Comment on "Insight into Organometallic Intermediate and Its Evolution to Covalent Bonding in Surface-Confined Ullmann Polymerization"

■ In a recent paper,[1] Di Giovannantonio *et al.* investigated the organometallic structures and covalent bonding mechanisms during the on-surface polymerization of 1,4-dibromobenzene on Cu(110), by using scanning tunneling microscopy (STM), X-ray photoelectron spectroscopy (XPS), low-energy electron diffraction (LEED), near-edge X-ray absorption fine structure (NEXAFS) spectroscopy, and first-principles calculations. The authors claimed the intermediate organometallic structure was extended to a conjugated polymeric phase polymerization by thermal annealing accompanied with the detaching of phenylene units from the copper substrate and the subsequent polymerization, which was also elaborated from the point of view of XPS analysis in the paper. However, in this comment, I want to point out that (1) the conclusion was not clearly substantiated by the XPS core level measurements, and (2) the discussion of XPS measurement was not properly developed.

I highlight two main points that were observed but not discussed by the authors: (1) the thorough shift of C 1s X-ray spectrum at varying temperatures from the higher binding energy range (LT, 100 K) to the lower range (RT, 300 K) and back to higher binding energy (500 K) again, and (2) the thorough shift of Br 3d core level spectrum as a function of exposure time to synchrotron radiation in Figure S3. For the C 1s spectrum, the shift was huge (around 1.6 eV as read from Figure 4) between the measurements at LT and RT, and there was no change of the chemical bonding for the C2 component which was assigned to the carbon–hydrogen bonded carbons in the benzene ring by the authors; the same applies to the comparison between measurements at RT and 500 K. This should be addressed and explained in the paper. In my opinion, the calibration was not properly done. Most importantly, the assignment of different carbon components from the fitting of spectra was not precise. As seen in the middle panel of Figure 4, the C 1s spectrum taken at RT should be fitted with only two components in such a situation: the copper-bonded carbon (component 1) and the sp^3-hybridized carbon in the aromatic ring (component 2), as reported in the previous finding[2] which the authors also cited in addition to other reports.[3,4] The authors mentioned that nonequivalent positions of carbon atoms could result in the splitting of the carbon peak, leading to a new component (component 3). Actually, this is not true and also contradicts their explanation for the spectrum taken at 500 K, where components 4 and 5 have similar shapes and ratios compared to components 2 and 3, but different interpretations were used. The physical position of atoms cannot contribute to the chemical environment change of core level electrons, which leads to the shift of binding energy in the spectrum, except that the chemical bonding is modified. The authors explained the distinct components 4 and 5 in the spectrum taken at 500 K as two different chemically bonded carbon atoms C1 (sp^2 graphite-like carbon) and C2 (sp^3-hybridized carbon), which agrees well with previous reports.[2−4] However, there is still the unignorable shift (around 0.5 eV seen from Figure 4) of the spectrum to be considered; specifically, the shift between the identical component 2 from the spectrum taken at RT and the component 4 at 500 K, which were assigned to the same sp^3-hybridized C2 carbons by the authors.

Second, there was also a general shift for the Br 3d spectrum as a function of exposure time to beam radiation as found in Figure S3, which leads me to wonder again whether the calibration has been properly done. Besides this, it is surprising to see such a clear Br 3d spectrum since it sits so close the Cu 3p region (binding energy around 75 eV). The background or satellite from the copper substrate can be very strong to bury the tiny Br 3d signal; therefore, the Br 3p peak was usually chosen instead to avoid such overlap, as reported in the previous paper.[5] Meanwhile, the authors also used this reference[5] to explain the modified state of Br 3d where the bromine was supposed to be linked to the copper substrate both at RT and 500 K. Interestingly, as mentioned before, no single Br 3d peak was measured or discussed by Folkesson *et al.* in their work,[5] but instead, the Br 3p peak was intensively investigated by them. Moreover, the authors introduced the explanation for the Br 3d spectrum taken at RT by saying that the weaker, higher binding energy component of Br 3d probably comes from one of the two distinct chemical environments of Br atoms; however, when looking at the STM measurements or density functional theory (DFT) simulated model (from Figure 3), one can easily figure out that these two distinct chemical bromine atoms hold roughly equal quantity with respect to each other. Therefore, it is expected that the higher binding energy component should have similar intensity as the main component, but not the tiny satellite-like peak in the present spectrum.

In all, it is apparent that the conclusion drawn from the XPS measurements and analysis is questionable and the discussion of the XPS section was not well addressed.

REFERENCES AND NOTES

1. Di Giovannantonio, M.; El Garah, M.; Lipton-Duffin, J.; Meunier, V.; Cardenas, L.; Revurat, Y. F.; Cossaro, A.; Verdini, A.; Perepichka, D. F.; Rosei, F.; Contini, G. Insight into Organometallic Intermediate and Its Evolution to Covalent Bonding in Surface-Confined Ullmann Polymerization. *ACS Nano* **2013**, *7*, 8190–8198.
2. Beamson, G.; Briggs, D. *High Resolution XPS of Organic Polymers-The Scienta ESCA300 Database*; Wiley: Chichester, UK, 1992.
3. Balog, R.; Andersen, M.; Jorgensen, B.; Sljivancanin, Z.; Hammer, B.; Baraldi, A.; Larciprete, R.; Hofmann, P.; Hornekaer, L.; Lizzit, S. Controlling Hydrogenation of Graphene on Ir(111). *ACS Nano* **2013**, *7*, 3823–3832.
4. Tai, F. C.; Lee1, S. C.; Wei, C. H.; Tyan, S. L. Correlation between I_D/I_G Ratio from Visible Raman Spectra and sp^2/sp^3 Ratio from XPS Spectra of Annealed Hydrogenated DLC Film. Materials. *Transactions* **2006**, *47*, 1847–1852.
5. Folkesson, B.; Sundberg, P.; Johansson, L.; Larsson, R. An ESCA Investigation of Some Copper Complexes. *J. Electron Spectrosc. Relat. Phenom.* **1983**, *32*, 245–256.

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