Surface charges of hexagonal boron nitride with carbon layers formed by plasma in hydroquinone aqueous solution

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Abstract

A carbon layer formation on hexagonal boron nitride (hBN) particles has been demonstrated using plasma processing in hydroquinone solution, which improve a dispersibility of hBN. This study investigates the surface charges of hBN particles modified with the carbon layer and evaluates the number of polar groups on the surfaces. By solving a Poisson-Boltzmann equation, the surface charge densities of the modified hBN are calculated from the reported zeta potentials, and converted to the corresponding number of ionized polar groups. These results show that the number of polar groups in the modified hBN clearly increase from that of untreated hBN, and is consistent with the estimation from acid-base neutralization.

1. Introduction

Hexagonal boron nitride (hBN) is a thermally conductive and electrical insulating material, and hBN/polymer composite materials have been developed for thermal management in electronic devices. In this application, surface modification of hBN is desired for preventing their aggregation[1)]. Plasma processing is an effective method for surface modification of hBN because the excited species can break the B–N bonds and functionalized the surfaces with polar groups[2)]. The polar groups are expected to improve their wettability and provide surface charges, resulting repulsion of hBN particles in solvent. For further surface modification, we have demonstrated a carbon layer formation on hBN particles by plasma processing in hydroquinone aqueous solution[3)]. Such hBN modified with a carbon layer showed high zeta potentials, and improved their dispersibility in water[4)] and a polymer matrix[5)]. These results suggest the modified hBN contain more polar groups on the carbon layer, but the surface charges and number of polar groups have not been discussed. In this study, surface charges of the modified hBN and the number of polar groups are estimated from their zeta potentials.

2. Experiment

Plasma processing, as demonstrated in previous studies[3,5)], was performed for hydroquinone aqueous solution containing hBN (Sigma-Aldrich) using a bipolar pulsed power supply (Kurita Seisakujo, MPP-HV-04-300 kHz) and a cavitation device (Nihon Spindle, Jetpaster). The modified hBN, containing a carbon layer[3)], were reported to show higher negative zeta potentials than those of untreated hBN, which were measured using particle tracking analysis (Particle-Metrix, ZetaView PMX 110) in pH 4–9 solution[5)]. Here, the reported zeta potentials of the modified hBN were used for calculation of the surface charge densities. The calculated surface charge densities were converted to the corresponding number of ionized polar groups, which were compared with the number of acidic groups in the modified hBN determined by an acid-base neutralization titration using 10^{-4} mol/L of KOH solution.

3. Results and discussion

The relationship between the surface charge density q of a flat particle in solution and the surface potential φ_0 (relative to bulk solution's potential far from a particle) is given by solving the Poisson–Boltzmann equation, as following.

$$q = (2n_0\varepsilon_r\varepsilon_0 k_B T)^{1/2}\left[\exp\left(\frac{ze\varphi_0}{2k_B T}\right) - \exp\left(-\frac{ze\varphi_0}{2k_B T}\right)\right] \quad (1)$$

where n_0 is the ion density in solution, ε_0 is the permittivity of vacuum, ε_r is the relative permittivity of solution, z is the valence of the ion, e is the elementary charge, k_B is Boltzmann's constant, T is the absolute temperature of solution, and the zeta potential $\zeta \cong \varphi_0$ is assumed. The calculated surface charge densities of the modified hBN and untreated hBN are plotted in Fig. 1 as a function of pH. The right axis shows the corresponding number of ionized monovalent groups per surface areas. This estimation indicates that the modified hBN increases the ionized groups with 1000 μm^{-2}. Assuming that pH dependence of surface charge corresponds to the acid dissociation of polar groups, the total number of polar groups is found in the value at a high pH. The modified hBN was estimated to have acidic groups of 9900 μm^{-2}, which were consistent with the result of the acid-base titration.

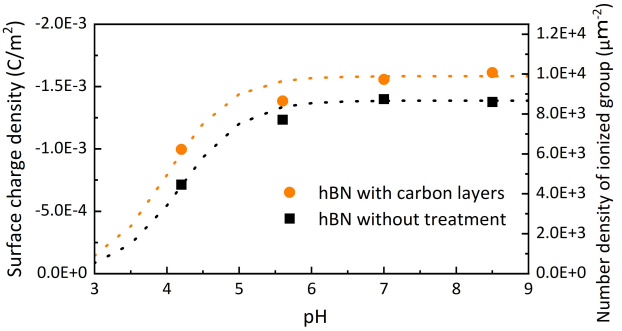

Fig.1 Surface charge density and number density of ionized groups on hBN calculated from their zeta potentials

4. Conclusion

This study demonstrates the estimation of surface charge densities and number of polar groups from the zeta potentials of modified hBN with the carbon layer, which showed considerable dispersibility in a polymer. The zeta potential not only has a key role in describing particle dispersion as using Derjaguin-Landau-Verwey-Overbeek (DLVO) theory, but can also be an indicator of the number of functionalized polar groups. This study suggests that surface states of plasma-modified particles and the resulting dispersion mechanism, which are still under investigation, can be discussed based on the zeta potential measurement.

References

1) Z. Zheng, M. Cox and B. Lin, Journal of Material Science, 53, 66-99 (2018). DOI: https://doi.org/10.1007/s10853-017-1472-0

2) A. Pakdel, Y. Bando and D. Golberg, ACS Nano, 8, 10631 (2014). DOI: https://doi.org/10.1021/nn5041729

3) K. Inoue, N. Sakakibara, T. Goto, T. Ito, Y. Shimizu, Y. Hakuta, K. Ishikawa, M. Hori and K. Terashima, ACS Applied Materials & Interfaces, accepted.

4) K. Inoue, T. Goto, M. Iida, T. Ito, Y. Shimizu, Y. Hakuta and K. Terashima, Journal of Physics D: Applied Physics, 53, 42LT01 (2020). DOI: https://doi.org/10.1088/1361-6463/ab97dd

5) K. Inoue, T. Goto, T. Ito, Y. Shimizu, Y. Hakuta, K. Ito and K. Terashima, Journal of Physics D: Applied Physics, 54, 425202 (2021). DOI: https://doi.org/10.1088/1361-6463/ac15d1