Electronic Supplementary Materials (ESI)

Green Synthesis of Crystalline Bismuth Nanoparticles Using Lemon Juice

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1. Materials and Instruments

Materials. $Bi(NO_3)_3{\cdot}5H_2O$, sodium borohydride and L-ascorbic acid were obtained from Kanto Chemical Co. Inc. (Tokyo, Japan). 4-NP was purchased from Tokyo Chemical Industry Co. Ltd. (Tokyo, Japan). All the materials were used without further purification.

Measurements. XRD analysis was conducted on a Rigaku (Tokyo, Japan) MiniFlex 600 diffractometer with Cu-Kα radiation. SEM measurements were conducted on a Hitachi (Tokyo, Japan) SU-8000 microscope at accelerating voltages of 10 and 15 kV. TEM measurements were conducted on a TEM-2100F (JEOL, Tokyo, Japan) field emission electron microscope. The hydrodynamic size was measured through DLS analysis conducted on a Malvern (Malvern, UK) Zetasizer Nano ZS instrument. FTIR spectra were recorded on a JASCO (Tokyo, Japan) FT/IR-460 plus spectrometer using a KBr pellet, and a Shimadzu (Tokyo, Japan) IRSpirit spectrometer equipped with a Shimadzu QATR-S single-reflection ATR accessory with a scan rate of 4 cm^{-1} s^{-1} at 25 °C. TGA was carried out on a Seiko Instruments (Tokyo, Japan) TG/DTA 6200 (EXSTER6000) at a heating rate of 10 °C min^{-1} under N_2. ^1H and ^{13}C NMR spectra were recorded on a JEOL (Tokyo, Japan) ECX-600 (600 MHz for ^1H, 125 MHz for ^{13}C) spectrometer. UV-vis spectroscopic analysis was carried out on a HACH DR 5000 (Colorado, USA) UV visible spectrometer. Centrifugation was performed on a KUBOTA 3700 (Osaka, Japan) micro refrigerated centrifuge machine.

2. Experimental

Temperature and pH play crucial roles in the formation of BiNPs. Below 60 °C, no black product was obtained at pH = 12.3 even after 24 h. Additionally, at pH < 9, no black product was obtained at temperature up to 120 ˚C even after 48 h. This result accord with previous reports on BiNPs synthesis under basic conditions, proceeding through the formation of $NaBiO_2$, which can be reduced by mild reducing agents.[1–5] Ascorbic acid with the amounts 25-75 mL of lemon juice equivalent to 12-36 mg (calculated by redox titration) was unable to produce any black product at same reaction conditions. Longer time does not increase the yields of the product.

3. Results and Discussion

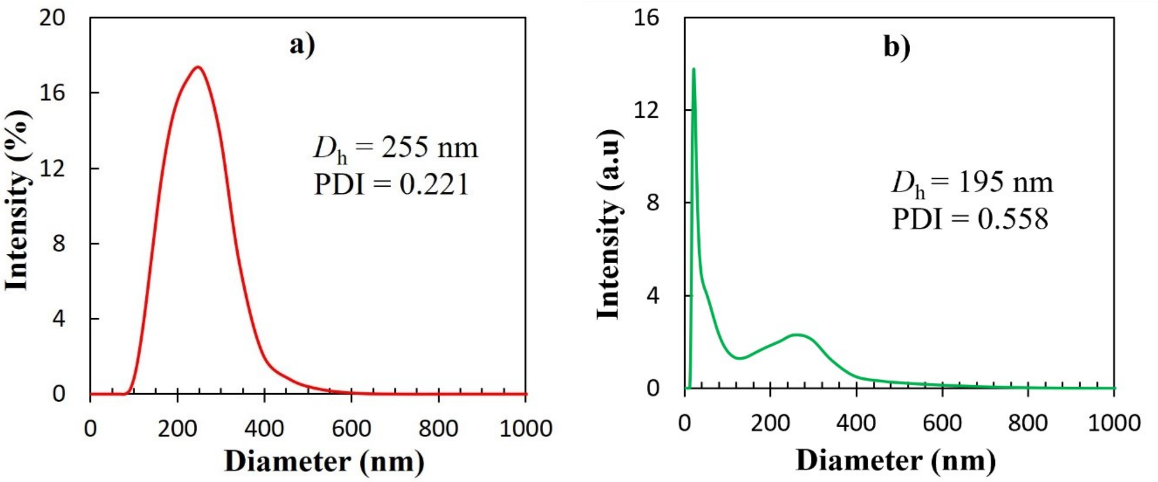

Fig. S1. DLS curves of dispersion of lemon-juice-based green synthesized BiNPs in distilled water (a) before and (b) after catalytic reduction.

The average hydrodynamic diameters (D_h) were calculated by the cumulants analysis on the histograms of diameter.

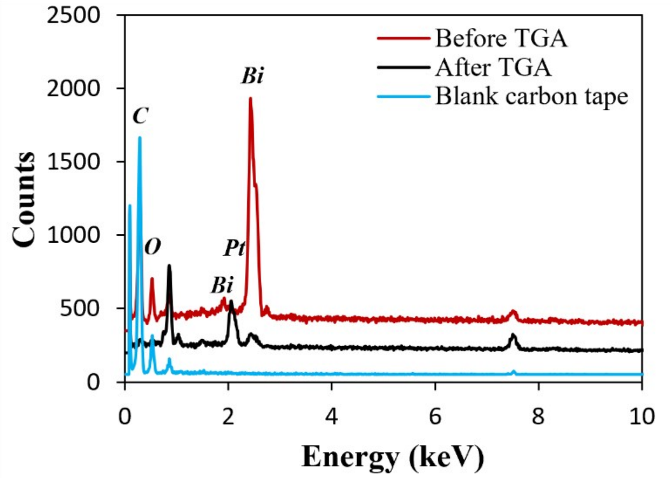

Fig. S2. EDX spectra of lemon-juice-based green synthesized BiNPs on before and after TGA on a Pt pan, and blank (carbon tape).

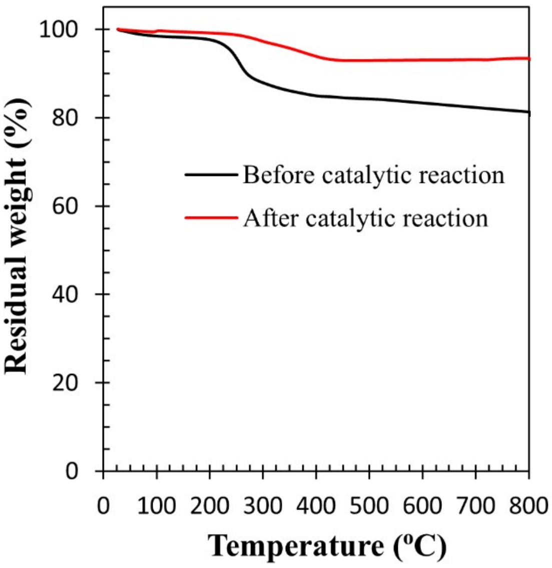

Fig. S3. TGA curves of lemon-juice-based green synthesized BiNPs on before and after the catalytic experiment (heating rate = 10 °C/min, N_2 flow).

The NMR (^{1}H and ^{13}C) and FTIR spectra of the ethanol and chloroform extracts were analyzed based on the reported data.[6–17] The ethanol extract of BiNPs can provide the information on hydrophilic components on BiNPs. The FTIR spectrum of the ethanol extract of BiNPs (Figure S4) shows a broad absorption band around 3050-3500 cm^{-1} corresponding to the O–H stretching of hydroxy groups. The absorption band at 2956, 2921, and 2851 cm^{-1} are assignable to $–CH_3$ antisymmetric, $–CH_2$ antisymmetric and $–CH_2$ symmetric stretching, respectively. The absorption band between 900-1160 cm^{-1} assignable to C–C and C–O stretching, and absorption around 1250-1460 cm^{-1} corresponding to O–C–H, C–C–H and C–O–H bending, are the characteristics FTIR absorption bands of polysaccharides[8,14] indicating the presence of polysaccharides on BiNPs.

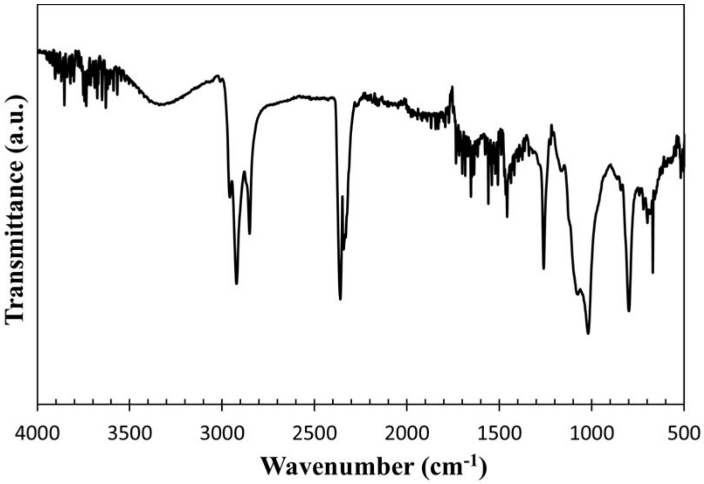

Fig. S4. FTIR spectrum of ethanol extract of BiNPs synthesized using lemon juice.

The ^{1}H-NMR spectrum of the ethanol extract of BiNPs (Figure S5) can be categorized into three regions. The first region (0-3.0 ppm) is assignable to the signals of saturated alkyl chains in fatty acids and amino acids.[12,13] The second region (3.0-5.5 ppm) is assignable to the signals of oxyalkyl groups of sugars and alkenyl groups of unsaturated fatty acids.[12,13,15,16] The third region (7.5-8.0 ppm) shows a small signal assignable to the aromatic groups of amino acids and phenolic compounds.[12,15] These ^{1}H-NMR and FTIR spectroscopic analyses suggest that polysaccharides is one of the key components on BiNPs.

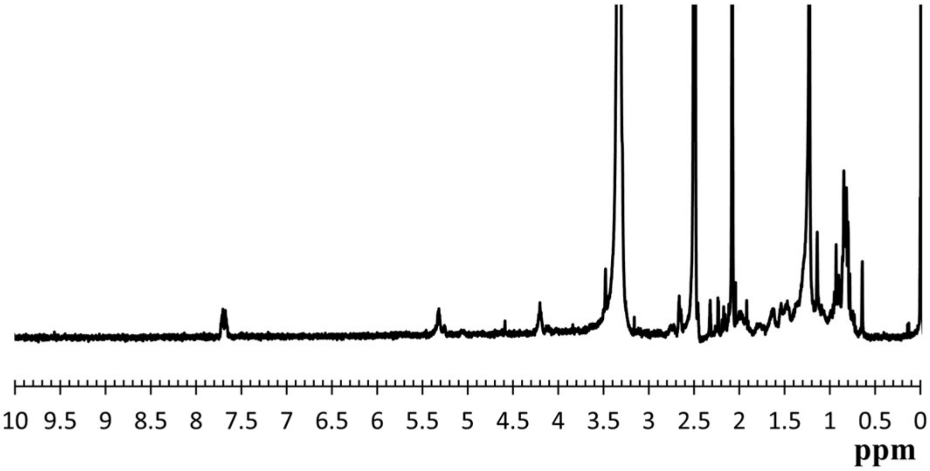

Fig. S5. ^{1}H-NMR spectrum of ethanol extract of BiNPs synthesized using lemon juice (600 MHz, d_6-DMSO).

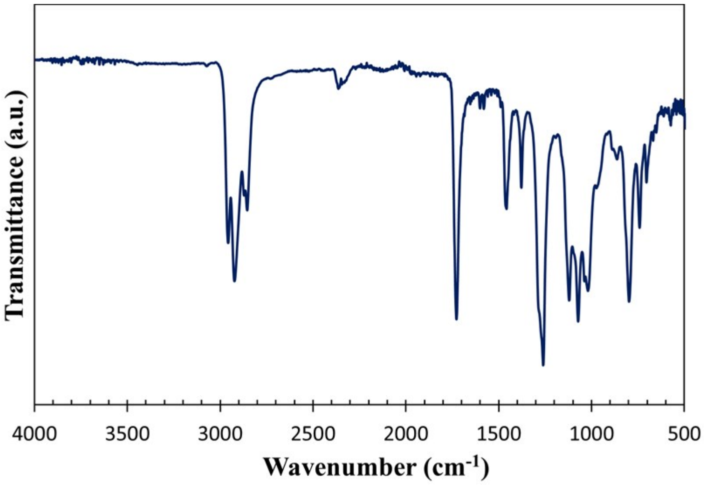

Fig. S6. FTIR spectrum of chloroform extract of BiNPs synthesized using lemon juice.

The FTIR spectrum of the chloroform extract of BiNPs (Figure S6) shows the absorption band at 2956, 2922, and 2871 cm^{-1} are assignable to $–CH_3$ antisymmetric, $–CH_2$ antisymmetric and $–CH_2$ symmetric stretching, respectively. A strong absorption band at 1727 cm^{-1} is assignable to the C=O groups in ester or carboxylic acid. The almost identical intensity with that of the C–H stretching band around 2870-2960 cm^{-1} suggests the presence of long carbon chains. All these absorption bands agrees well with those of fatty acids,[6,7] suggesting that the major components should be derivatives of fatty acids. In addition, the absence of O–H stretching bands of carboxy groups around 2500-3000 cm^{-1} suggests the esterified forms of fatty acids. Tiny absorption bands at 3072 cm^{-1} corresponds to =C–H stretching and around 1580-1600 cm^{-1} assignable to C=C stretching suggest the presence of trace amount of unsaturated chain. The absorption band between 860-1180 cm^{-1} assignable to C–C and C–O stretching, and absorption around 700-800 cm^{-1} and 1250-1460 cm^{-1} corresponds to –C–H bending. These agree with the characteristic bands of fatty acids esters.

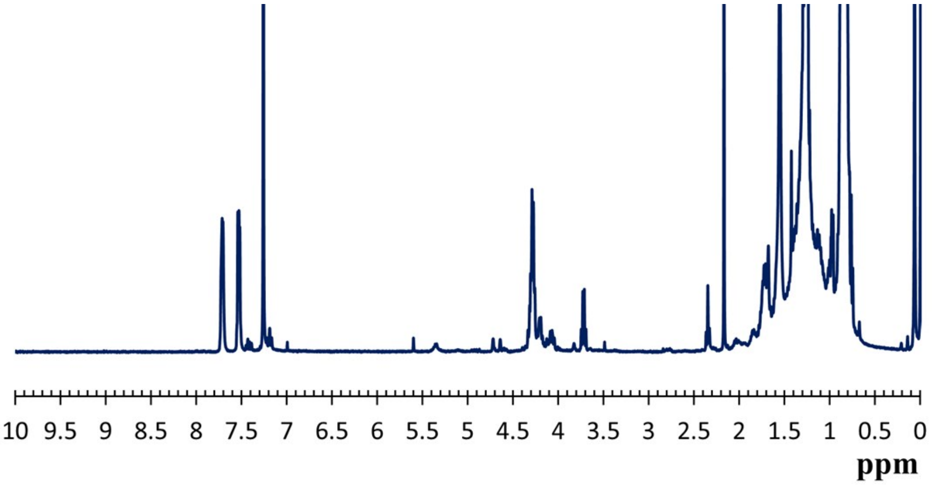

Fig. S7. ^{1}H-NMR spectrum of chloroform extract of BiNPs synthesized using lemon juice (600 MHz, $CDCl_3$).

The ^{1}H-NMR spectrum of the chloroform extract of BiNPs (Figure S7) was also categorized into the three regions. The first region (0-3.0 ppm) is assignable to the signals of alkyl protons of fatty acid chains and terpenes such as limonene, γ-terpinene, β-pinene, and limonoids. The second region (3.0-6.0 ppm) is assignable to the signals of $–C\underline{H}=C\underline{H}–$, $>C\underline{H}–O–CO–$, and $–C\underline{H}_2–O–CO–$ protons of fatty acids ester and terpenes. The third region (6.5-8.0 ppm) assignable to the characteristic signals of limonoids and phenolic compounds.[9,12,17]

The ^{13}C-NMR spectrum (Figure S8) also shows the presence of aliphatic carbons in the region of 10-40 ppm, C–O carbons at 50-70 ppm, olefinic carbon around 130 ppm, and >C=O carbon at 168 ppm. These spectroscopic data of the chloroform extract of BiNPs suggest that fatty acid derivatives and possibly terpenes are also the surface components of BiNPs. These be attached to the surface of BiNPs through the hydrophobic interaction.

Overall, the spectroscopic analysis of the ethanol and chloroform extracts of BiNPs suggests that polysaccharides and fatty acid derivatives are major components on BiNPs, and that polysaccharides are predominant. Possible minor components include amino acids, terpenes, and phenolics.

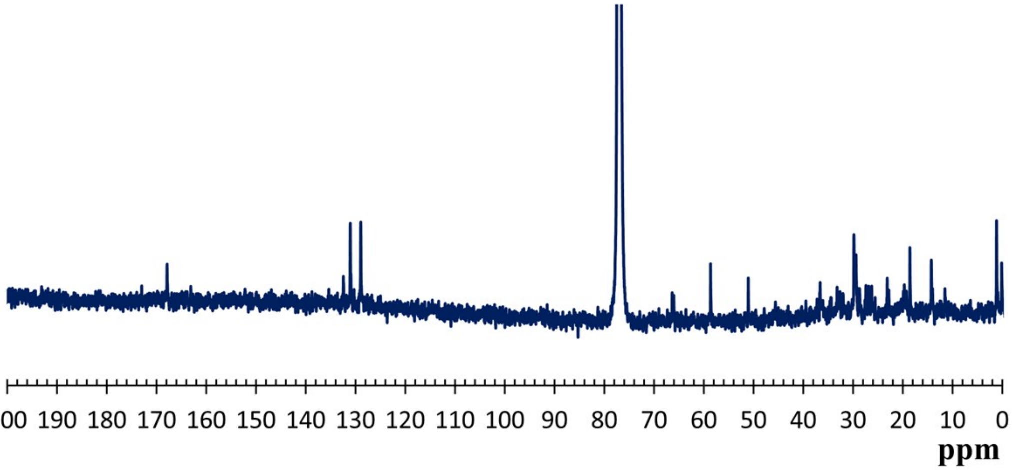

Fig. S8. ^{13}C-NMR spectrum of chloroform extract of BiNPs synthesized using lemon juice (125 MHz, $CDCl_3$).

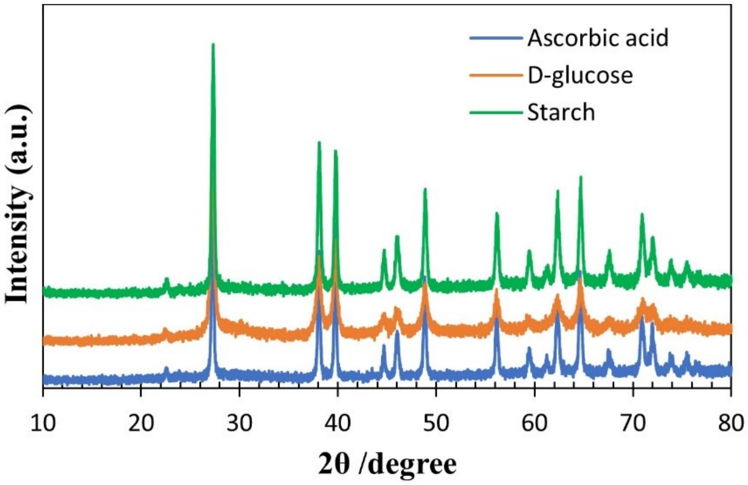

Fig. S9. XRD patterns of reduced product of Bi^{3+} using ascorbic acid, D-glucose, and starch without any stabilizing agents.

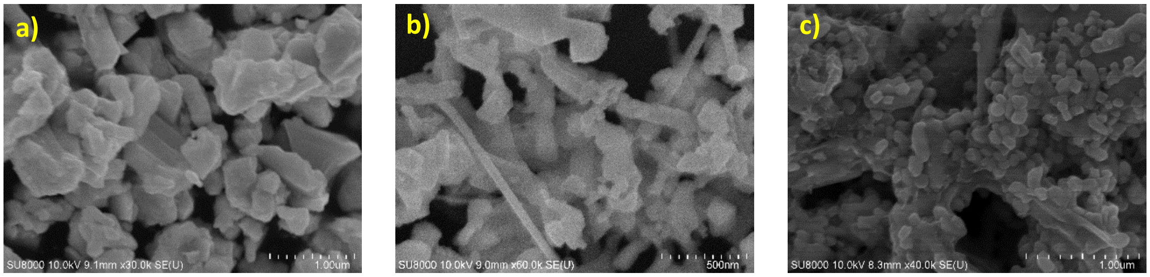

Fig. S10. SEM images of the reduced product of Bi^{3+} using (a) ascorbic acid; (b) D-glucose; and (c) starch without any stabilizing agents.

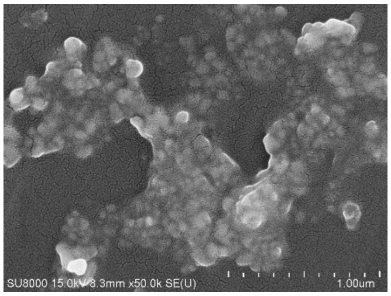

Fig. S11. SEM image of lemon-juice based green synthesized BiNPs after the catalytic reaction.

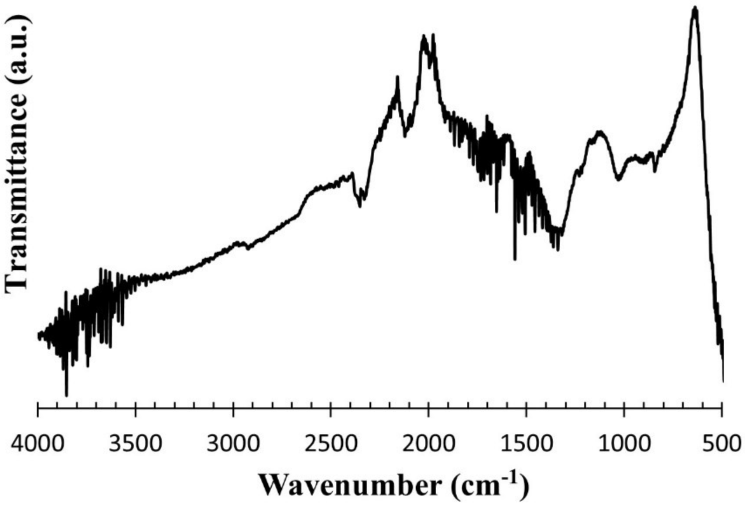

Fig. S12. FTIR spectrum of lemon-juice based green synthesized BiNPs after the catalytic reaction.

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