

Will Any Crap We Put into Graphene Increase Its Electrocatalytic Effect?

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Supporting Information

The doping of graphene with a plethora of elements has been reported as enhancing its electrocatalytic performance.^{1,2} It has become almost a paradigm that the once fantastic graphene for electrocatalysis³ is not so fantastic anymore and that we need to add something to it (*i.e.*, a dopant) to make it great again.^{4–10} Following this trend, graphene has been doped with many different elements, including N, S, P, B, *etc.*; in all cases, the electrocatalytic effect of the doped graphene was enhanced.^{1,11–13} It apparently *did not matter* whether the doping atom/group was electron donating or electron withdrawing; the effect was *always* claimed to be electrocatalytic.¹⁴ Only a few experimental and theoretical studies have found that B or S doping actually *inhibits* electrochemical reactions.^{11,15–17} After doping with individual atoms, it was apparently again not enough for electrocatalysis (one may be surprised that there is *always* room for improvement) and two-element-doped graphene was claimed to be a better catalyst than graphene doped with one element due to a so-called “synergistic effect”.^{18–23} Multi-elemental (*i.e.*, three or more “heteroatoms” other than carbon) doped graphene became a trend.^{24–31} It seems that whatever “crap” we put into graphene, electrocatalysis increases.² One may exaggerate only a little by saying that if we spit on graphene it becomes a better electrocatalyst. Having 84 reasonably stable elements (apart from noble gases and carbon), one can produce 84 articles on mono-elemental doping of graphene; with two dopants we have 3486 possible combinations, with three dopants we can publish 95,284 combinations, and with four elements there are close to 2×10^6 combinations. One may start wondering whether there is any reason to do so, whether all the efforts in graphene doping for electrochemistry are justified. We decided to take this argument a step forward and to show experimentally that such efforts often do not bring significant insight. We demonstrate in the following text the meaninglessness of the never-ending co-doping of graphene. We decided to follow the hyperbole of ever multiplying dopants; however, instead of using expensive and toxic chemicals such as ammonia, fluorine, chlorine, boranes, *etc.*, we took a page from the pre-Haber–Bosch era and sought natural materials for the fertilization of graphene and used guano as a dopant. Guano has a great advantage for doping over using synthetic chemicals. It is available at low cost, it contains a plethora of elements (including N, P, S, Cl, *etc.*), and its use for graphene doping can be handled by a nonchemist. We show that we can create high-entropy,

multiple-element-doped graphene with *outstanding* electrocatalytic properties for two industrially important reactions: oxygen reduction used in fuel cells and hydrogen evolution used in electrolyzers. If we follow the claims of previously published doped graphene for electrocatalysis articles regarding “metal-free catalysis”, one can envision an era in which guano-doped graphene is used instead of platinum in fuel cells and electrolyzers, with huge societal impact not only in clean energy production and a cleaner environment but also on rural economies as guano once again becomes a valuable and highly sought-after product.

To make our point of the meaninglessness of efforts to co-dope graphene with various elements experimentally, we evaluate in this work if guano-doped graphene poses any advantages over nonguano-doped graphene. We prepared guano-decorated graphenes *via* thermal exfoliation with different kinds of graphite oxide precursors. The reference graphenes were synthesized with the same method, but in the absence of guano. We then characterized the prepared graphenes and guano-doped graphenes by scanning electron microscopy (SEM) for morphology and elemental mapping, Raman spectroscopy for defect density, X-ray photoelectron spectroscopy (XPS) for elemental compositions and bonding information, combustible elemental analysis for elemental compositions and, finally, studied the electrochemistry properties toward the oxygen reduction reaction (ORR) and the hydrogen evolution reaction (HER) of prepared graphenes *via* the voltammetric method. We labeled the prepared materials by following the method of precursor synthesis, abbreviating the graphite oxide synthesized *via* Hoffmann method as “Ho-GO” and Hummers method as “Hu-GO”, and by suffix “BD” as decorated with bird droppings (*e.g.*, Hu-GO and Hu-GO-BD).

The morphologies of the graphenes were obtained *via* SEM and are presented in Figure 1. All samples showed typical exfoliated structures in agreement with previous studies and confirmed successful thermal exfoliation of all samples. Interestingly, the decorated graphenes showed the same structures as the control graphenes, and no extra small flakes

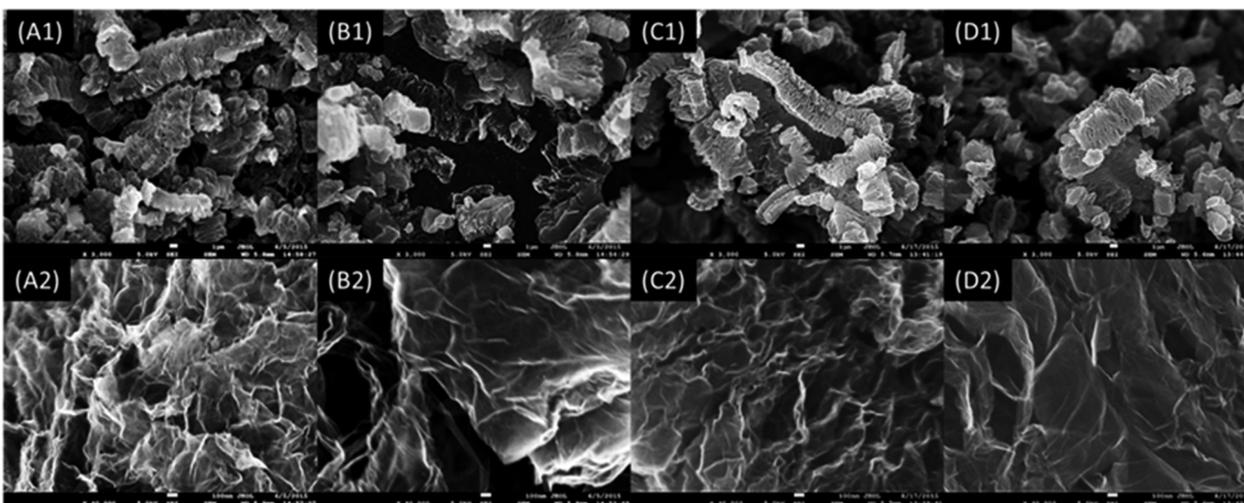


Figure 1. SEM images of (A) Ho-GO-BD, (B) Hu-GO-BD, (C) Ho-GO, and (D) Hu-GO with magnification of 3000 \times and 40,000 \times with scale bars of (top row) 1 μ m and (bottom row) 100 nm.

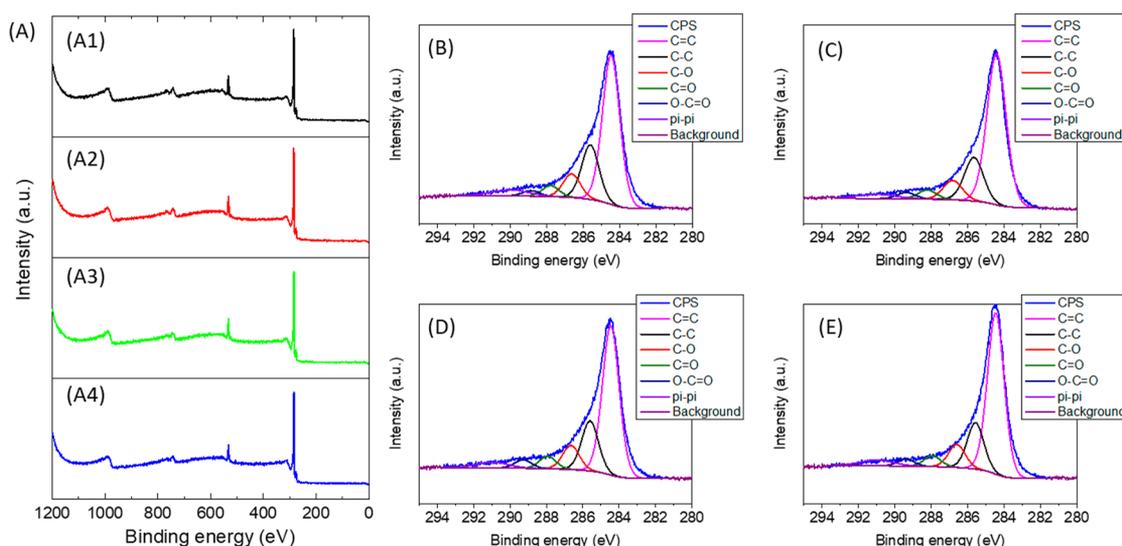


Figure 2. Elemental and bonding analysis *via* XPS. (A) Survey XPS of (A1) Ho-GO-BD, (A2) Hu-GO-BD, (A3) Ho-GO, and (A4) Hu-GO and high resolution XPS of C 1s of (B) Ho-GO-BD, (C) Hu-GO-BD, (D) Ho-GO, and (E) Hu-GO.

or powders were observed, which, in this case, indicates that the added droppings exfoliated together with the graphene and can form structures similar to exfoliated graphenes. In addition, elemental maps for all prepared samples are shown in Figure S1 and indicate that the bird dropping-decorated graphenes do contain significant amounts of N, S, and P and that the reference graphenes only show clean C and O content.

Next, we investigated the defect density of the prepared graphenes by Raman spectroscopy (shown in Figure S2). The G band at approximately 1560 cm^{-1} indicates the presence of sp^2 lattice carbon atoms in the graphene sheet and a D band at approximately 1350 cm^{-1} reflects the defects caused by the sp^3 hybridized carbon atoms. The intensity ratios between the D and G bands are 0.87, 0.90, 0.93, and 0.94 for Ho-GO-BD, Hu-GO-BD, Ho-GO, and Hu-GO, respectively. Interestingly, the dropping-decorated graphenes showed a relatively lower I_D/I_G ratio than the control materials, which means the graphenes decorated with bird droppings have relatively fewer defects than the control materials.

We employed XPS to investigate the elemental composition and bonding of the prepared materials and the results are shown in Figures 2 and S3. Figures A1–A4 show graphenes that mainly consist of C and O, only Hu-GO-BD contains 0.83 at. % S. The ratio of intensity of C and O is 11.1 for Ho-GO-BD, 10.9 for Hu-GO-BD, 10.7 for Ho-GO, and 13 for Hu-GO, which indicates comparable reduction levels for all prepared graphenes. Residual oxygen-containing groups were investigated by high-resolution C 1s binding energies, such as C=C bonds at 284.5 eV, C–C bonds at 285.4 eV, C–O bonds at 286.3 eV, C=O bonds at 287.4 eV, O–C=O bonds at 288.5 eV, and π – π interactions at 290 eV. On the other hand, in high-resolution N 1s, S 2p, and P 2p, the bird dropping-decorated graphenes exhibit peaks in those ranges, which means the bird dropping-decorated graphenes do contain N, S, and P, further confirming the successful decoration and elemental mapping results.

Because the amount of decorated N, S, and P cannot be reliably detected in wide scan XPS, we employed combustible elemental analysis to obtain accurate measurements of the

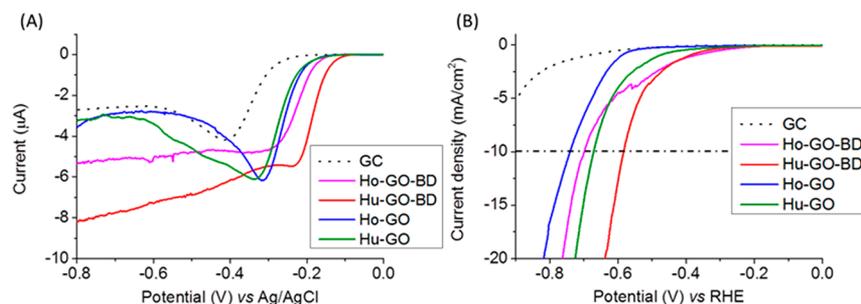


Figure 3. Linear sweep voltammograms of (A) ORR and (B) HER at the bare GC electrode, decorated graphenes and control graphenes in (A) 0.1 M KOH and (B) 0.5 M H₂SO₄ with scan rates of 10 mV/s and 2 mV/s, respectively.

concentrations of these trace elements. We found that Ho-GO-BD contains 0.90 at. % of N, 1.58 at. % of S, and 2.06 at. % of P, while Hu-GO-BD contains 0.91 at. % of N, 2.26 at. % of S, and 2.10 at. % of P. The amounts of decorated N and P are approximately the same for decorated graphenes, and Hu-GO-BD has a little bit more S than Ho-GO-BD.

Due to the relatively low detection limits of XPS (≈ 0.1 at. %), we also performed inductively coupled plasma optical emission spectrometry (ICP-OES) to obtain the information on the trace metal impurities within the graphenes decorated in bird waste. The ICP-OES result shows that Ho-GO-BD contains 3.5 ppm of Co, 1562 ppm of Fe, 72.3 ppm of Mn, and 13.1 ppm of Ni, and Hu-GO-BD contains 25.8 ppm of Co, 1519 ppm of Fe, 3766 ppm of Mn, and 11 ppm of Ni. In this case, the results also confirm that graphene synthesized *via* the Hummers method is more contaminated with Mn-based impurities than the graphene prepared *via* the Hofmann method.^{32–34}

The electrocatalytic properties toward ORR and HER at the bare glassy carbon electrode, decorated graphenes, and control graphenes were recorded and are shown in Figure 3. According to Figure 3A, the recorded onset potentials are -273 mV (vs Ag/AgCl) for GC, -207 mV for Ho-GO, -210 mV for Hu-GO, -173 mV for Ho-GO-BD, and -139 mV for Hu-GO-BD. All graphene samples showed much improved electrocatalytic properties toward ORR than the bare GC electrode. Both the Ho-GO-BD and Hu-GO-BD showed lower onset potentials compared with non-doped graphene.

Then for HER, again, all prepared graphenes performed much better than the bare GC electrode and the overpotentials at 10 mA/cm² are 0.96 V (vs RHE) for GC, 0.74 V for Ho-GO, 0.67 V for Hu-G, 0.69 V for Ho-GO-BD, and 0.58 V for Hu-GO-BD. Bird dropping-doped Hu-GO-BD shows the lowest overpotential of all samples due to additional dopants present from the bird droppings.

In summary, we demonstrated that bird dropping-treated graphenes indeed make graphene more electrocatalytic than nondoped graphene. Both bird-dropping-decorated graphenes and control nondoped graphenes show the same morphology. Graphenes decorated with bird droppings contain additional N, S, and P in the material. These decorated graphenes exhibit much better electrocatalytic properties toward both oxygen reduction and hydrogen evolution, and, in this case, it can be considered as a potential multifunctional catalyst for both ORR and HER. Because doping graphene with cheap bird droppings produces more electrocatalytic materials than many complex multielemental doping procedures, we do not see any justification for such efforts, and we believe that researchers should focus their energy on other research directions. To

conclude in a positive (and a bit satiric) tone, we speculate that the chemical composition of chicken guano can be tailored by feedstock (chick feed), and, therefore, the quality of the resulting doped catalyst can be further improved. We believe that there is potential for the bird dropping-doped graphene for fuel cells and in a hydrogen economy, and we believe that bird droppings can become a high-value-added product such as guano was in the past. One can only hope that with such dramatic advantages, no wars (even trade wars) will be started over bird droppings this time.^{35–38}

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsnano.9b00184>.

Scanning electron microscope images, elemental mapping, Raman spectra, high resolution XPS of N 1s, S 2p, and P 2p of the prepared samples as well as experimental details are available from the authors (PDF)

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Notes

Views expressed in this Perspective are those of the authors and not necessarily the views of the ACS.

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