Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Experimental Section

Synthesis of honeycomb nanostructure porous silicon (hp-Si). The hp-Si was prepared by reaction of silicate with magnesium according to magnesiothermic reduction reaction under the stainless autoclave. $Na_2SiO_3{\cdot}9H_2O$ (2.84g, crystal) and Mg (1.44g, 100-200 mesh) were mixed and added into an 20 mL stainless autoclave before sealed. Subsequently, the autoclave was maintained at 200 ^{0}C for 10 h and cooled to room temperature. The samples were immersed in hydrochloric acid (1 mol L^{-1}) for several hours to remove NaOH and other impurities. The resultant solution was washed with distilled water and centrifuged (3000 rpm, 10 min) to collect silicon. The obtained silicon was dissolved in 10 wt% dilute HF solution for 10 min to remove unreacted silica during reduction. The dark brown precipitate was collected by centrifuge and dried for overnight at 60 ^{0}C in vacuum oven to evaporate rest solvent.

Synthesis an Aqueous dispersion of Graphene Oxide (GO). GO solution was prepared according to a modified Hummer's method,[S1] and the synthetic details of graphene oxide can be found in our earlier publication.[S2] The homogeneous GO suspension in the supernatant solution had a concentration of about 1 mg mL^{-1}.

Fabrication of graphene-coated honeycomb nanostructure porous silicon (hp-Si@G). The hp-Si@G was synthesized by covalently grafting aniline onto the surface of naturally oxidized Si nanoparticles via a diazotization reaction,[S3, S4] followed by hydrothermal aggradational process under an autoclave with GO solution. Typically, 0.3 g of p-phenylenediamine (98.5%, Benchmark Chemical Reagent Co., Ltd., China) was firstly dissolved in 50 ml of distilled water contained 6 ml of concentrated hydrochloric acid under continuous stirring. 0.2 g of hp-Si was then added under the aid of sonication for 5 min at a power of about 4 W using a UH-100A probe-type sonicator (Tianjin AutoScience Instrument Co., Ltd, China). Subsequently, 10 ml of a 1.0 M sodium nitrite (99.0%,Benchmark Chemical Reagent Co., Ltd., China) solution was added dropwise into the above mixture. After this, the mixture was kept continuously stirring for 12 h. Unless otherwise stated, the diazotization reaction was performed in an ice-water bath. The resulting reaction solution was centrifugated, washed repeatedly with ethanol and distilled water until the supernatant solutions were colourless. Then, the hp-Si@GO was obtained by disperse with GO solution and then hydrothermal reaction at 180 °C for 5 h. Finaly, hp-Si@G could be obtained from the hp-Si@GO by simply removing the organic functional groups via pyrolysis process in a flow of Ar at 700 °C for 1 h.

Material Characterization. The morphology of the reaction product were characterized by scanning electron microscopy (SEM, JEOL-JSM-6700F), Transmission electron microsocopy (TEM, Hitachi H7650 and HRTEM, JEOL 2010). X-ray diffractometer (XRD) was performed on a Philips X' Pert Super diffract meter with Cu Kα radiation (λ=1.54178 Å). The nitrogen adsorption and desorption isotherms were measured with a VELSORP-mini II (BEL Japan, Inc.) at 473 K in the relative pressure range of P/P_0 from 0 to 1 to determine the Brunauer–Emmett–Teller (BET) surface areas and pore size distribution. Raman spectrum was performed with 514.5 nm wavelength to check the compositions and the carbon content of the product was check by EA (Vario EL-III).

Electrochemical Measurement. The electrochemical properties of hp-Si and hp-Si@G electrodes were measured with coin-type half cells (2016 R-type) which assemble under an argon-filled glove box (H_2O, O_2 < 1 ppm). Working electrode was prepared by mixing the active material, super P carbon black and sodium carboxymethyl cellulose (CMC) in a weight ratio of 75:20:5 in water solvent. The slurry was pasted onto a Cu foil and then dried in a vacuum oven at 80 ^{0}C for 10 h and then 120 °C for 2 h. The active material density of each cell was determined to be around 1.0~1.5 mg cm^{-2}. Metallic Li sheet was used as counter electrode, and 1 M $LiPF_6$ in ethylene carbonate/dimethylcarbonate (EC/DMC; 1:1 by Volume; Merck) as electrolyte. Galvanostatic measurements were made using a LAND-CT2001A instrument that were cycled between 0.005 V and 1.00 V at a rate of 0.4 – 7.2 A g^{-1}.

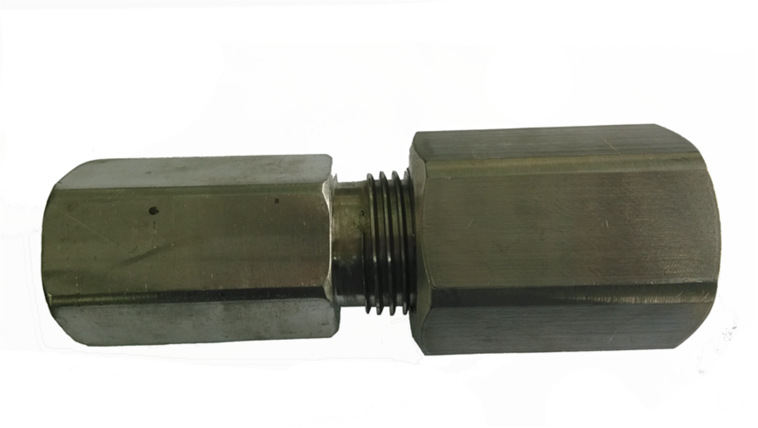

Figure S1. Images of the autoclave reactor used to carry out low temperature chemical reduction of sodium metasilicate nonahydrate in this report.

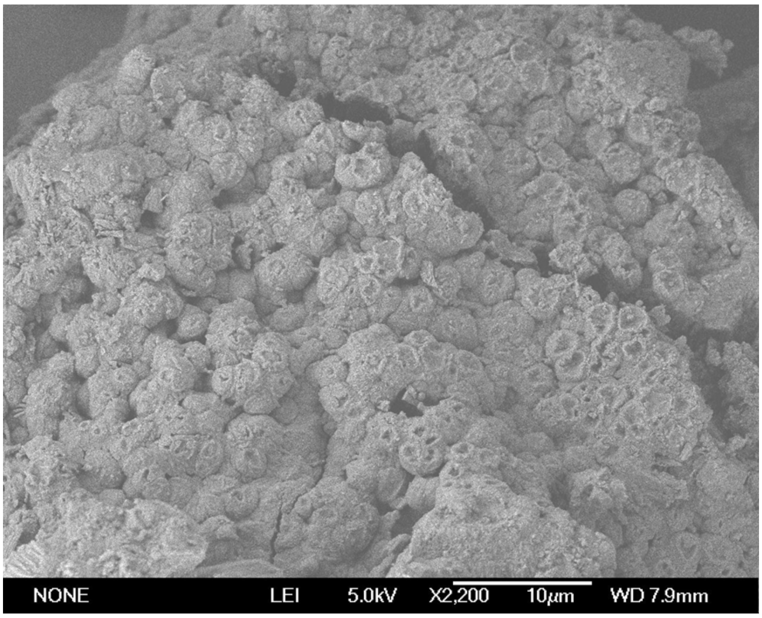

Figure S2. Large scale SEM image of agglomerated as-prepared reacted products.

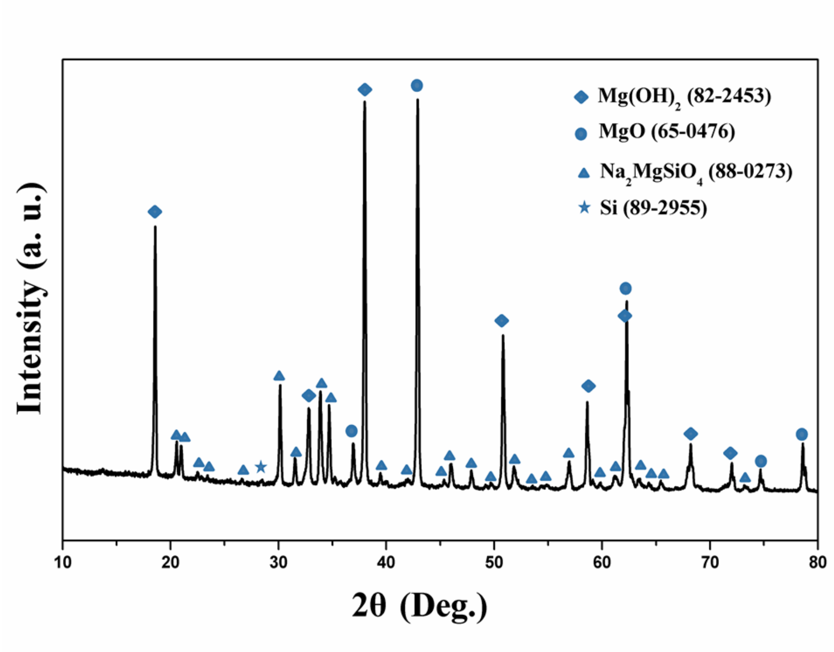

Figure S3. XRD pattern of agglomerated as-prepared reacted products under the synthesis temperature of 200 ^{0}C.

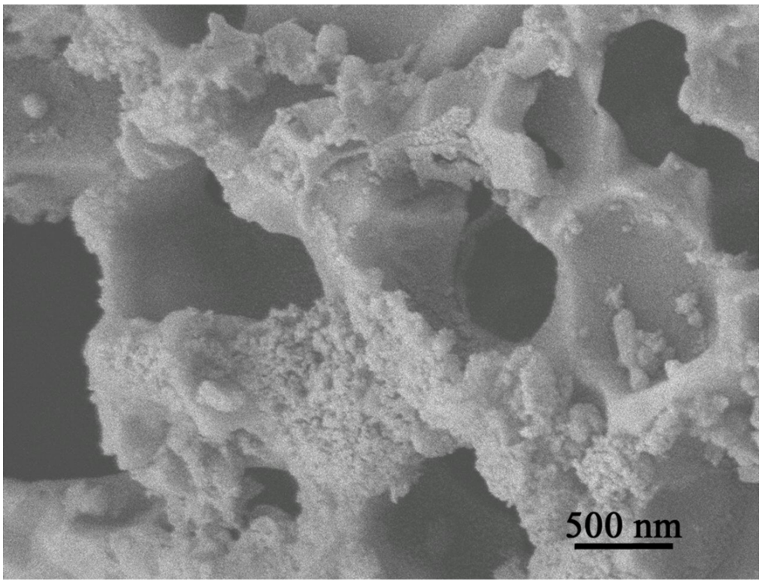

Figure S4. Large scale SEM image of agglomerated as-prepared reacted products.

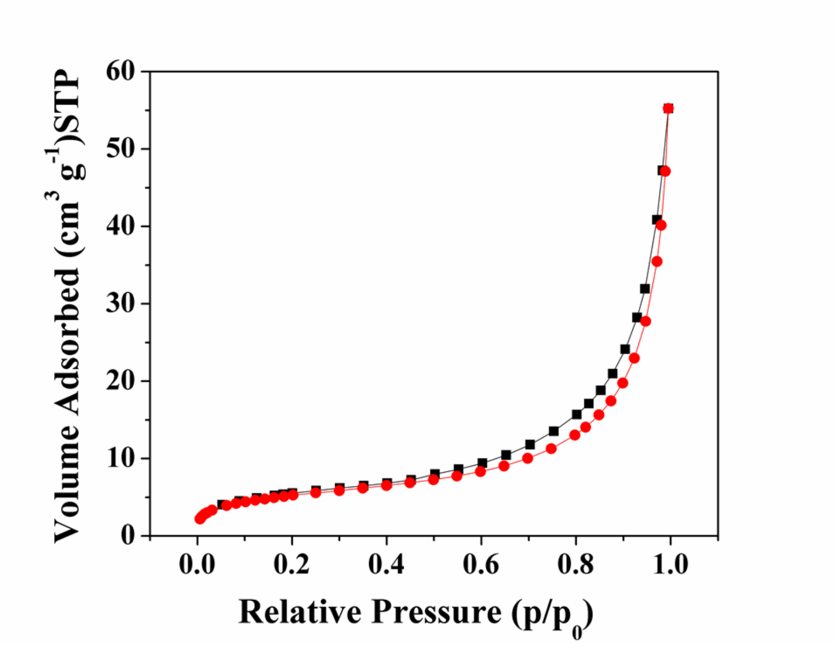

Figure S5. Nitrogen adsorption and desorption isotherms of hp-Si.

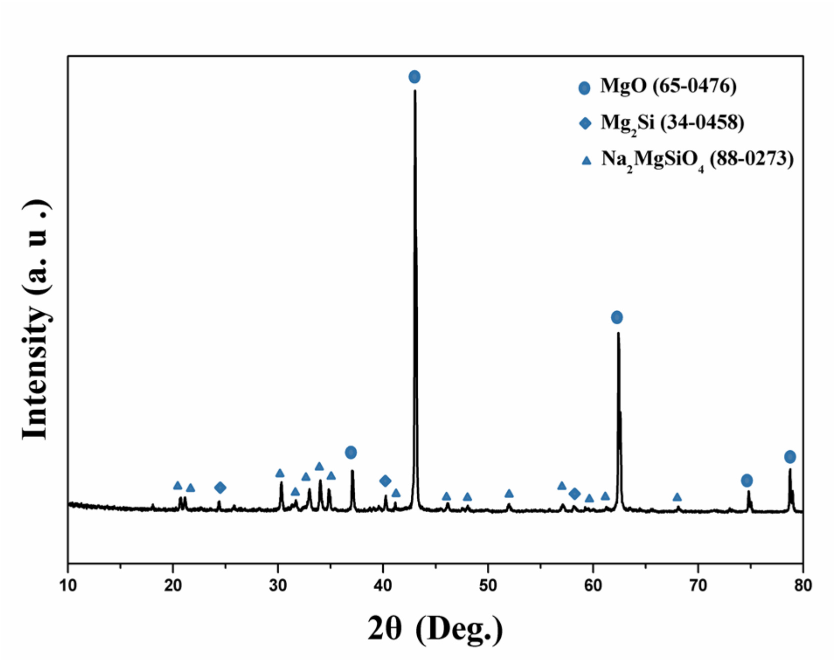

Figure S6. XRD pattern of agglomerated as-prepared reacted products under the synthesis temperature of 400 ^{0}C.

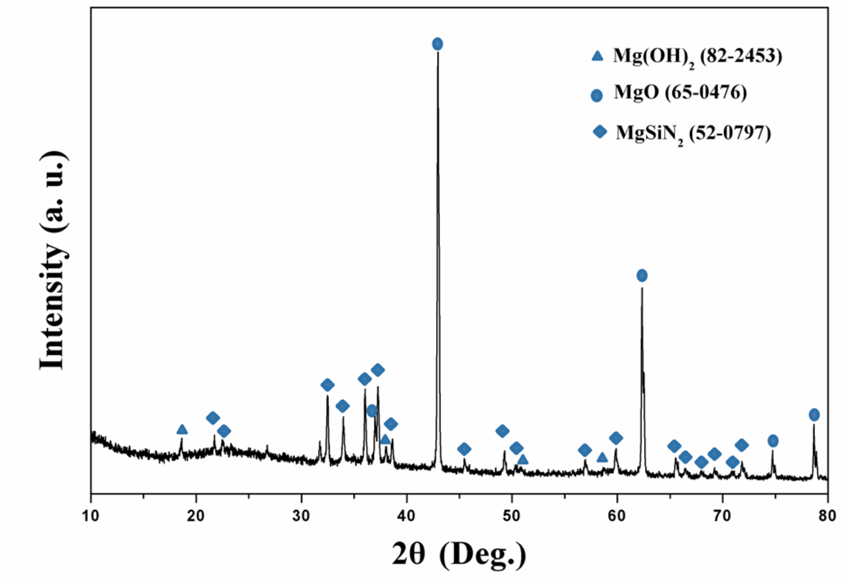

Figure S7. XRD pattern of MgSiN$_2$ production. The MgSiN$_2$ production was prepared by reaction of silicate with magnesium and NaN$_3$ according to similar procedure of this hp-Si. Typically, $Na_2SiO_3 \cdot 9H_2O$ (2.84g, crystal), Mg (7.2g, 100-200 mesh) and NaN$_3$ (1.44g, 100-200 mesh) were mixed and added into an 20 mL stainless autoclave before sealed. Subsequently, the autoclave was maintained at 300 ^{0}C for 10 h and cooled to room temperature. The reaction produc was directly measured with XRD.

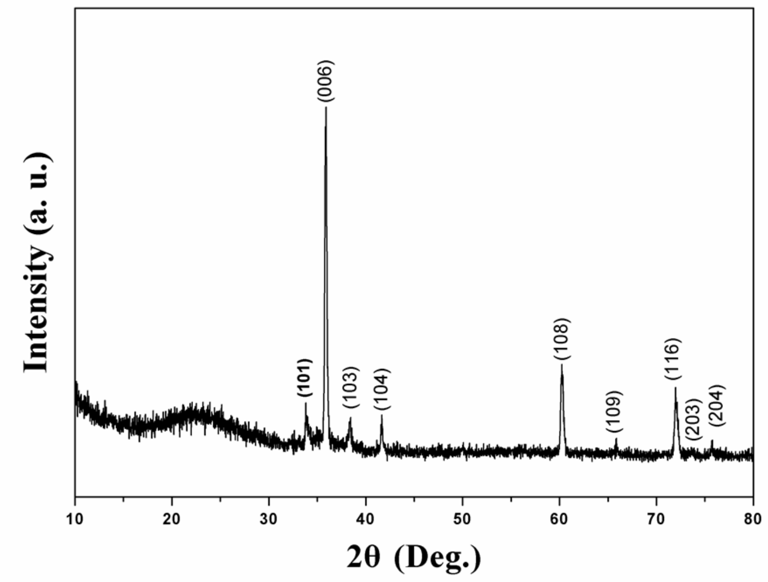

Figure S8. XRD pattern of SiC. The SiC production was prepared by reaction of silicate with magnesium and glocuse according to similar procedure of this hp-Si. Typically, $Na_2SiO_3 \cdot 9H_2O$ (2.84g, crystal), Mg (1.44g, 100-200 mesh) and glocuse (1.44g, 100-200 mesh) were mixed and added into an 20 mL stainless autoclave before sealed. Subsequently, the autoclave was maintained at 200 ^{0}C for 10 h and cooled to room temperature. The samples were immersed in hydrochloric acid (1 mol L^{-1}) for several hours to remove NaOH and other impurities. The resultant solution was washed with distilled water and centrifuged (3000 rpm, 10 min) to collect SiC.

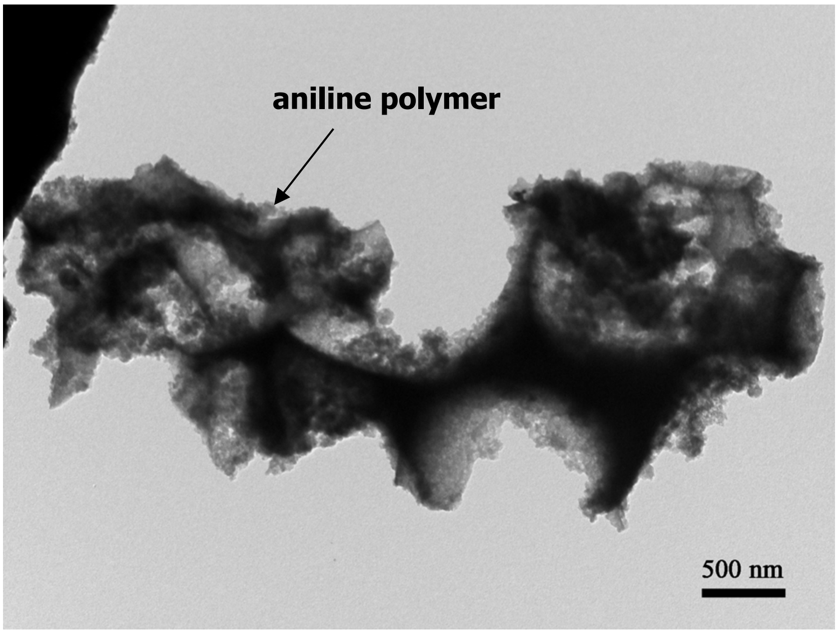

Figure S9. TEM image of aniline polymer based decoration of hp-Si. The anilinel polymer was uniformly distributed on the surface of hp-Si.

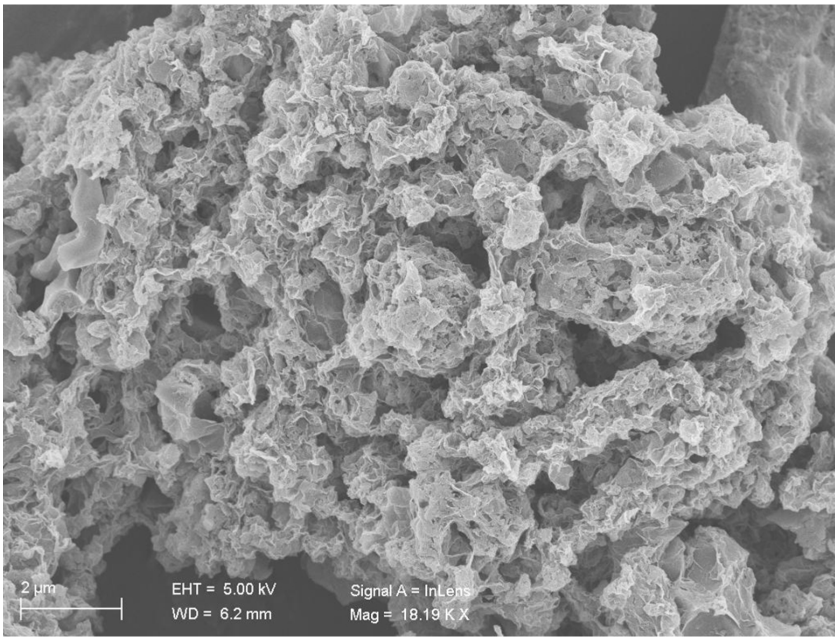

Figure S10. Low magnification SEM image of hp-Si@G.

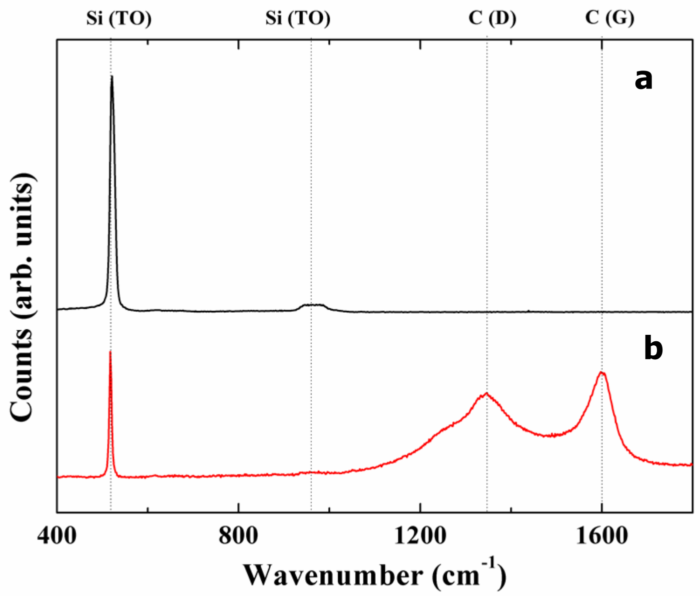

Figure S11. Raman spectra of hp-Si (top, a) and hp-Si@G (bottom, b).

References

S1. S. Park, J. An, R. D. Piner, I. Jung, D. Yang, A. Velamakanni, S. T. Nguyen and R. S. Ruoff, *Chem. Mater.*, 2008, **20**, 6592-6594.
S2. D. Wei, J. Liang, Y. Zhu, Z. Yuan, N. Li and Y. Qian, *Part. Part. Syst. Charact.*, 2013, **30**, 143-147.
S3. R. A. Messing and H. R. Stinson, *Mol. Cell. Biochem.*, 1974, **4**, 217-220.
S4. C. Du, M. Chen, L. Wang and G. Yin, *J. Mater. Chem.*, 2011, **21**, 15692-15697.