Work function lowering of photo- and thermionic-cathode by two-dimensional nanomaterial coating beyond anti-corrosion protection

Two-dimensional (2D) nanomaterials such as graphene possesses attractive material properties as anti-corrosion coatings [1]. Graphene is a carbon sheet that is only one atom thick, yet is mechanically and chemically stable, and possesses packed atomic structure in the in-plane direction with geometric pore size of 0.64 Å, which is smaller than the smallest gas molecule, namely the hydrogen molecule. Utilizing the unique capability of supersonic molecular beam (SSBM) at SPring-8 **BL23SU**, we have studied the effectiveness of graphene anti-corrosion coating on copper substrates by X-ray photoelectron spectroscopy (XPS). SSBM is based on free jet expansion and generates gas molecules such as oxygen with imparted kinetic energy of up to ~2 eV with narrow energy distributions with widths that are as low as 1/10 of those generated thermally. We have successfully demonstrated high anti-corrosion performance of monolayer graphene and published the results in 2020 [2]. Our article was featured as one of the cover graphics for the Journal of Physical Chemistry Letters and was publicized in news releases.

Our next goal was to demonstrate an additional functionality for the 2D material coating. Discussion with our theoretical collaborators indicated that we may be able to lower the work function of material surfaces by 2D material coating. This could benefit electron sources of particle accelerators including SPring-8 because lowering the work function would increase the number of emitted electrons and hence the brightness of the beams. Furthermore, long lifetime is another critical performance factor for the electron sources for which anti-corrosion coating by 2D materials would be beneficial [3]. We chose lanthanum hexaboride (LaB_6) for our study because using LaB_6, both photo- and thermionic-cathode performance can be tested with a single material. LaB_6 is an established thermionic cathode that is widely used in electron sources for electron microscopes and particle accelerators. Moreover, its low work function of ~2.4 eV makes it attractive as a photo-cathode. We used photoemission electron microscopy (PEEM) and thermionic emission electron microscopy (TEEM) to investigate the work function of LaB_6. Both techniques probe work function of material surfaces with spatial resolution of few tens nm and show low work-function regions through high intensity of emitted electrons. PEEM and TEEM utilize photoemission and thermionic emission, respectively. We used Xe lamp as the light source for PEEM. The sample preparation was as follows. We purchased a LaB_6 (100) single crystal with a diameter of 3 mm and coated half of the crystal with chemical vapor deposited (CVD) monolayer graphene via the established wet-transfer method. We then coated CVD monolayer hexagonal boron nitride (hBN) via the wet-transfer method such that a quarter of the circle is covered by just hBN and half of graphene was covered with hBN (Fig. 1). When we performed

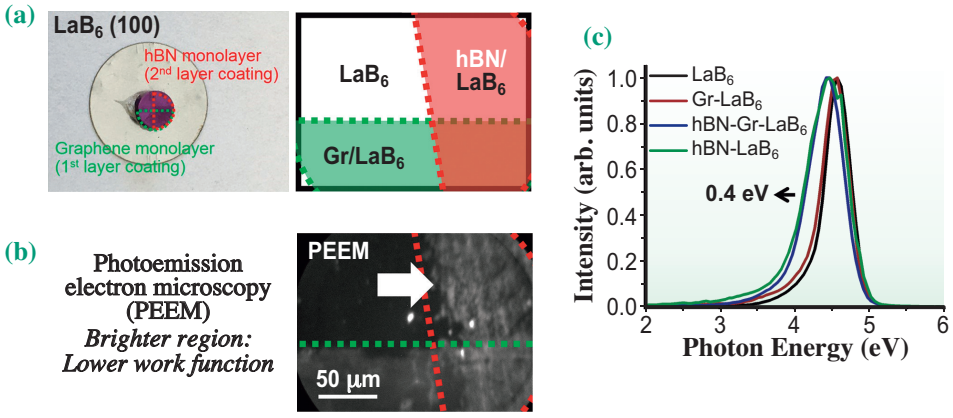

Fig. 1. **(a)** Top view photograph of graphene- and hBN-coated LaB_6 (100). LaB_6 is fixed onto a nickel (Ni) substrate using silver paint. Regions of 2D material coatings are indicated by green (graphene) and red (hBN) dotted lines. Top view schematic illustration of the LaB_6 geometry. White, green, and red regions are bare LaB_6, graphene-coated LaB_6, and hBN-coated LaB_6, respectively. **(b)** PEEM image taken at room temperature after heating up to 905°C. **(c)** PES spectra of LaB_6 coated with graphene and hBN taken at room temperature after heating up to 905°C. The black arrow indicates a shift of low-energy cutoff of the spectra for hBN-coated LaB_6 compared to bare and graphene-coated LaB_6.

PEEM at the center of LaB_6 where four different types of bare, graphene-coated, hBN-coated and graphene/hBN-coated surfaces intersect, the hBN-only coated region exhibited the highest intensity of photoelectrons (i.e., brightest color) [4]. Graphene-only-coated region had similar intensity as the bare region, and graphene/hBN-coated region exhibited intensity between those of hBN-only and graphene-only. TEEM results were consistent with the PEEM results. hBN-only and graphene/hBN-coated regions exhibited measurable intensity at 905°C while no intensity was detected from other regions. A broad and uniform brighter image of the hBN-coated region in PEEM was quantitatively supported by a 0.4 eV decrease of the work function in the photoelectron spectra compared to the bare region. The work function of 4.2 eV that we observed for non-coated LaB_6 (100) (extrapolated low energy cut-off of the spectra) was higher than the value of ~2.4 eV reported for its clean surfaces. This is due to native oxidized layer on top that persists even after annealing at 905°C, which we confirmed by XPS. The work function is also consistent with a reported value of ~4.0 eV for the LaB_6 (100) surface with an oxide layer. A larger decrease of the work function for hBN-coated LaB_6 (100) compared to graphene-coated LaB_6 (100) was qualitatively supported by our density functional theory (DFT) calculations. For both the hBN- and graphene-coating, the degree of work function modification on the oxidized surfaces was smaller compared to the clean surfaces, indicating that the oxide layer reduces the change transfer between LaB_6 and 2D materials.

Band diagrams illustrating the work function changes of oxidized LaB_6 (100) by graphene- and hBN-coating are shown in Fig. 2. For the semi-metallic graphene, the charge transfer from LaB_6 to the conduction bands of the coating materials induces inward-pointing dipoles, which increase the work function (Figs. 2(a) and 2(b)). Figure 2(c) shows the electron transfer at the interface of oxidized LaB_6 (100) surface and graphene. Blue and yellow regions indicate electron depletion and accumulation, respectively. In contrast to graphene, for monolayer hBN, because of its large bandgap, an outward dipole is formed at the interface originating from exchange repulsion, which decreases the work function (Figs. 2(d) and 2(e)). Comparison of Figs. 2(f) and 2(c) clearly shows that the surface dipole has different directions for the graphene- and hBN-coated surfaces.

In summary, we demonstrated that functionalities beyond anti-corrosion protection such as work function lowering of material surface can be provided by 2D material coating.

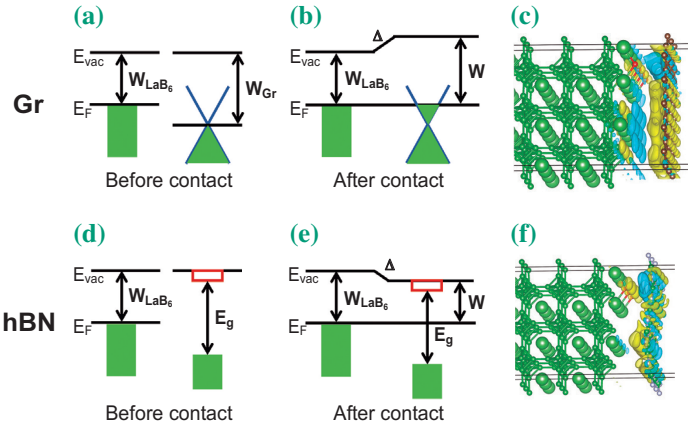

Fig. 2. Schematic band alignment of graphene with the oxidized LaB_6 (100) surface: **(a)** before contact and **(b)** after contact. **(c)** Charge redistribution. Schematic band alignment of hBN with the oxidized LaB_6 (100) surface: **(d)** before contact and **(e)** after contact. **(f)** Charge redistribution. Large green, small green, brown, red, and white spheres in insets of (c) and (f) represent lanthanum (La), boron (B), carbon (C), oxygen (O), and hydrogen (H) atoms, respectively.

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References

[1] H. Yamaguchi *et al.*: Adv. Energy Mater. **4** (2014) 1300986.
[2] S. Ogawa *et al.*: J. Phys. Chem. Lett. **11** (2020) 9159.
[3] L. Guo *et al.*: Sci. Rep. **13** (2023) 2412.
[4] *H. Yamaguchi, R. Yusa, G. Wang, M. T. Pettes, F. Liu, Y. Tsuda, A. Yoshigoe, T. Abukawa, N. A. Moody, S. Ogawa: Appl. Phys. Lett.* ***122*** *(2023) 141901.*