

## Supporting Information

### **Phase Segregation Assisted Morphology Sculpting - Growth of Graphite and Silicon Crystals via Vapor-Solid Reactions**

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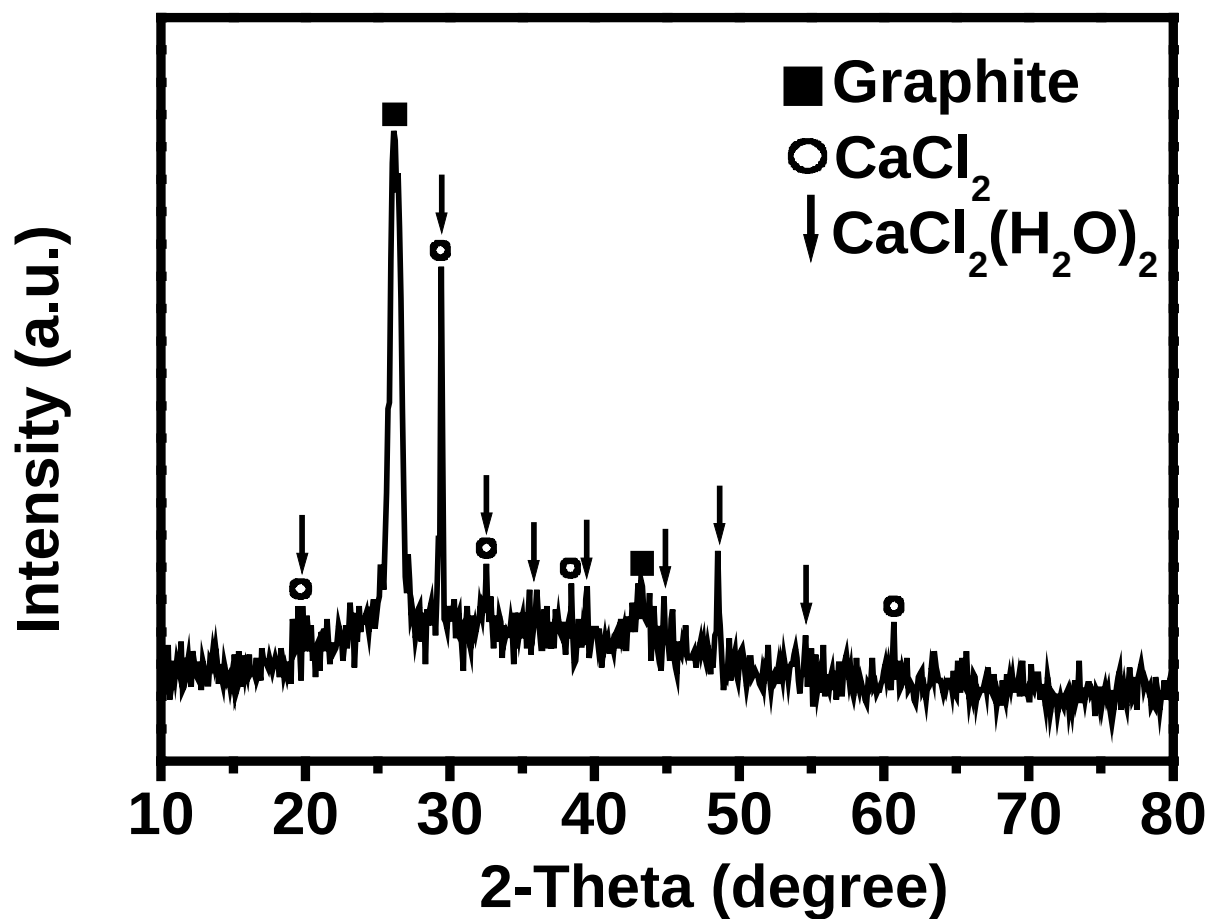
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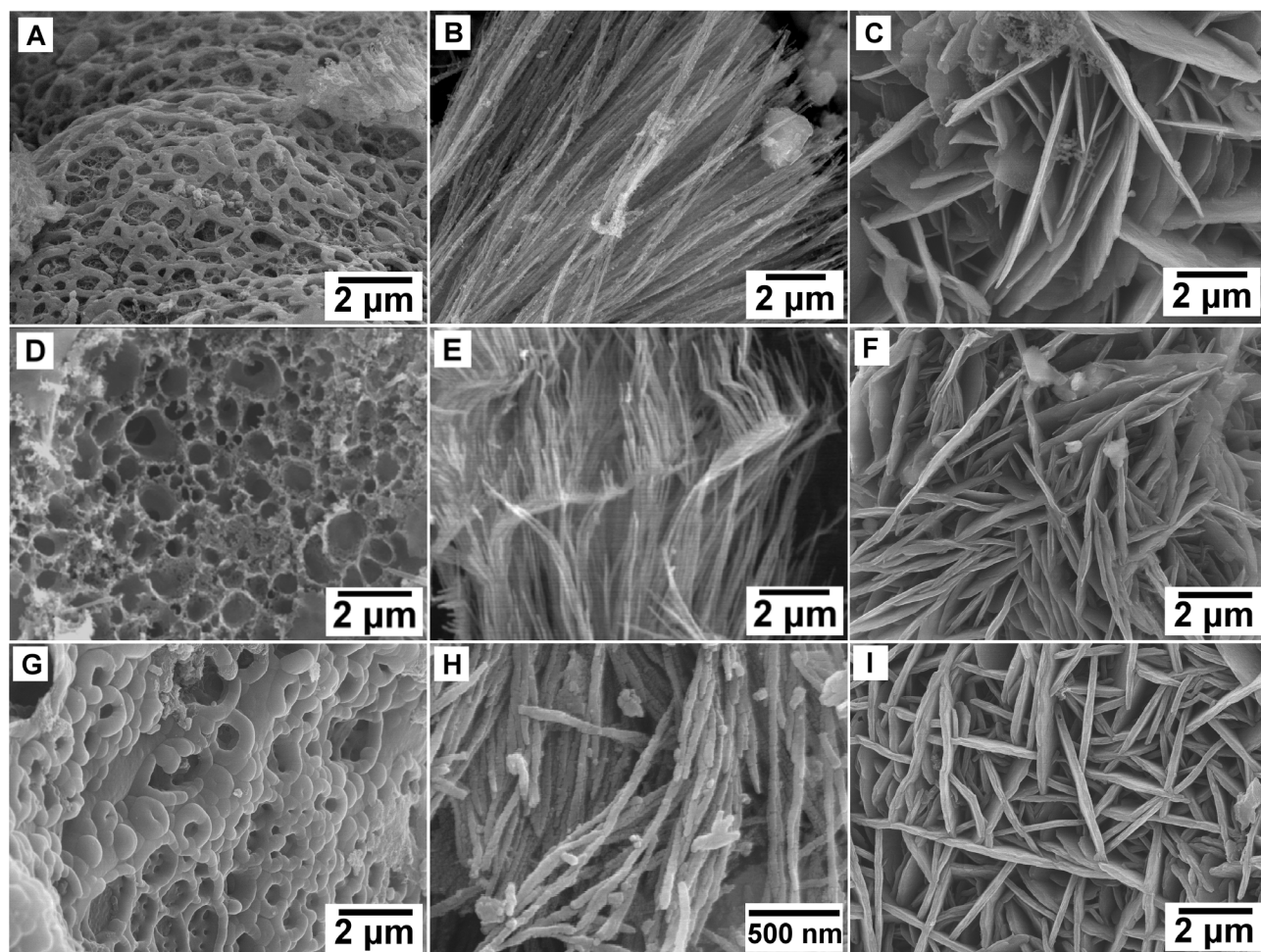
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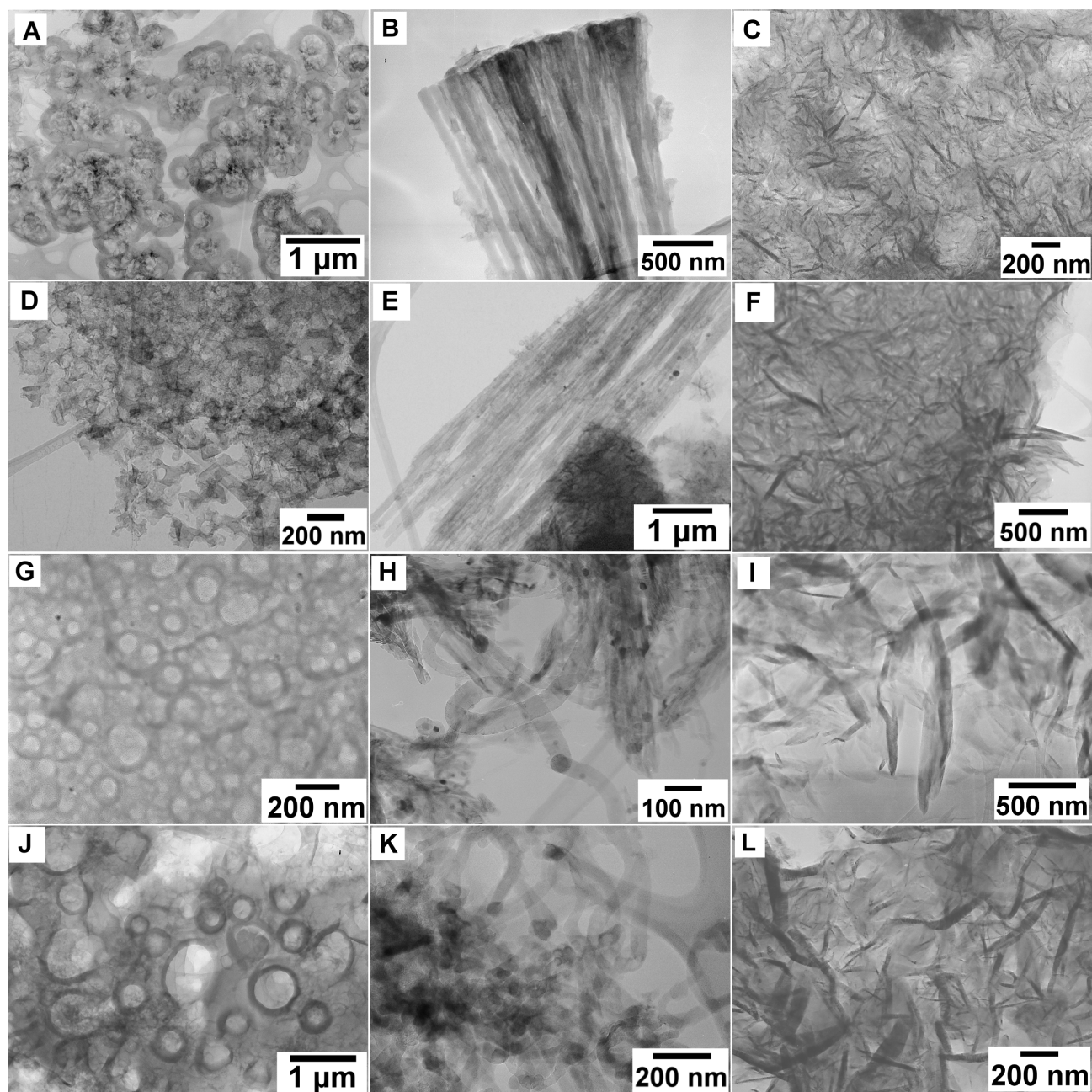


**Figure S1.** XRD of products grown from  $\text{CaC}_2$  and  $\text{C}_4\text{Cl}_6$  at 1223 K showing formation of graphite and  $\text{CaCl}_2(\text{H}_2\text{O})_x$ . JCPDS file number: graphite:23-0064,  $\text{CaCl}_2$ : 74-0522,  $\text{CaCl}_2(\text{H}_2\text{O})_2$ : 70-0385.



|                                    |                      |                      |                      |
|------------------------------------|----------------------|----------------------|----------------------|
| <b>CCl<sub>4</sub></b>             | (A)<br><b>1023 K</b> | (B)<br><b>1123 K</b> | (C)<br><b>1223 K</b> |
| <b>C<sub>2</sub>Cl<sub>4</sub></b> | (D)<br><b>973 K</b>  | (E)<br><b>1023 K</b> | (F)<br><b>1123 K</b> |
| <b>C<sub>5</sub>Cl<sub>6</sub></b> | (G)<br><b>1023 K</b> | (H)<br><b>1123 K</b> | (I)<br><b>1223 K</b> |

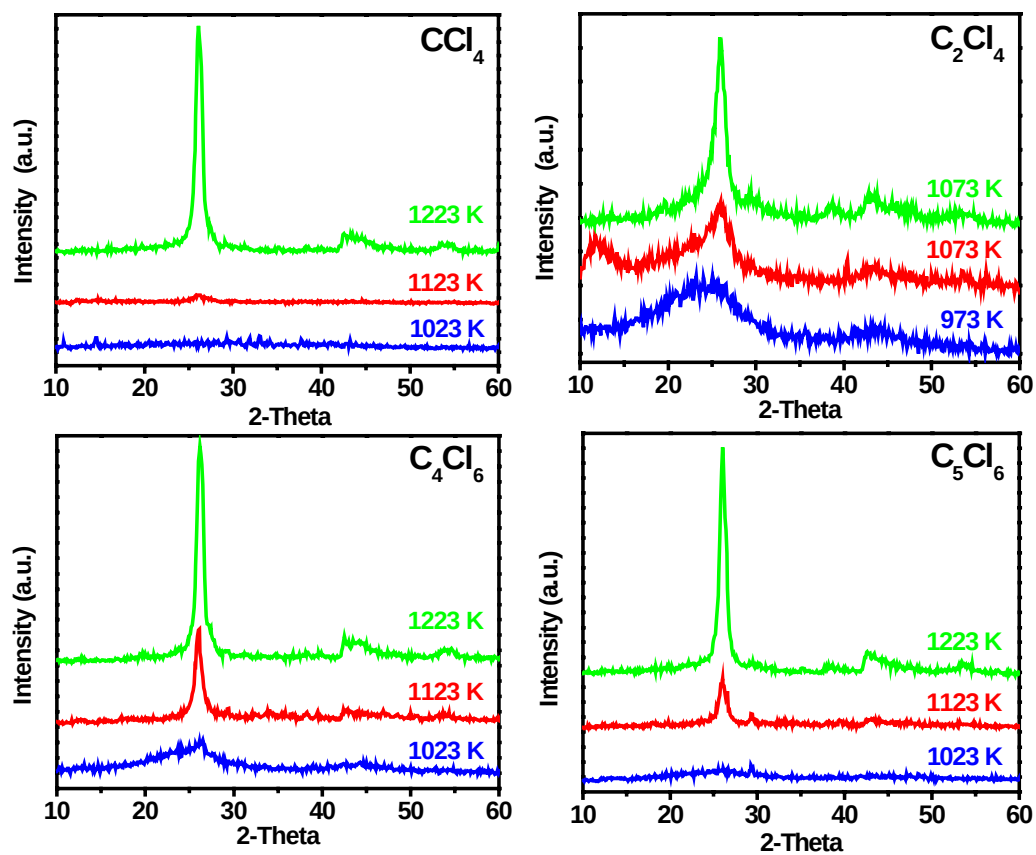
**Figure S2.** SEM images of graphite products prepared from  $\text{CaC}_2$  and  $\text{C}_x\text{Cl}_y$  at different temperatures.



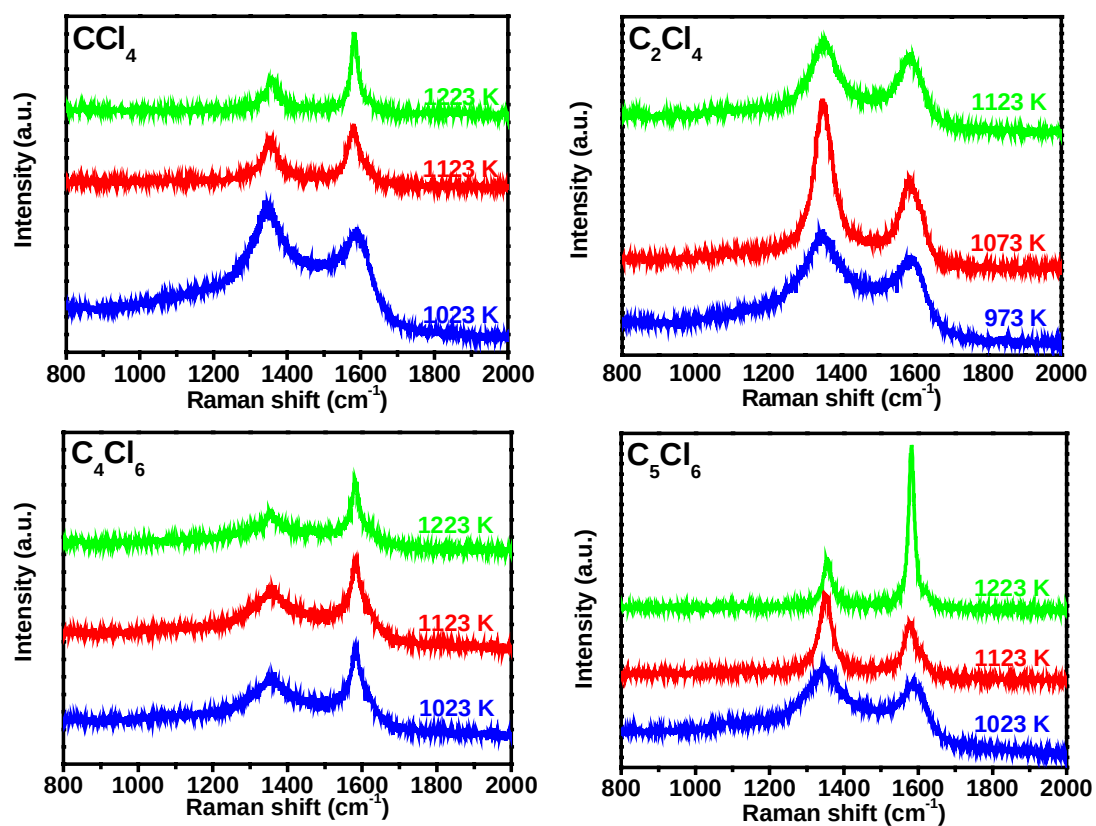
|                                    |                             |                             |                             |
|------------------------------------|-----------------------------|-----------------------------|-----------------------------|
| <b>CCl<sub>4</sub></b>             | <b>(A)</b><br><b>1023 K</b> | <b>(B)</b><br><b>1123 K</b> | <b>(C)</b><br><b>1223 K</b> |
| <b>C<sub>2</sub>Cl<sub>4</sub></b> | <b>(D)</b><br><b>973 K</b>  | <b>(E)</b><br><b>1023 K</b> | <b>(F)</b><br><b>1123 K</b> |
| <b>C<sub>4</sub>Cl<sub>6</sub></b> | <b>(G)</b><br><b>1023 K</b> | <b>(H)</b><br><b>1123 K</b> | <b>(I)</b><br><b>1223 K</b> |
| <b>C<sub>5</sub>Cl<sub>6</sub></b> | <b>(J)</b><br><b>1023 K</b> | <b>(K)</b><br><b>1123 K</b> | <b>(L)</b><br><b>1223 K</b> |

**Figure S3.** TEM images of graphite products prepared from CaC<sub>2</sub> and C<sub>x</sub>Cl<sub>y</sub> at different temperatures.

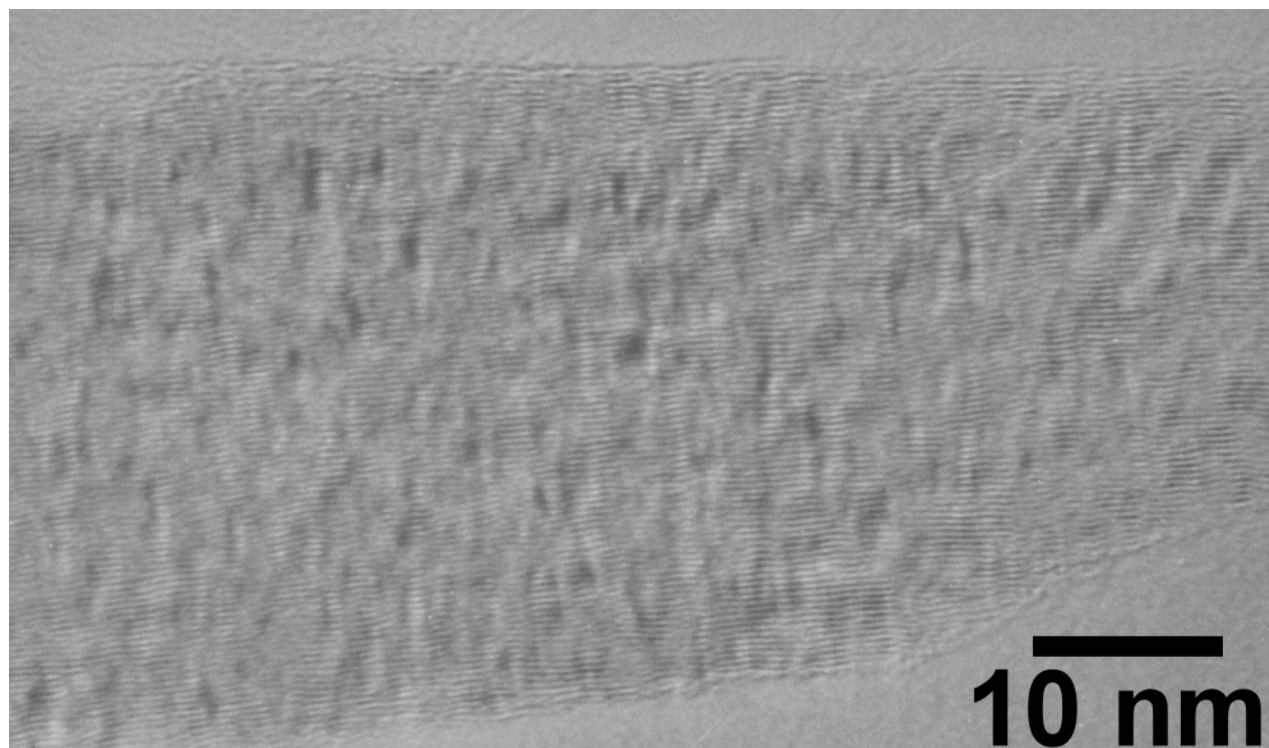




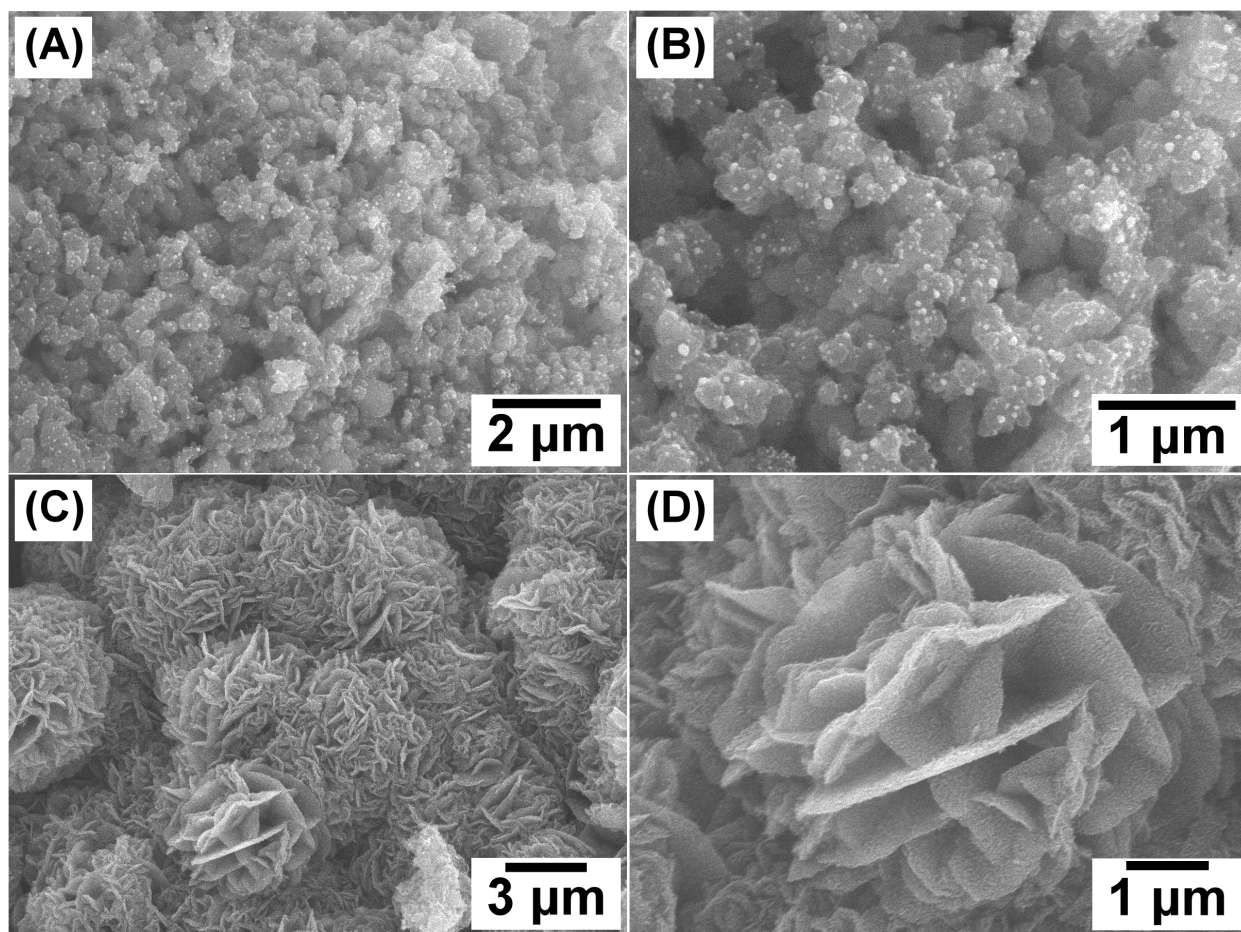
**Figure S4.** XRD of graphite products grown at 973 K – 1223 K from  $\text{CaC}_2$  and  $\text{C}_x\text{Cl}_y$ .



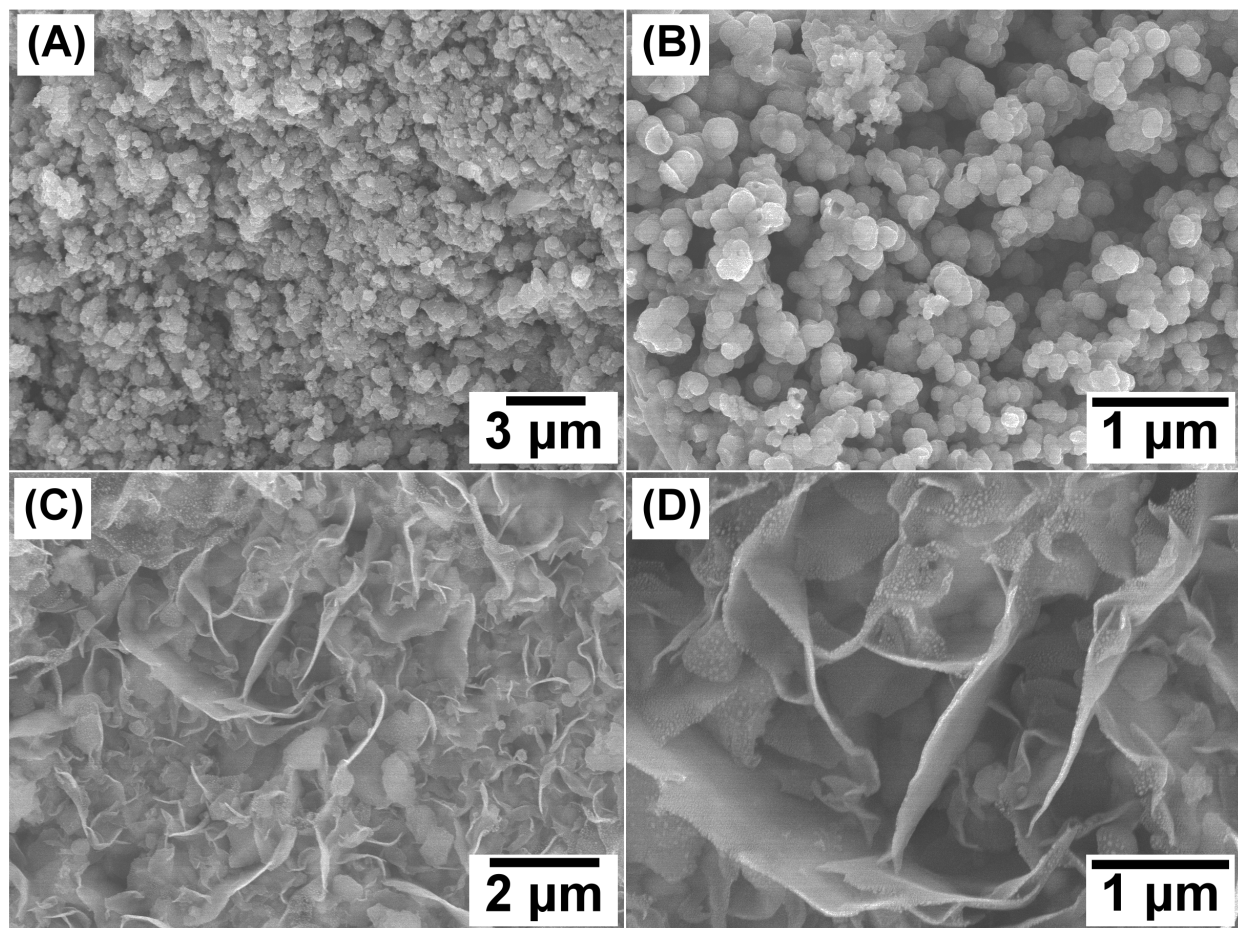
**Figure S5.** Raman spectra of graphite products grown at 973 K – 1223 K from CaC<sub>2</sub> and C<sub>x</sub>Cl<sub>y</sub>.



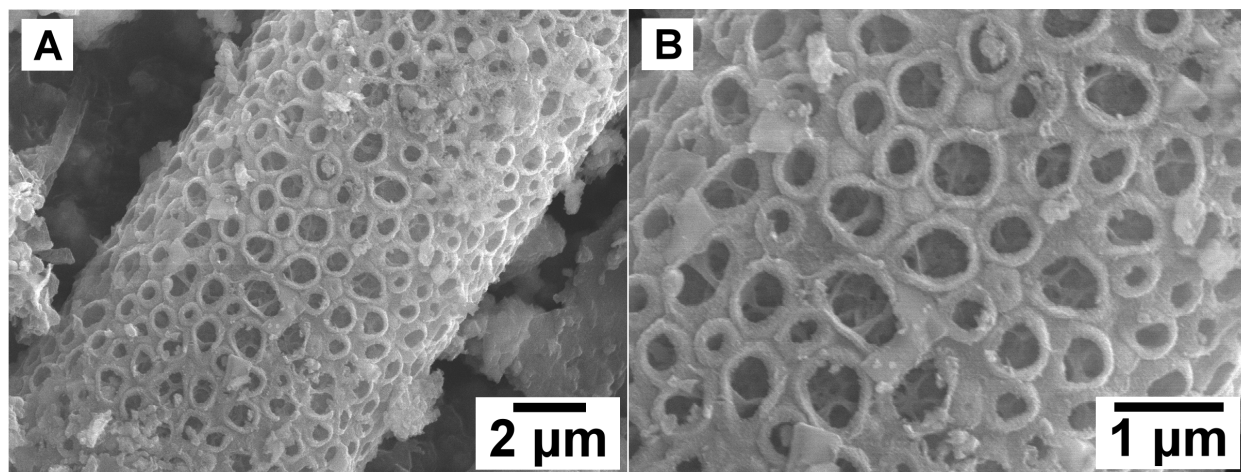
**Figure S6.** HRTEM of a sample prepared from  $\text{CaC}_2$  and  $\text{C}_4\text{Cl}_6$  at 1023 K, showing nearly one hundred graphene layers.



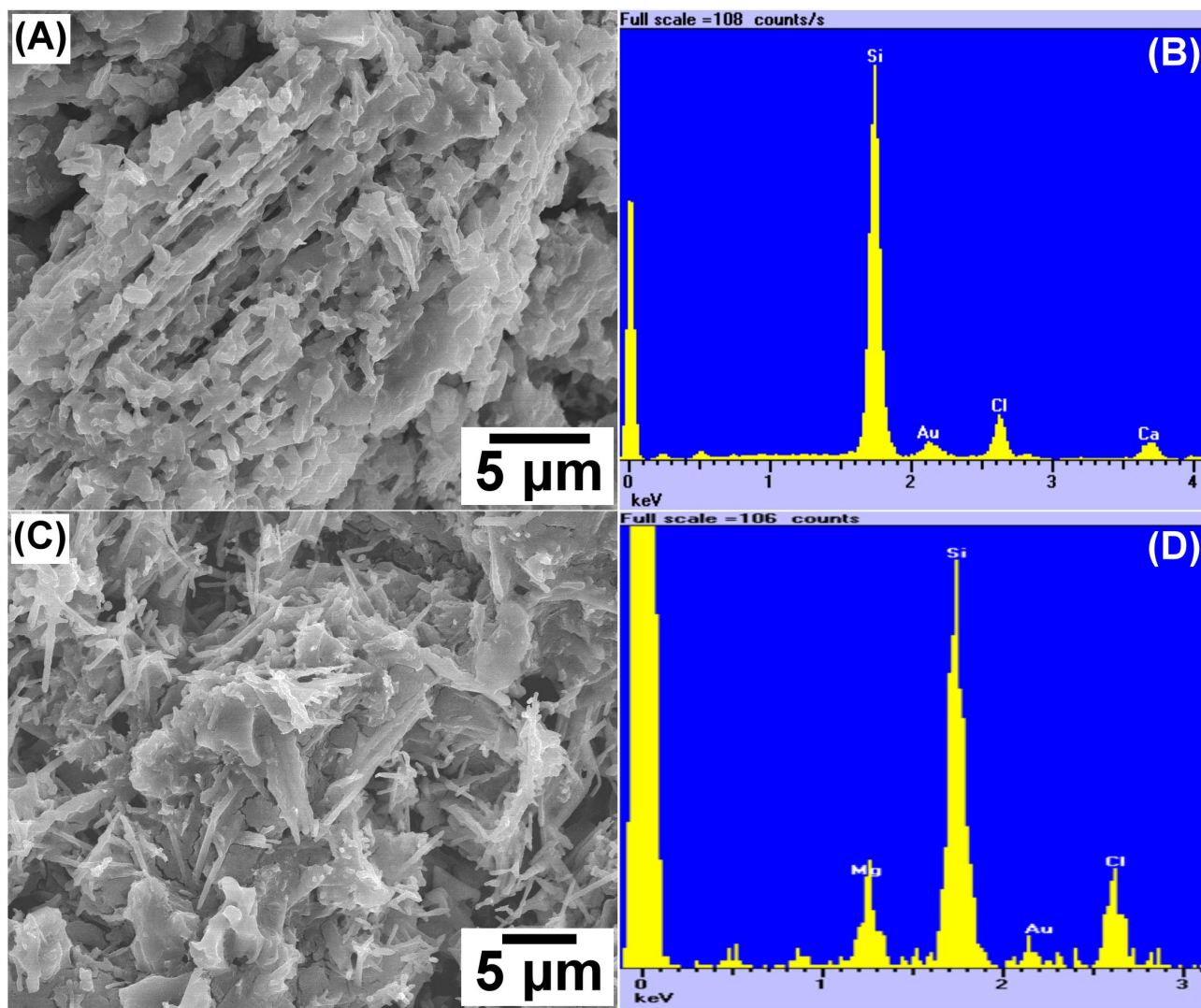
**Figure S7.** SEM images of products prepared from  $\text{CaC}_2$  and  $\text{Br}_2$ . (A) Low and (B) high magnification carbon particles, prepared at 1023 K; (C) Low and (D) high magnification planar carbon, prepared at 1223 K.



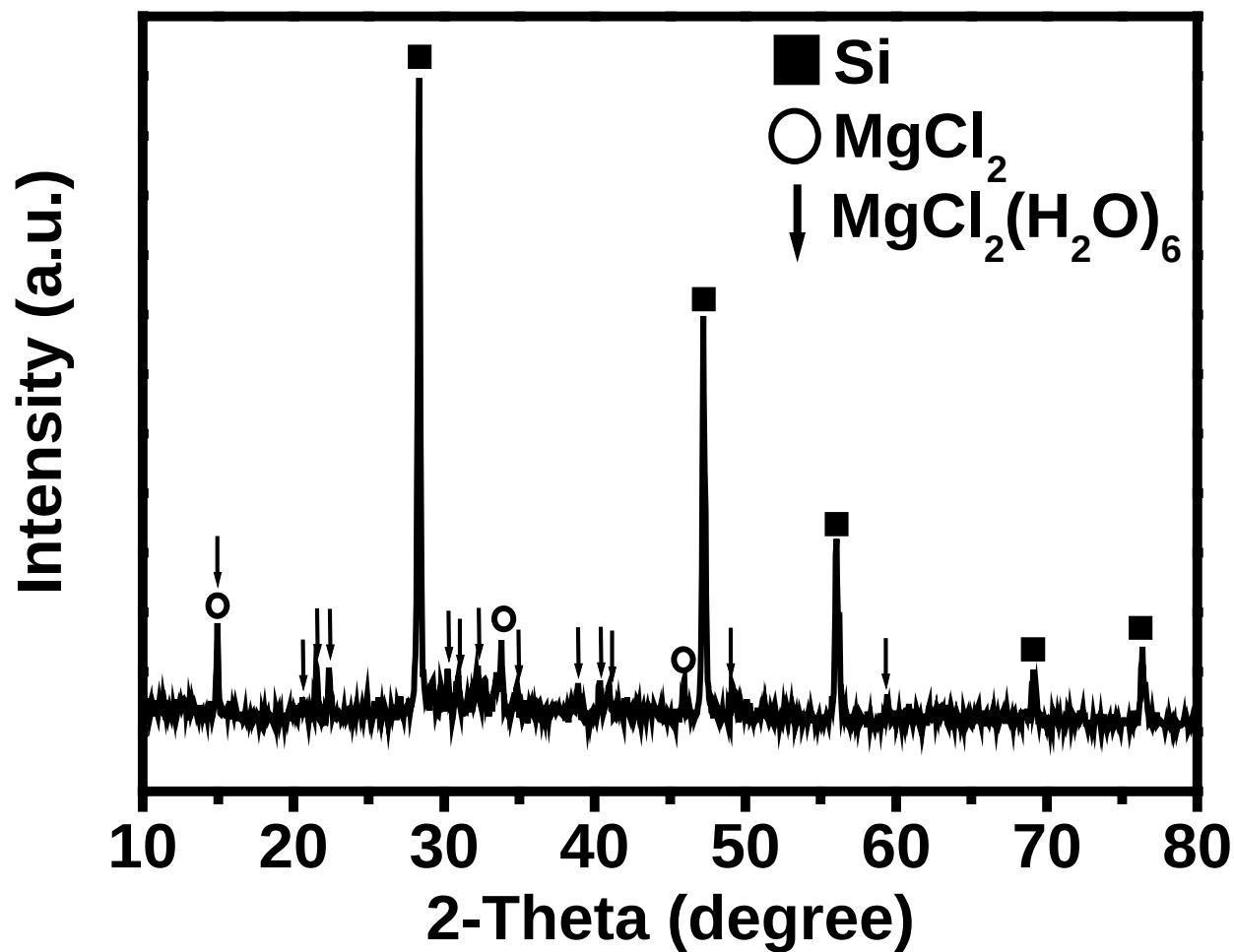
**Figure S8.** SEM images of products prepared from  $\text{CaC}_2$  and  $\text{I}_2$ . (A) Low and (B) high magnification carbon particles, prepared at 1023 K; (C) Low and (D) high magnification planar carbon, prepared at 1223 K.



**Figure S9.** SEM images of products prepared from  $\text{CaC}_2$  and  $\text{C}_6\text{Cl}_6$ . (A) Low and (B) high magnification porous carbon, prepared at 1023 K.

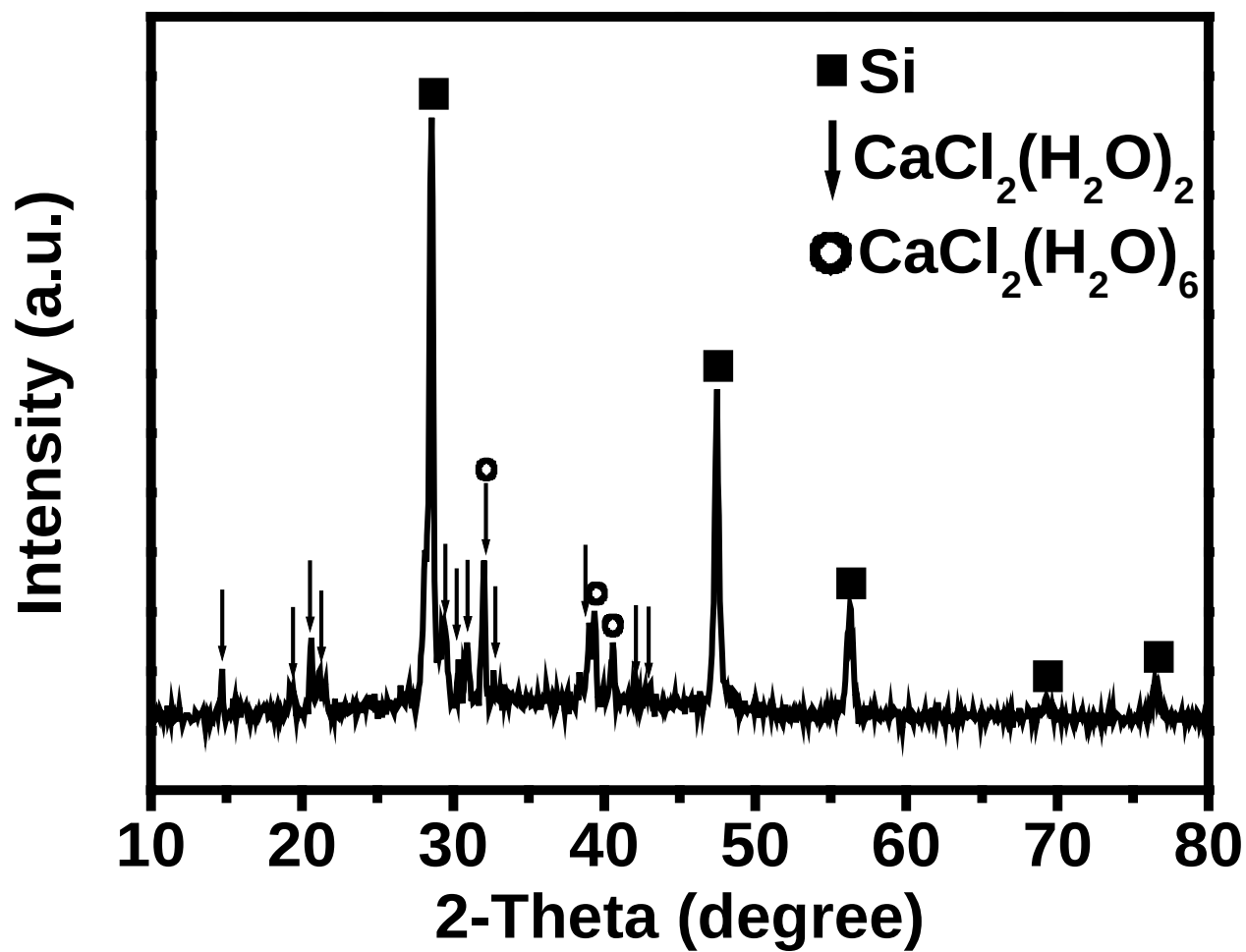


**Figure S10.** (A) SEM and (B) EDX of products synthesized from  $\text{SiCl}_4$  and  $\text{CaSi}_2$  at 1123 K showing formation of Si and  $\text{CaCl}_2$ . (C) SEM and (D) EDX of products synthesized from  $\text{SiCl}_4$  and  $\text{Mg}_2\text{Si}$  at 1123 K showing formation of Si and  $\text{MgCl}_2$ .

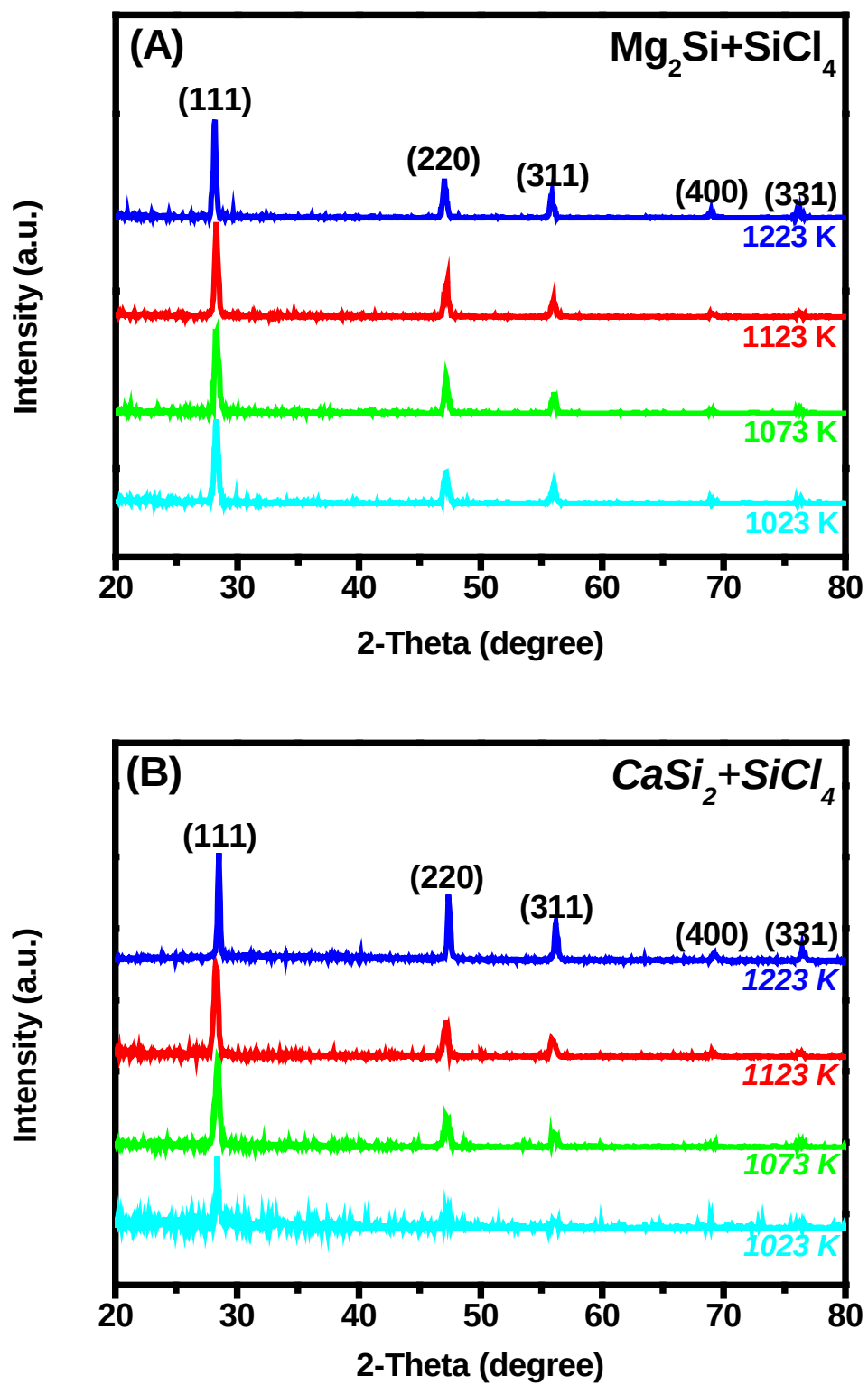


**Figure S11.** XRD of products grown from  $\text{SiCl}_4$  and  $\text{Mg}_2\text{Si}$  at 1123 K showing formation of Si,  $\text{MgCl}_2$  and  $\text{MgCl}_2(\text{H}_2\text{O})_6$ . JCPDS file number: Si, 89-5012;  $\text{MgCl}_2$ , 89-1567;  $\text{MgCl}_2(\text{H}_2\text{O})_6$ , 74-1039.

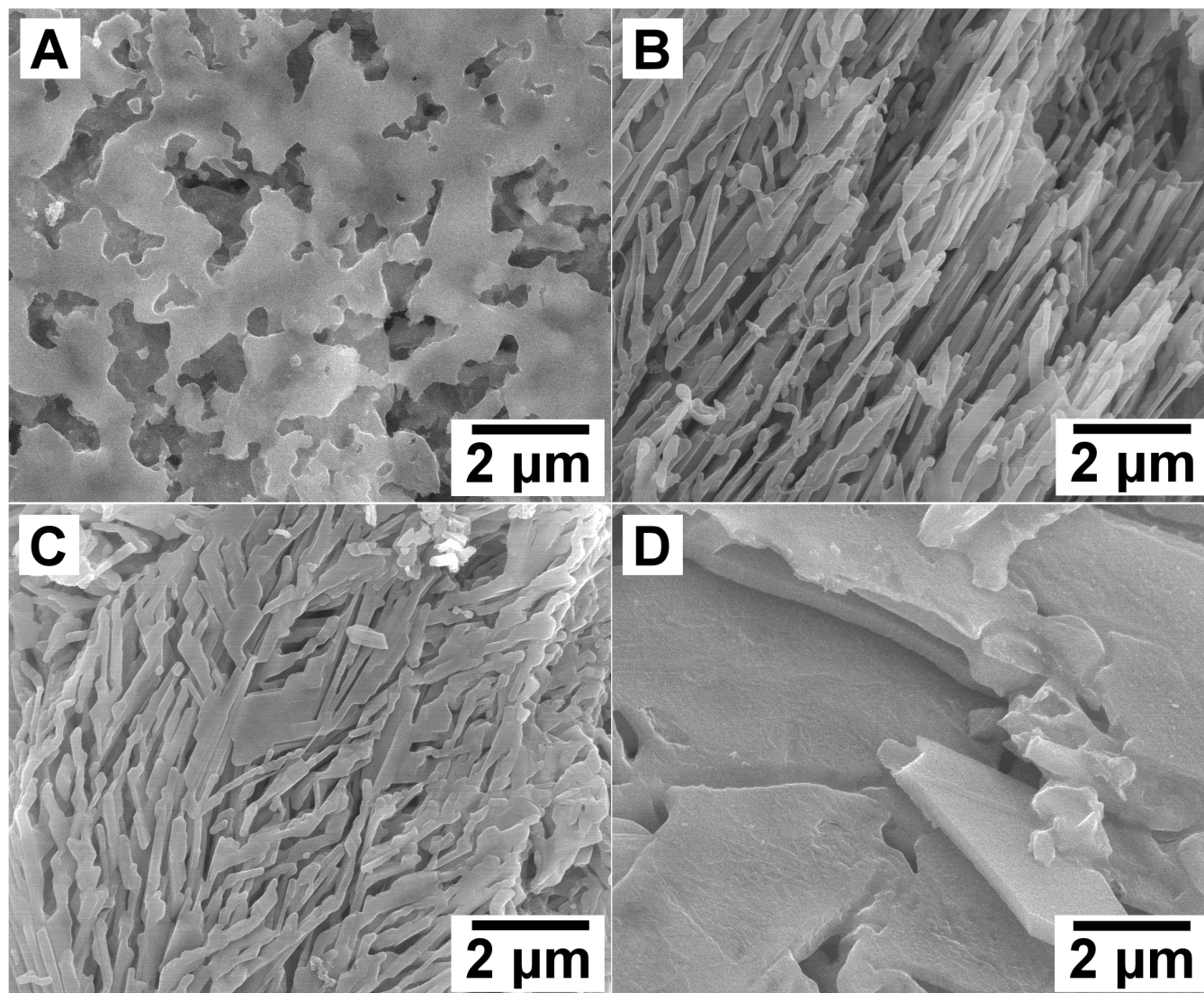




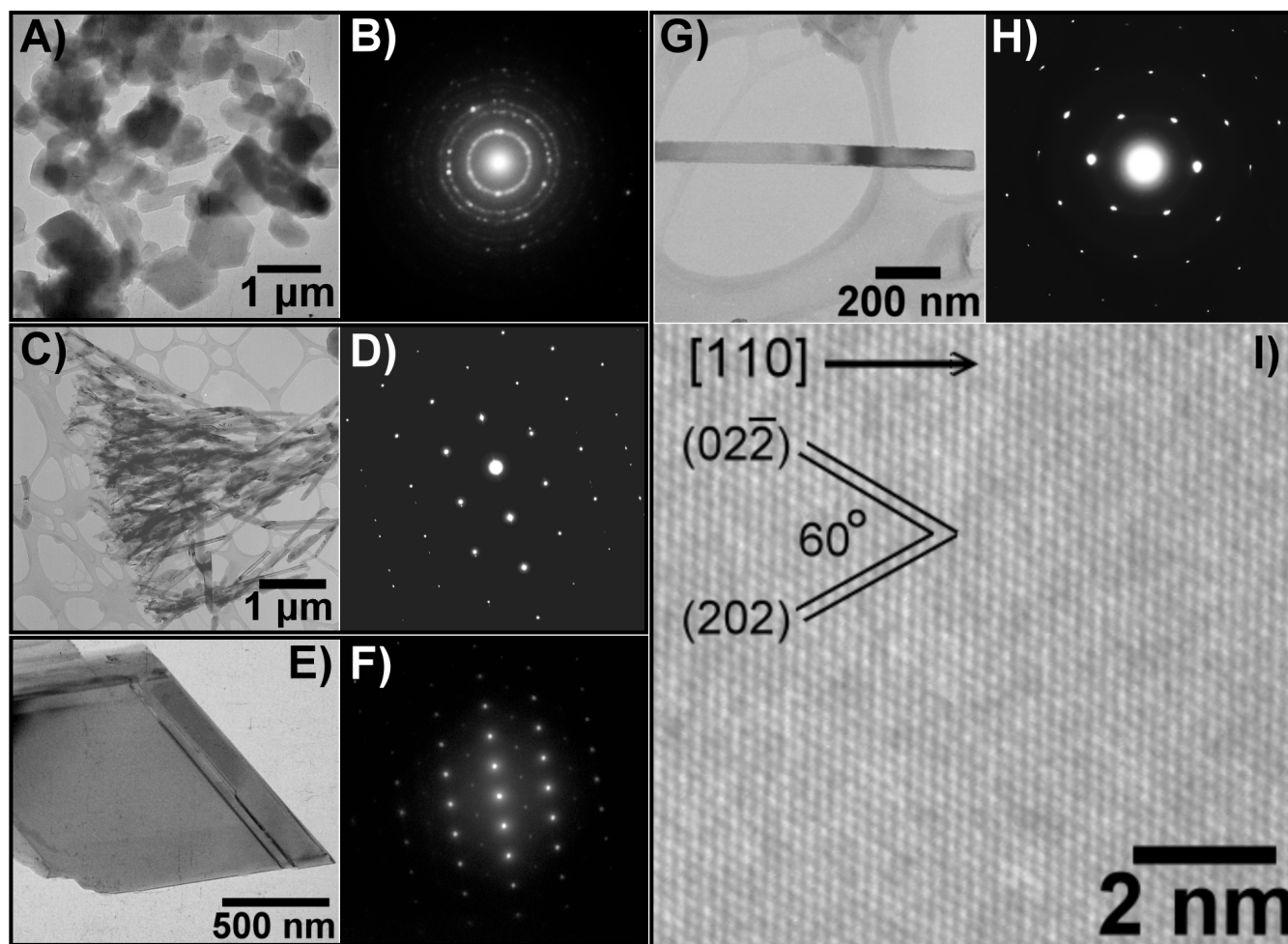
**Figure S12.** XRD of products grown from  $\text{SiCl}_4$  and  $\text{CaSi}_2$  at 1123 K showing formation of Si and  $\text{CaCl}_2(\text{H}_2\text{O})_x$ . JCPDS file number: Si, 89-5012;  $\text{CaCl}_2(\text{H}_2\text{O})_2$ , 70-0385;  $\text{CaCl}_2(\text{H}_2\text{O})_6$ , 77-1782.



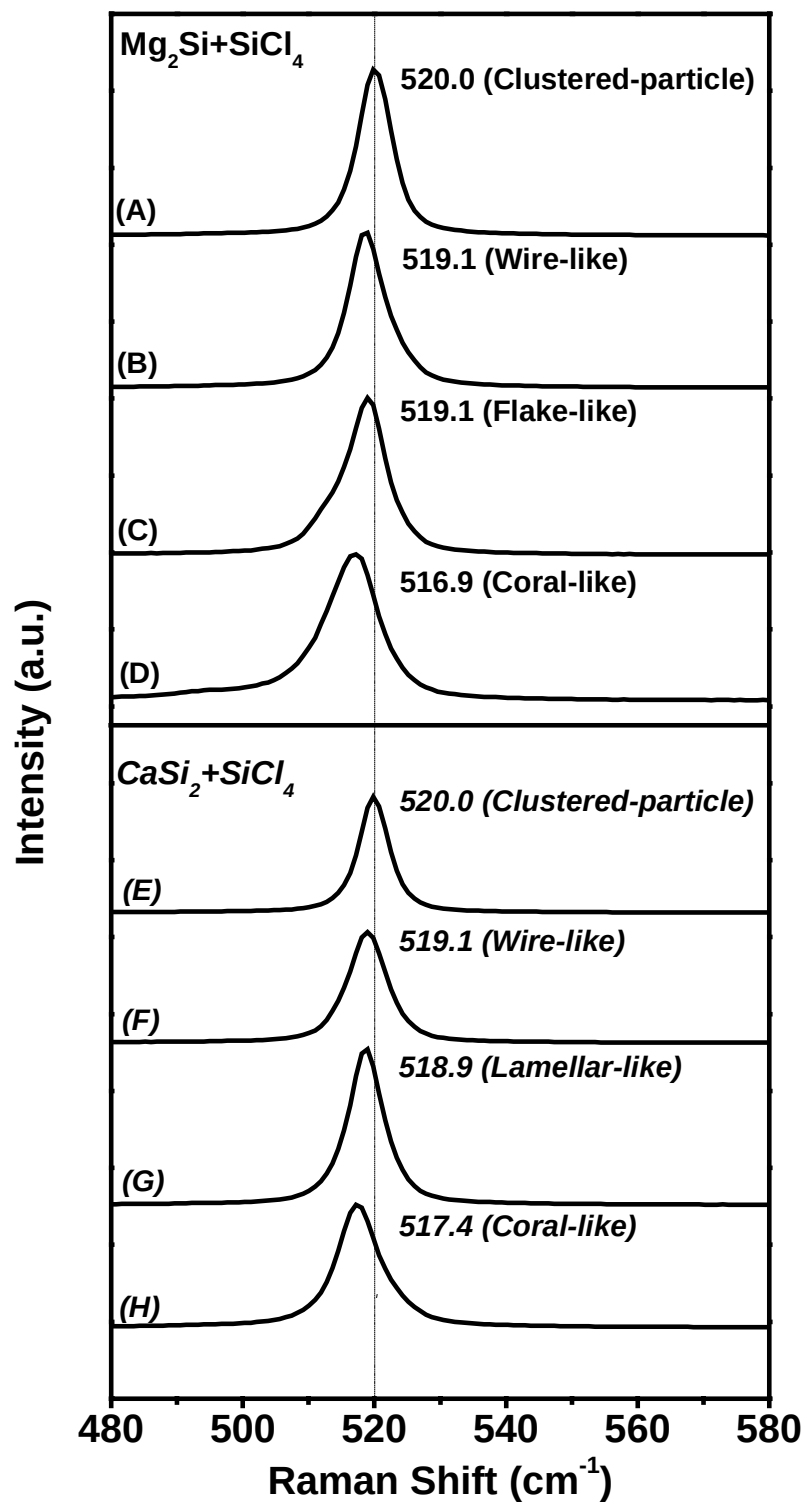
**Figure S13.** XRD of silicon products grown at 1023 K – 1223 K from  $\text{SiCl}_4$  and (A)  $\text{Mg}_2\text{Si}$ , (B)  $\text{CaSi}_2$  after removal of the salts. JCPDS file number: Si, 89-5012.



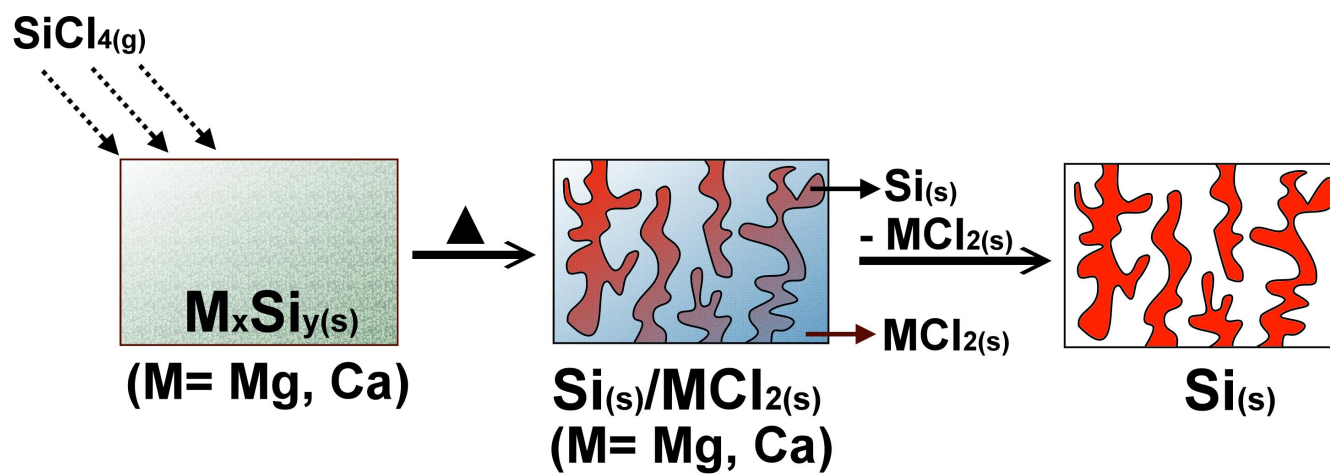
**Figure S14.** SEM images of silicon products prepared from  $\text{CaSi}_2$  and  $\text{SiCl}_4$ . (A) Porous silicon, prepared at 1023 K; (B) silicon nanowires, prepared at 1073 K; (C) coral-like silicon, prepared at 1123 K; (D) planar silicon, prepared at 1223 K.



**Figure S15.** Various morphology of silicon products prepared from  $\text{CaSi}_2$  and  $\text{SiCl}_4$ . (A) TEM image and (B) SAED of porous structure prepared at 1023 K; (C) TEM image and (D) SAED taken along the  $[0\ 1\ 1]$  zone axis of coral-like silicon prepared at 1123 K; (E) TEM image and (F) SAED taken along the  $[1\ -1\ -2]$  zone axis of planar silicon prepared at 1223 K; (G) TEM (low magnification) image and (H) SAED taken along the  $[-1\ 1\ 1]$  zone axis and (I) HRTEM image of a single silicon nanowire prepared at 1073 K.



**Figure S16.** Raman spectra of Si products with different structures prepared from  $\text{SiCl}_4$  and  $\text{Mg}_2\text{Si}$  at (A) 1023 K, (B) 1073 K, (C) 1123 K, (D) 1223 K; and  $\text{CaSi}_2$  at (E) 1023 K, (F) 1073 K, (G) 1123 K, (H) 1223 K.



**Figure S17.** An illustration of formation of textured silicon from  $SiCl_4$  and metal silicides (metal = Mg, Ca). The products  $MCl_2$  and Si act as self-templating mold and cast