

Preparation of pillared carbon

Preparation of GO

Natural graphite powder (Madagascar, purity >99.7%, 57- 74 μm , 10 g) was put in a beaker and fuming nitric acid (200 mL) was added. This mixture was heated in a water bath to 60°C and then potassium chlorate (80 g) was gradually added. (*Caution!* Do not add a large amount of KClO_3 at one time, otherwise explosion may occur. Ventilation is necessary during reaction because of the generation of chlorine gas.) The mixture was kept for 3 h at 60 °C and then, it was added to 2 L of water. The resulting solution was filtered and washed with water several times. The product was dried overnight. This procedure was repeated for 5 times. The elemental analysis data of carbon and hydrogen (56.40 and 1.74%, respectively) indicated that the composition of GO was $\text{C}_8\text{H}_{3.0}\text{O}_{4.5}$. The content of oxygen was calculated by subtracting those of carbon and hydrogen from 100%.

Silylation of GO and preparation of pillared carbon

GO (100 mg) was mixed with *n*-butylamine ($\text{C}_4\text{H}_9\text{NH}_2$, hereafter abbreviated as C_4 , 2 ml; 32 molecules per GO unit) as an exfoliating reagent in a sealed glass vial under an Argon atmosphere and the resulting solution was sonicated, then heated at 60 °C for 1 h. Dry toluene (5 ml, water content <30 ppm) was added to this solution and the solution was again sonicated. Methyltrichlorosilane (0.86 mL, 13 molecules per GO unit) was added to the resulting and then allowed to stand for 2 day at 60 °C. After centrifugation at 4000 rpm for 20 min, the precipitate was washed with dry toluene, ethanol and finally acetone. This procedure was repeated for 3 times. The composition of silylated GO was determined from the weight of residual SiO_2 after thermogravimetric analysis, assuming that 0. 4 *n*-butylamine molecules per GO were included. Fig.S1 shows the X-ray diffraction patterns of GO and silylated GO samples. The diffraction peak at $2\theta=12.76^\circ$ observed for pristine GO shifted to lower angle of $2\theta=8.16, 6.52$ and finally 5.14° . The content of silylating reagent per GO which was estimated from the weight of residual SiO_2 after thermogravimetric measurement increased from 0.83 to 2.3 as shown in Table S1. Here, the thermogravimetric measurement (Shimadzu TGA-50) was performed under ambient atmosphere at the temperature increase rate of 5 °C/min from room temperature to 800 °C.

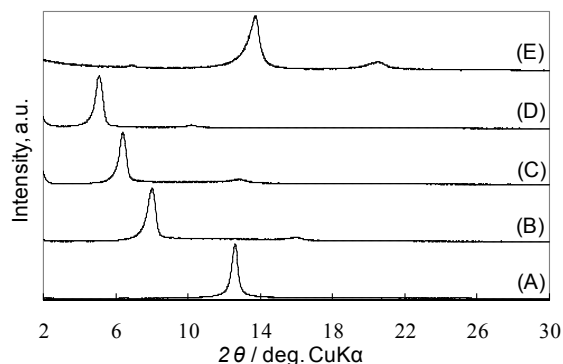


Fig. S1 X-ray diffraction patterns of graphite oxide (A): before and after silylated with methyltrichlorosilane for (B): 1, (C): 2 and (D): 3 times, together with (E): that of pillared carbon.

The resulting silylated GO was heated at 500 °C under dynamic vacuum. The temperature increase rate was 1 °C/min and the amount of the sample was less than 200 mg in order to avoid the deflagration of GO layers due to the heat generate during the removal oxygen from GO layers.

The diffraction peak at $2\theta=7.12$, 13.76 and 20.78 ° are indexed as (001), (002) and (003), respectively and the interlayer spacing was calculated to be 1.39 nm. The composition determined based on the elemental analysis data of carbon (50.81%) and hydrogen (2.52%), together with that of silicon estimated from the weight of residual SiO₂ after thermogravimetric measurement (23.0%) was C_{4.1}(CH₃SiO_{1.8}).

Table S1 Composition of silylated GO samples

sample	Si / wt. %	x in (CH ₃ Si(OH) ₂) _x GO
(B)	10.1	0.83
(C)	14.0	1.6
(D)	16.6	2.3

SEM and TEM observations of the pillared carbon

The SEM and TEM observations were performed using JEOL JSM-5500 and JEM2100F with the accelerating voltages of 15 and 80 kV, respectively. The sample was ground in a pestle and then it was dispersed in ethanol in case of the TEM observation. Fig.S2 shows the SEM images of pillared carbon. The sample was consisting of thin plate-like particles with the lateral size of 50 μm and the thickness of 5 μm, reflecting size of the starting graphite.

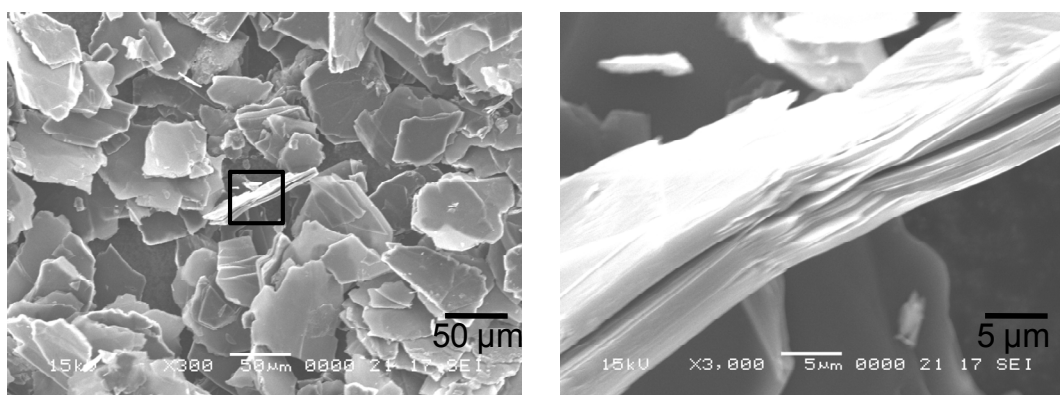


Fig. S2 SEM images of pillared carbon. Right: lower magnification, left: higher magnification.

Fig.S3 shows the TEM image of the pillared carbon. The layers with the lattice spacing of 0.56 nm was observed, which is almost consistent with the separation of (002) plane of pillared carbon (0.64 nm) which was observed in the X-ray diffraction measurement. These observations confirm the

layered structure of the pillared carbon. Together with the lattice spacing of 0.21 nm due to the (100) plane of carbon, the layers with the lattice spacing of 0.35 nm was observed perpendicularly to the (002) plane of as shown at the bottom right of the image. This could be due to the in-plane super structure of pillars, though further investigation should be needed.

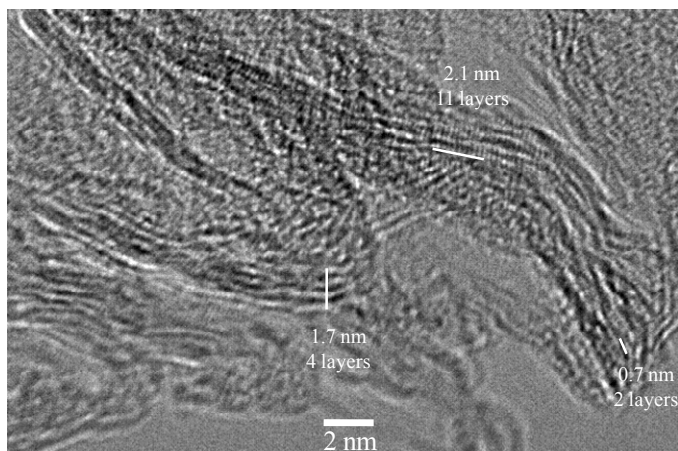


Fig. S3 TEM image of pillared carbon.