**Supporting information** 

## Porous graphene frame supported silicon@graphitic carbon *via in-situ* solid-state synthesis for high-performance lithium-ion anodes

<sup>5</sup> Li Zhang<sup>a\*</sup>, Weiwei Hao<sup>a</sup>, Haibo Wang<sup>a</sup>, Longfei Zhang<sup>a</sup>, Xiaomin Feng<sup>a</sup>, Yibo Zhang<sup>a</sup>, Weixiang Chen<sup>b</sup>, Huan Pang<sup>a</sup> and Honghe Zheng<sup>a\*</sup>

<sup>a</sup>School of Energy, Soochow University, Suzhou, Jiangsu, 215006, P. R. China

<sup>10</sup> <sup>b</sup>Department of Chemistry, Zhejiang University, Hangzhou, 310027, P. R. China

E-mail: zhangli81@suda.edu.cn, hhzheng@suda.edu.cn



**Figure S1.** The Schematic drawing of the dual-temperature zone tube furnace for synthesizing the porous N-doped graphene and NGSi@G granules.



Figure S2. XPS spectrum of the as-prepared porous N-doped graphene sheets.



**Figure S3.** TEM micrograph of the as-prepared porous N-doped graphene and the inset is the corresponding selected area electron diffraction (SAED) pattern.



**Figure S4.** TGA curves of the bare SiNPs, porous N-doped graphene and NGSi@G S1-S3 under the air atmosphere.

TGA was carried out to estimate the Si content (wt %) in the NGSi@G granules. Under an air atmosphere, the bare SiNPs sample has an increased weight of 7 wt% up to 750 °C due to the partial oxidation of Si particles. However, for the NGSi@G granules, there is very little oxidation of the inner SiNPs until 550 °C because the graphene frame and the graphitic carbon coating layer act as the sacrificial materials and consume oxygen first, therefore it's very convenient to calculate the Si content (wt %) in the NGSi@G S1-S3 granules by dividing the mass retained at 550 °C by the mass retained at 150°C where the absorbed water was completely subtracted.



**Figure S5.** (a) SEM micrograph of the as-prepared NGSi@G granules; (b)-(c) SEM micrographs of the NGSi@G S1 granules consist of 85.4% Si and 14.6% carbon at different magnification; (d) SEM micrograph of the as-prepared NGSi@G S2 granules at high magnificatin.



**Figure S6**. Reversible charge (delithiation) capacity and Coulombic efficiency versus cycle number profiles of NGSi@G S1 and NGSi@G S2 granules.



**Figure S7.** Nyquist plots of (a) pristine SiNPs and (b) NGSi@G S3 granules after different cycles with a DOD (delithiated state) of 60%.