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Supplementary Information for:

A Novel Bismuth-based Anode Material with Stable Alloying Process by the Space Confinement of in-situ Conversion Reaction for Rechargeable Magnesium Ion Battery

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Experimental Section

Synthesis of BiOF nanosheets

2 mmol of [BMIM]P was added in 15 mL water and continuously stirred until a homogeneous solution was obtained. 0.485g bismuth nitrate pentahydrate and 0.37g NH_4F is gradually added in the mixture while stirring. Then the magnetic stirring holds for 35 minutes. Finally the above solution was transferred into a Teflon-lined autoclave, maintained at 130 ^oC for 24 h and cooled down naturally. The obtained white-colored precipitate was washed with ethyl alcohol and deionized water for 3 times respectively. After the washing the product was dried at 80 ^oC in an oven for 12 h.

Materials characterizations

SEM (JEOL 6701F) operated at 10 kV and TEM (Tecnai F20) with an accelerating voltage of 200 kV were applied to characterize the morphology of the as-prepared BiOF. EDX-STEM-mapping was also carried out with the Tecnai F20 TEM. The XRD test uses a Regaku D/Max-2500 diffactometer with a Cu Kα1 radiation (λ = 1.54056 Å). XPS measurement was carried out with a ESCALAB 250Xi spectrometer, with the non-monochromatised Al Kα X-radiation (hν = 1486.6 eV) and a power of 150 W (10 mA×15 kV).

Electrochemical tests. Electrochemical measurements were carried out by using Swagelok-type cells assembled in an argon-filled glove box. For preparing the working electrode, a mixture of BiOF nanosheets, super-P (SP), and poly(vinyl difluoride) (PVDF, Aldrich) at a weight ratio of 80:10:10 was pasted on a pure Cu foil (99.6%, Goodfellow). Mg foil (100-150 μm thick) was used as the counter electrode. Both working and counter electrodes were electronically separated by a Whatman GF/D borosilicate glass-fiber sheet. The 0.25M $Mg(AlCl_2BuEt_2)_2$/THF electrolyte solution was prepared according to reference 10. Galvanostatic charge/discharge measurements were carried out on an Arbin BT2000 system at different current rates between voltage limits of 0.01 to 1.5 V under room temperature. Cyclic voltammetry (CV) was carried out using an Autolab PG302N at a scan rate of 0.1 mV s^{-1} in the potential range of 0.01-1.5 V (vs. Mg^{2+}/Mg). The specific capacities were calculated based on the mass of active material BiOF. All of the weight values were obtained with a high-precision electronic balance (Sartorius AG, BT 25S).

***Ex situ* characterizations.** To get insight view of the mechanism during electrochemical reaction, the Swagelok-type cells in which active electrode materials at different charge/discharge states were disassembled in the glove box and the electrode active materials were washed by tetrahydrofuran (THF) five times to remove the residual electrolyte. After evacuating the THF, the electrode plates were transferred to some special designed devices for *ex situ* X-ray photoelectron spectroscopy (XPS), Energy dispersive X-ray (EDX) or XRD characterizations. The electrode plates were sealed in argon to avoid exposing to air during XRD measurement using a Regaku D/Max-2500 diffactometer equipped with a Cu $K\alpha_1$ radiation ($\lambda = 1.54056$ Å); a vacuum transfer sample stage was applied for *ex situ* XPS analysis.

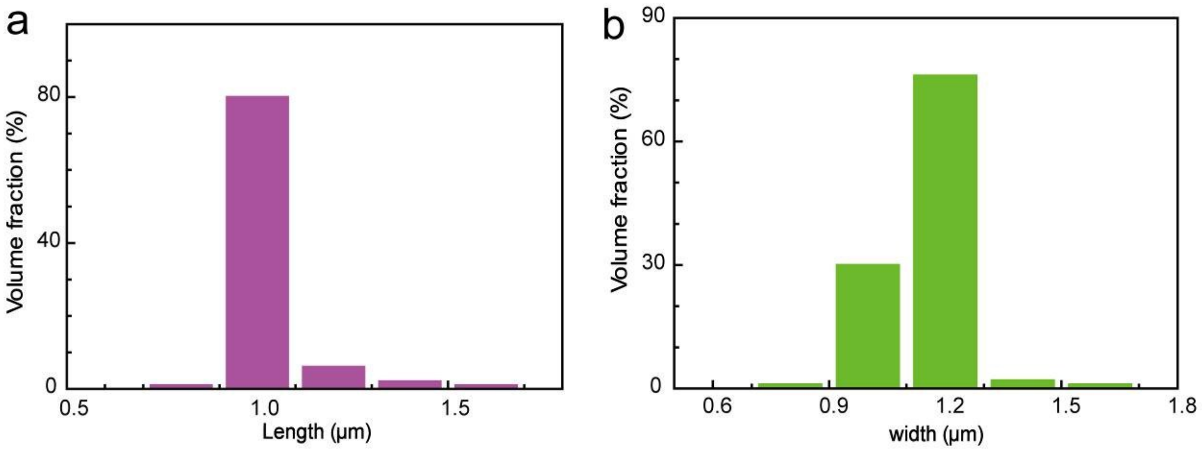

Figure S1. The size distributions (length and width) of square-like BiOF nanosheets .

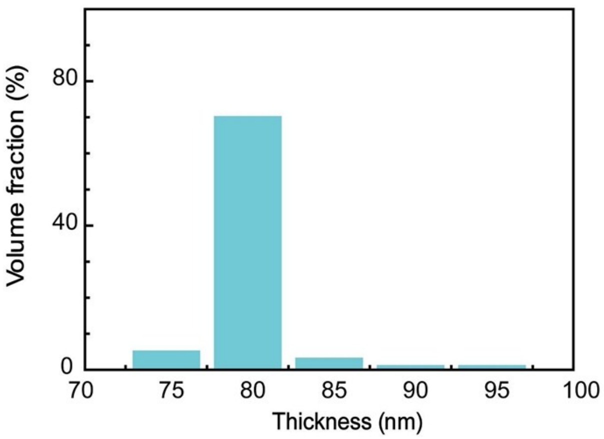

Figure S2. The thickness distributions of the BiOF nanosheets.

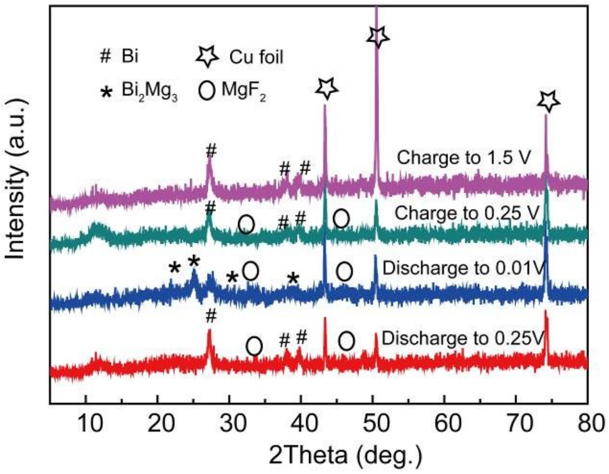

Figure S3. The ex situ XRD patterns of the BiOF electrode with different charge-discharge states of the 5th cycle in rechargeable Mg battery.

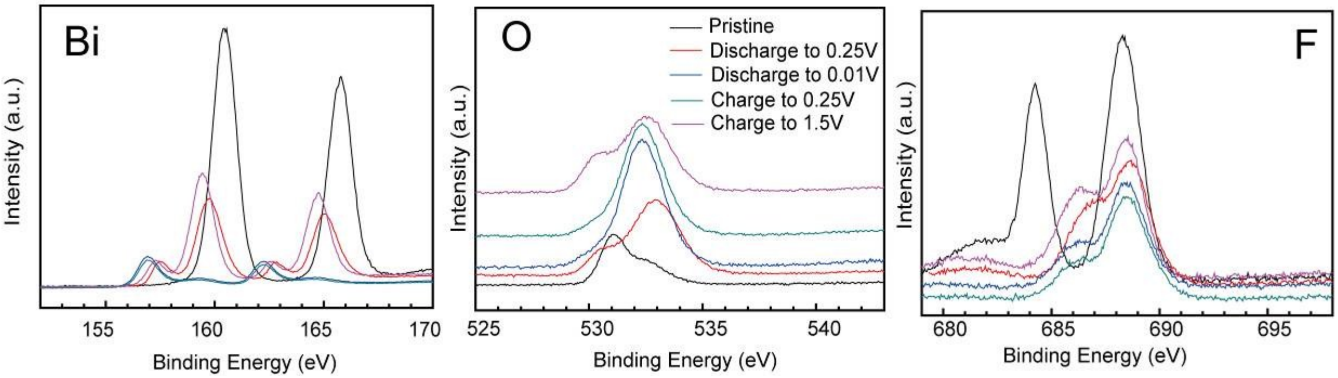

Figure S4. The ex situ XPS spectrum of the BiOF electrode with different charge-dicharge states of the 5th cycle.

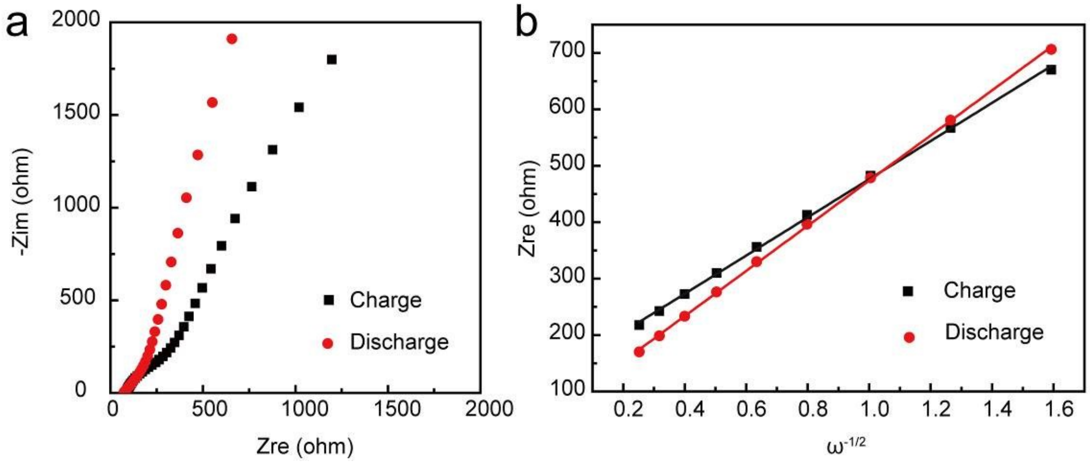

Figure S5. (a)The typical Nyquist plots of the BiOF electrode with different charge-dicharge states of the 5th cycle (b) The variations and fittings between Zre and the reciprocal square root of the angular frequency in the low frequency region of the BiOF electrode with different discharge states.

According to *R*ct of the EIS of the BiOF electrode with cycled in different states, the apparent Mg diffusion coefficients (D) are calculated from the inclined lines in the Warburg region by the equation as follows: $D= R^2T^2/2A^2n^4F^4C^2\sigma^2$

(R is the gas constant, T is the absolute temperature, A is the surface area of the electrode, n is the number of electrons per molecule during the reaction, F is the Faraday constant, C is the molar concentration of Mg^{2+} ions (C (mol cm^{-3}) = n_{Mg} (mol)/V (cm^3) = [(I × t) C/1.6 × 10^{-19} C/6.02 × 10^{23} mol^{-1}]/V (cm^3) with V = 3.2 × 10^{-6} cm^3), and σ is the Warburg factor associated with *Z*re (*Z*re $\propto \sigma\omega^{-1/2}$). After obtained the Warburg factor σ by linear fitting the relation plot between *Z*re and the reciprocal square root of the angular frequency ω, the *D* could be obtained from the above equation.