, pp. 8346-8352, 2015.
- [12] A. P. Caricato, V. Arima, M. Catalano, M. Cesaria, P. D. Cozzoli, M. Martino, A. Taurino, R. Rella, R. Scarfiello, T. Tunno, A. Zacheo, "MAPLE deposition of nanomaterials," *Appl. Surf. Sci.*, vol. 302, pp. 92-98, 2014.