

Supplementary Information

Controlled self-assembly of graphene oxide on a remote aluminum foil

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Experimental section

1. Materials Expandable graphite powders were provided by Yingtai Co. (China). Carboxyl-functionalized carbon nanotubes (CNT-COOHs) were purchased from ChengDu Organic Chemicals Co., Ltd., Chinese Academy of Science. Unless otherwise stated, all the other reagents were purchased from commercial suppliers and were used as received.

2. Preparation of samples

2.1 Preparation of graphite oxide 5 g of expandable graphite powders and 115 mL of concentrated H₂SO₄ were mixed and agitated in an ice bath. Then, 15 g of potassium permanganate was added to the suspension slowly to prevent a rapid rise in temperature (less than 20 °C). After keeping in the ice bath for 2 h, the reaction mixture was heated to 35 °C and stirred continuously for 0.5 h. 115 mL distilled water was slowly added to the reaction vessel. The diluted suspension was stirred for another 15 min and further diluted with 700 mL warm distilled water (40 °C) before adding 50 mL 30% H₂O₂. The resulting suspension was then filtered, washed with 5% HCl and dialyzed for 7 days in the dark. Subsequently, the wet form of graphite oxide was freeze-dried, pulverized and finally vacuum dried at 60 °C for 24 h.¹

2.2 Collection of the evaporated liquor of aqueous GO dispersion

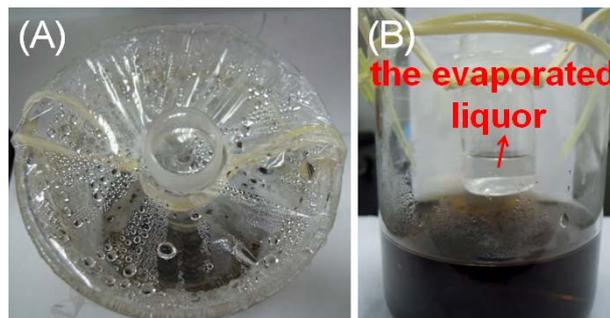


Fig. S1. The digital photos of the equipment we used to collect the evaporated liquor of aqueous GO dispersion.

10mg of graphene oxide sheets (GOSs) were dispersed in 100 mL of deionized water in a glass beaker (150ml) and the mixture was agitated for 0.5 h at room temperature to obtain a stable dispersion. Then a weighing bottle was hung in the air just above the surface of aqueous GO dispersion with the aid of elastics (as presented in Fig. S1). After being sealed with preservative film carefully, the glass beaker was placed in an oven at 45 °C for 120h. At last, the evaporated liquor that condensed in the weighing bottle was kept carefully for later characterizations (UV-Visible (UV-Vis), fluorescence and transmission electron microscopic (TEM)) without further purification.

2.3 Evaporation of the aqueous GO dispersion Similarly, 10mg of GOSs were dissolved in 100 mL of deionized water in a glass beaker (150ml) and the mixture was agitated for 0.5 h at room temperature to obtain a stable dispersion. The glass beaker containing the resulting aqueous GO dispersion (0.1mg/ml) was covered by the aluminium foil (the aluminium surface I in Fig. S3 or the surface II in Fig. S19), or 50nm Al₂O₃ coated silicon slice (the aluminium surface III in Fig. S25), or 50nm Al₂O₃ coated glass (the aluminium surface IV in Fig. S27) plainly and then sealed with preservative film carefully. The whole system was placed in an oven at certain evaporation temperature for designed evaporation time. At last, the aluminum surface on which the “evaporated” GOSs deposited was dried gradually at room temperature.

2.4 Evaporation of the aqueous CNT-COOH dispersion (0.16mg/ml) It was prepared via the same method as that of GO (section 2.3).

3. Characterizations. The UV-Vis absorptions were determined by a Shimadzu UV-3150 spectrophotometer, and the luminescence emission spectrum was taken on a Shimadzu RF-5301PC spectrofluorometer. The morphologies of the self-assembled structure of GO and CNT-COOH on the remote aluminum foil surfaces (including the aluminum surface I, II, III and IV) were observed with a scanning electron microscopy (SEM, XL 30 ESEM-TMP PHILIP) and/or a field emission scanning electron microscopy (FE-SEM, Hitachi, S-4800). All samples were coated with gold before SEM observation. Energy dispersive X-ray fluorescence spectrometer (EDX) analyses of the evaporated GOSs on the aluminum foil surface I at 35/45 °C for 48h were also obtained by the field emission scanning electron microscopy (FE-SEM, Hitachi, S-4800). These samples were not coated with gold in the EDX characterization. Atomic force microscopic (AFM) images were obtained using a Multimode Nano 4 in the tapping mode. Transmission electron microscopy (TEM) images and energy dispersive spectrometer (EDS) analyses were recorded on a JEOL JEM2100 TEM instrument operated under an acceleration voltage of 200 keV. Raman spectra were collected on a Renishaw inVia Reflex micro-Raman spectrometer with 633 nm laser excitation. The “evaporated” GOSs on aluminium surface I at 35/45 °C for 48h were obtained by dissolving the aluminum foil with HCl and then dialyzing the resulting acidic aqueous solution for 7 days before TEM, Raman and UV-Vis measurements. X-ray diffraction (XRD, PANalytical X’pert diffractometer with Cu K α radiation) was utilized to characterize the structure of the GO deposit layer on the aluminum foil surfaces. The static water contact angles (CAs) of the surface of the GO deposit layer (before and after modification) were measured according to the sessile droplet method using a drop shape analysis system (DSA100, Kruss Company Ltd., Germany) with a computer-controlled liquid dispensing system. Deionized water droplets with volume of 3 μ l were employed as the source for the CA measurement.

Supporting Results

1. The perfect beaker-mouth shaped deposit layers of GOSs on the aluminum foil surfaces (aluminum surface I) with different evaporation temperature or time are shown as digital photos in Fig. S2, exhibiting the uniformity of the “evaporation” of GOSs.

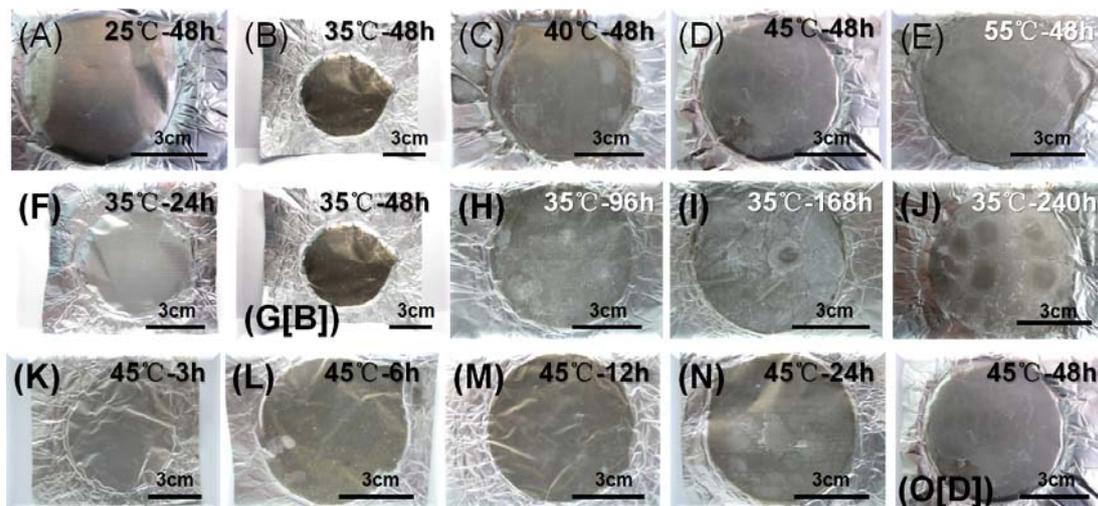


Fig. S2. The digital photos of GO deposit layers on the aluminum foil surface I under different evaporation conditions. (The photos are marked by “temperature-time”, where “temperature” means the evaporation temperature and “time” corresponds to the evaporation time.)

2. The fresh aluminum foil surface I, whose SEM images are shown in Fig. S3, was used for the deposit of GO or CNT-COOH as their SEM images shown in Fig. S2, Fig. S4-S18 and Fig. S34-S48.

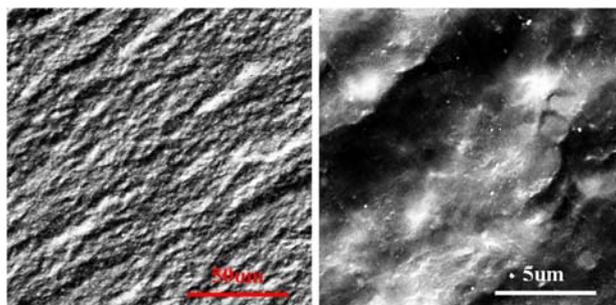


Fig. S3. The SEM images of the fresh aluminum foil surface I.

3. The time-resolved experiment of GO at 45 °C illustrates that it would eventually evolve from the hole-like structure to the cylindrical-like structure on the aluminum foil surface. Similarly, just as the FE-SEM images shown in Fig.S4.

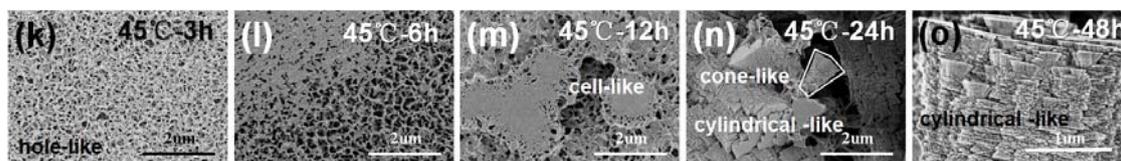


Fig. S4. The FE-SEM images of the self-assembled structure (GO) of the time-resolved experiment at 45°C on the aluminum surface. I .

We provide more (FE-) SEM images of the self-assembled structure of GO on the aluminum surface I under different evaporation conditions (Fig. S5-S18) to help understand the proposed mechanism of the self-assembly of GO. Although we observe variability for these SEM studies, the overall trend of the self-assembled structure evolution of GO was consistent throughout.

The images marked by “1-” in Fig. S5-S18 and Fig. S36-S47 are the SEM images, and those images marked by “2-” are the FE-SEM images.

4.

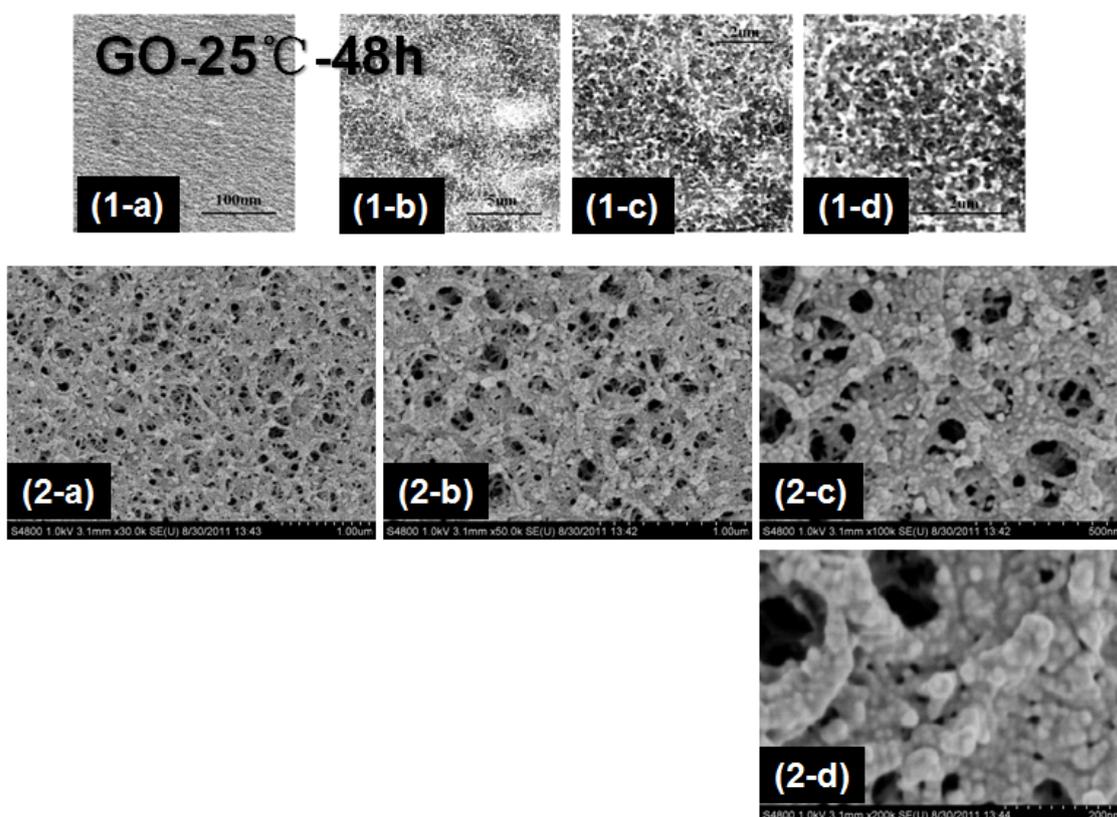


Fig. S5. More (FE-) SEM images of the self-assembled structure (GO) of the temperature-resolved experiment at 25 °C for 48h. (on the aluminum surface I)

5.

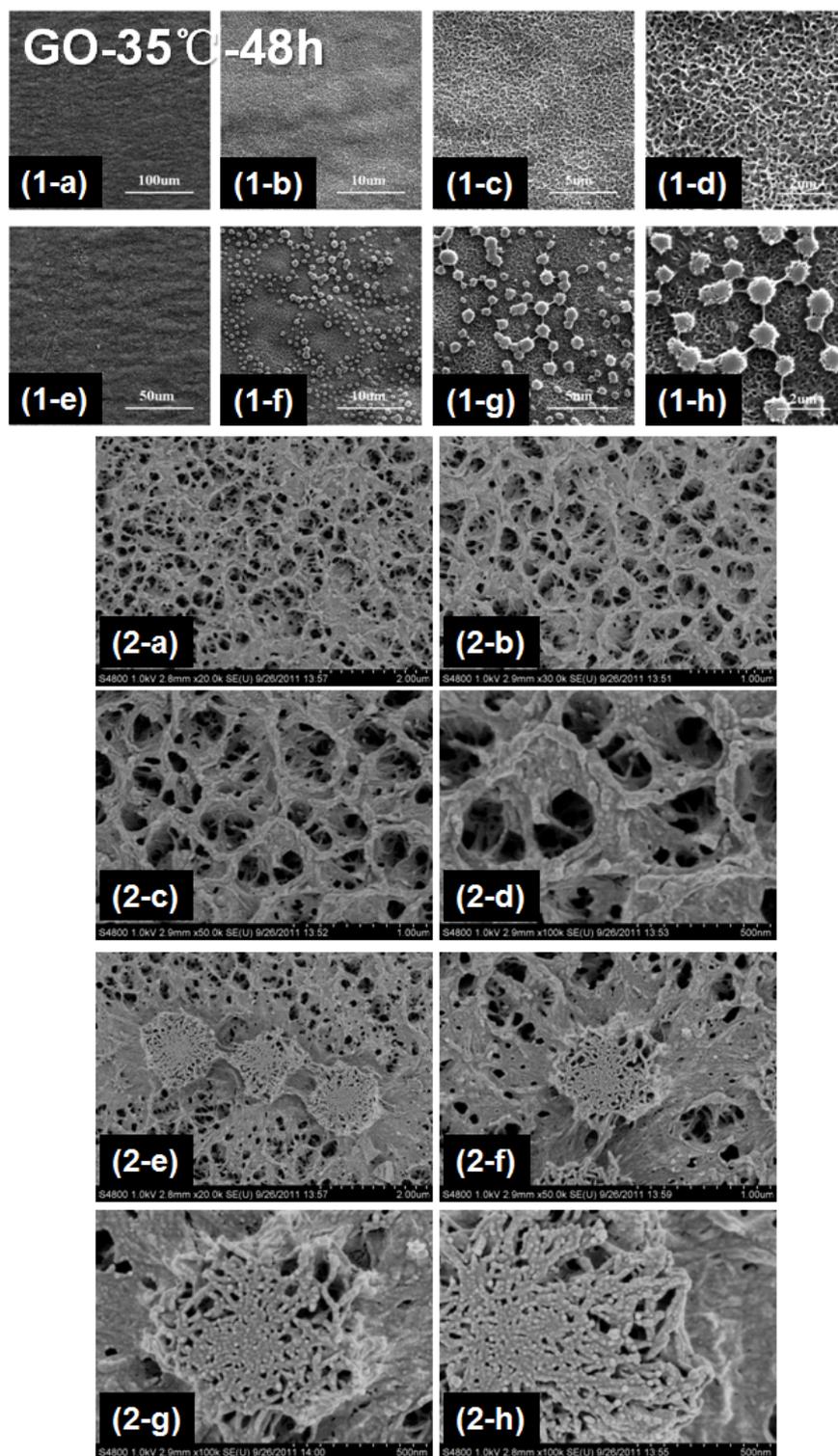


Fig. S6. More (FE-) SEM images of the self-assembled structure (GO) of the temperature-resolved experiment at 35 °C for 48h. (on the aluminum surface I)

6.

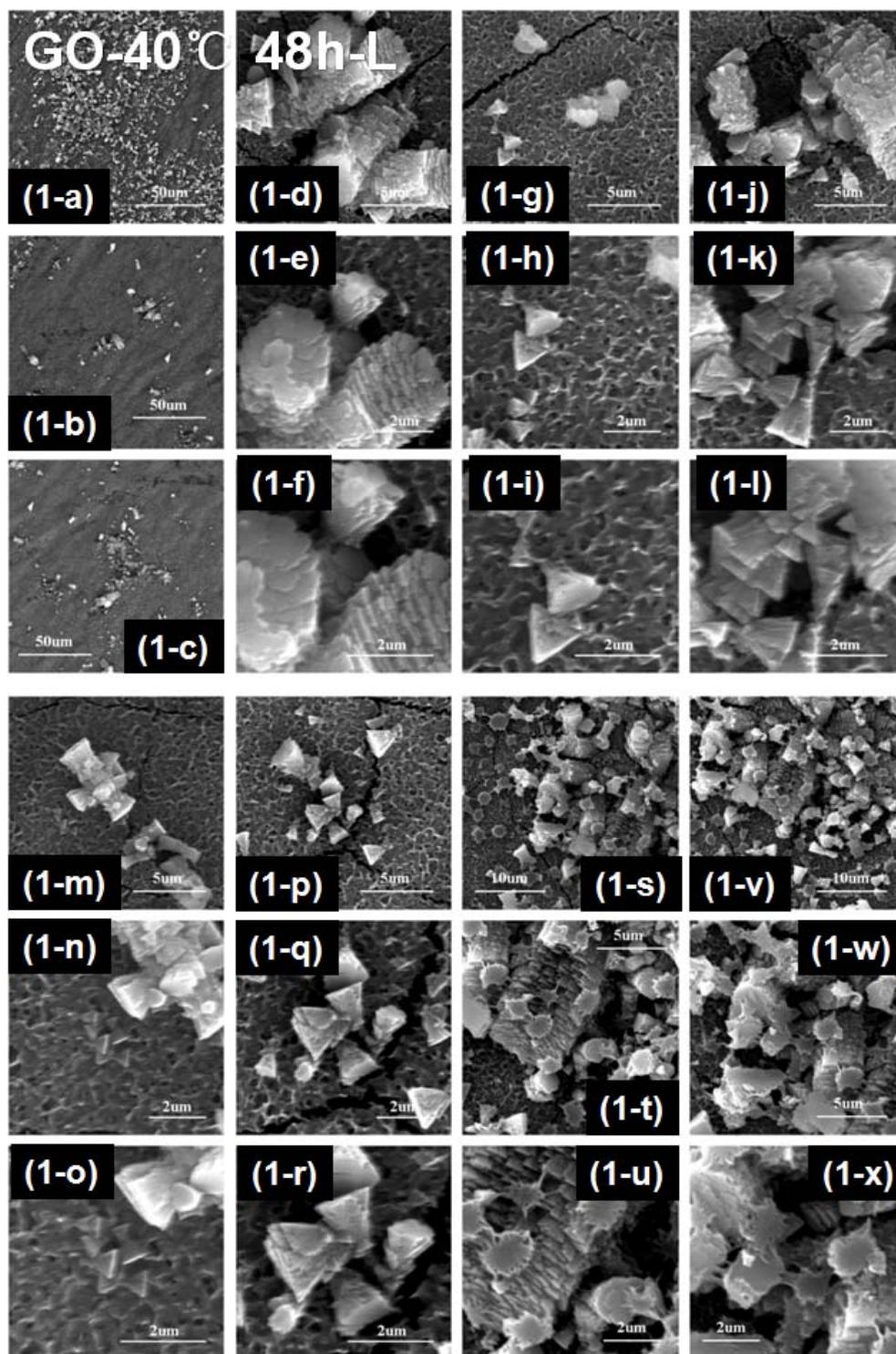


Fig. S7. More SEM images of the self-assembled structure (GO) of the temperature-resolved experiment at 40 °C for 48h. (on the aluminum surface I)

7.

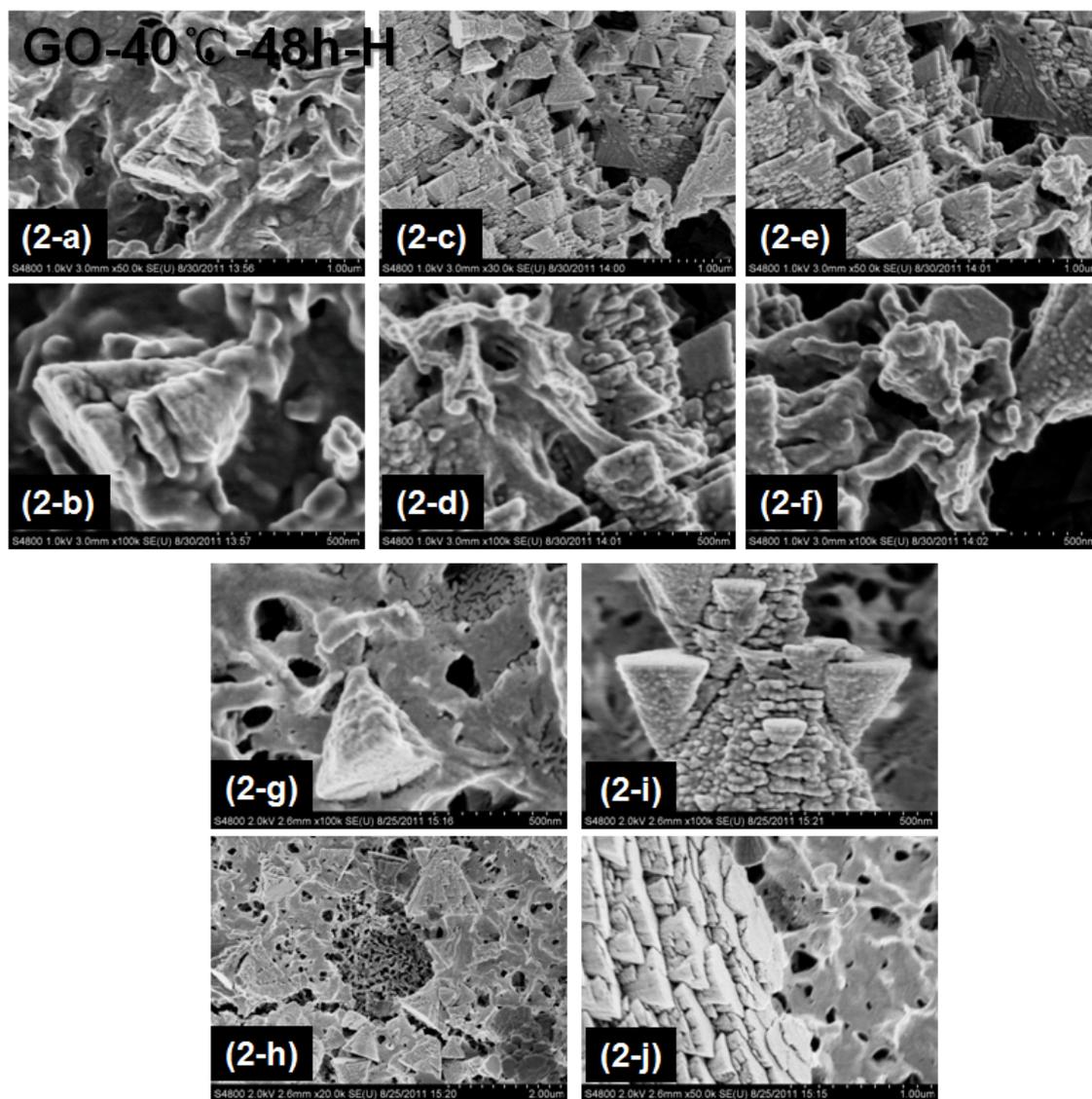


Fig. S8. More FE-SEM images of the self-assembled structure (GO) of the temperature-resolved experiment at 40 °C for 48h. (on the aluminum surface I)

8.

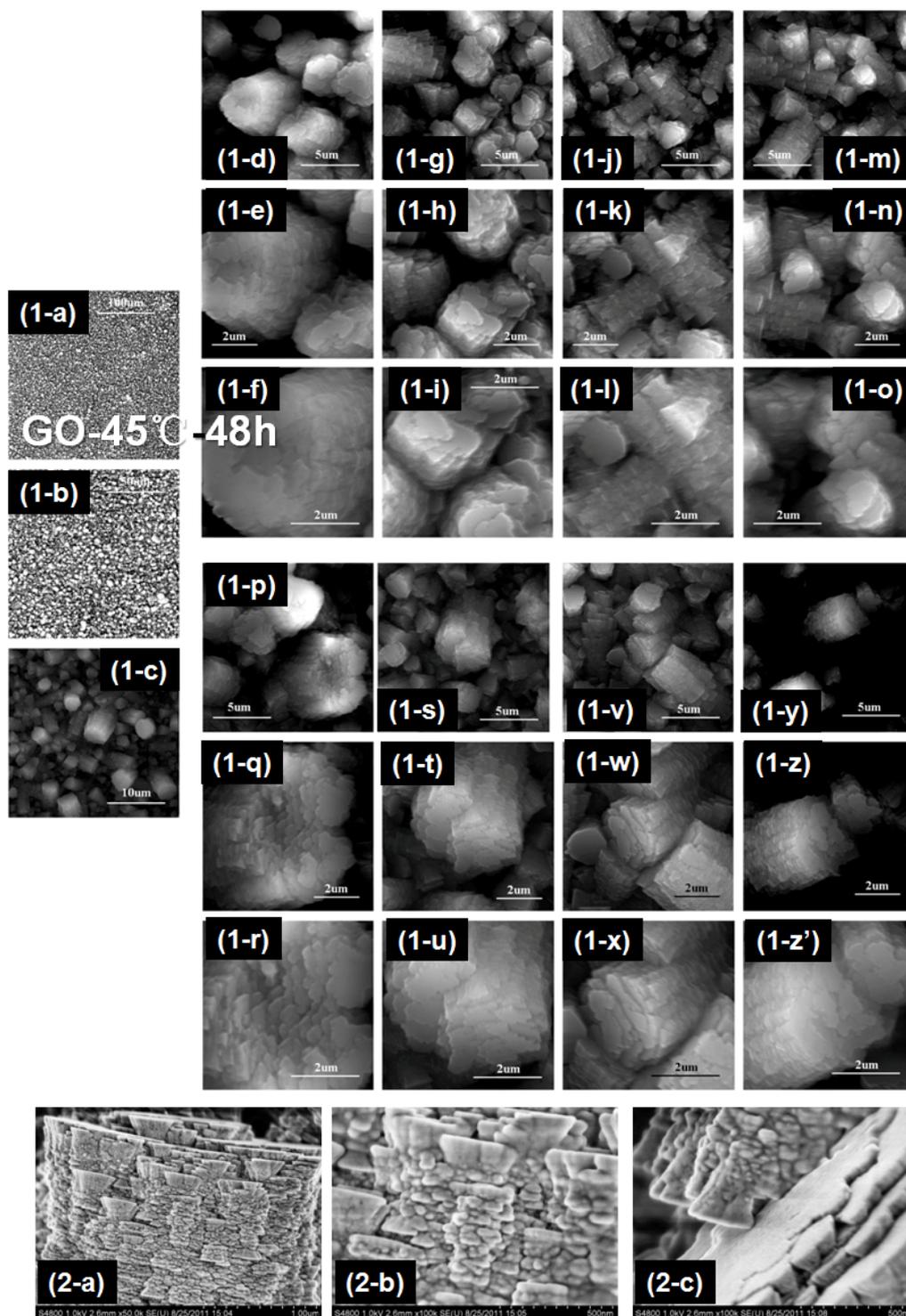


Fig. S9. More (FE-) SEM images of the self-assembled structure (GO) of the temperature-resolved experiment at 45 °C for 48h. (on the aluminum surface I)

9.

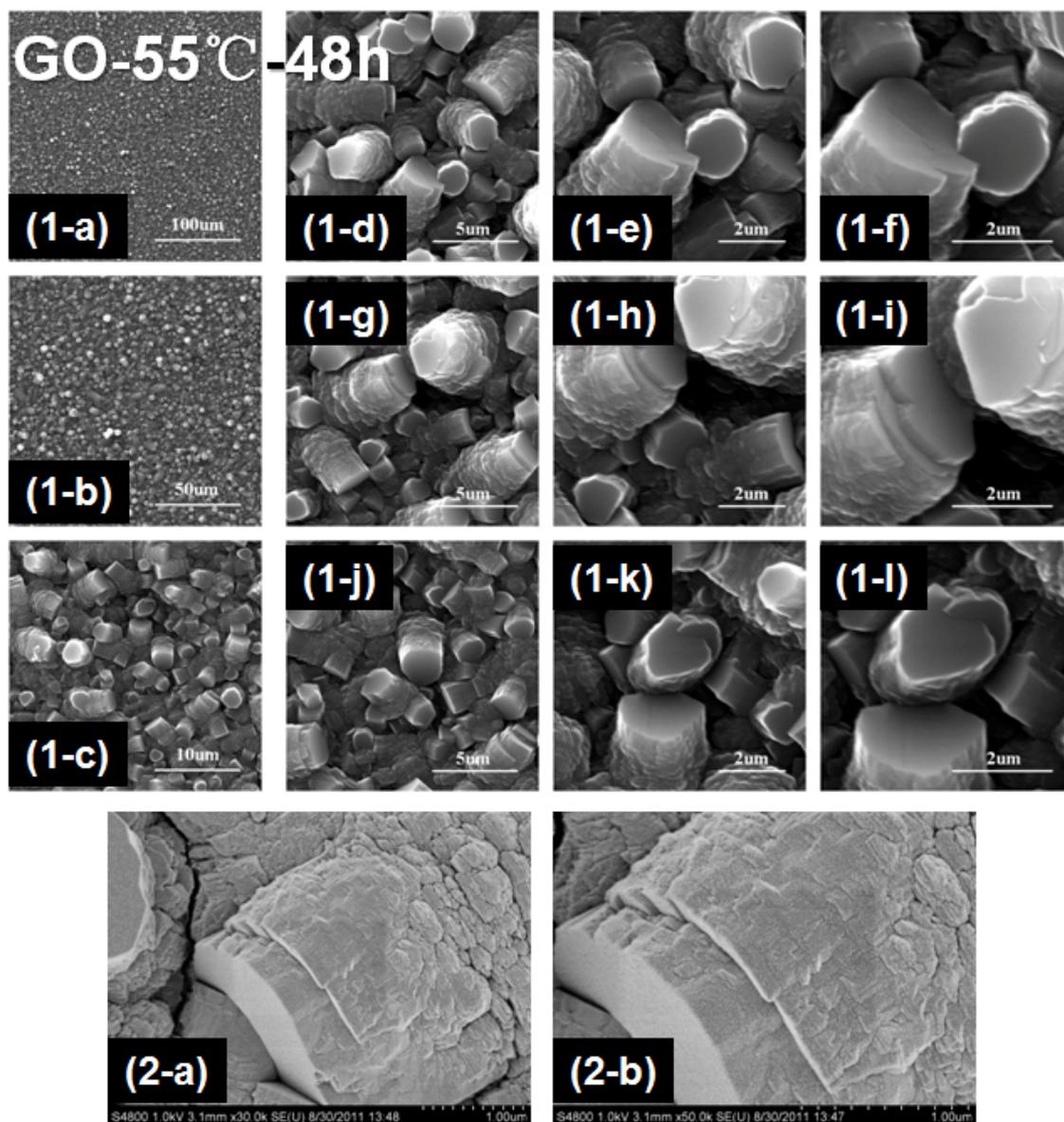


Fig. S10. More (FE-) SEM images of the self-assembled structure (GO) of the temperature-resolved experiment at 55 °C for 48h. (on the aluminum surface I)

10.

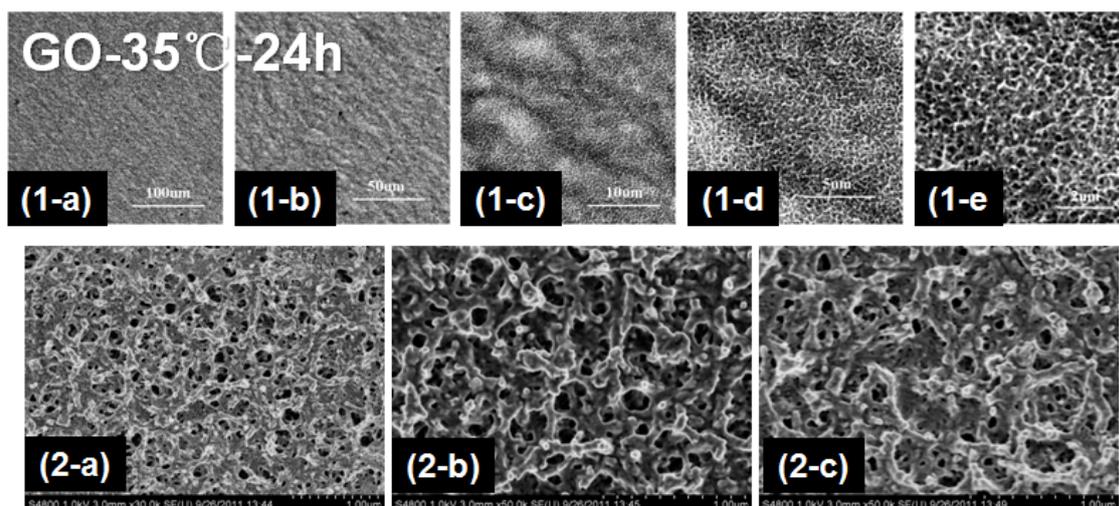


Fig. S11. More (FE-) SEM images of the self-assembled structure (GO) of the time-resolved experiment at 35 °C for 24h. (on the aluminum surface I)

11.

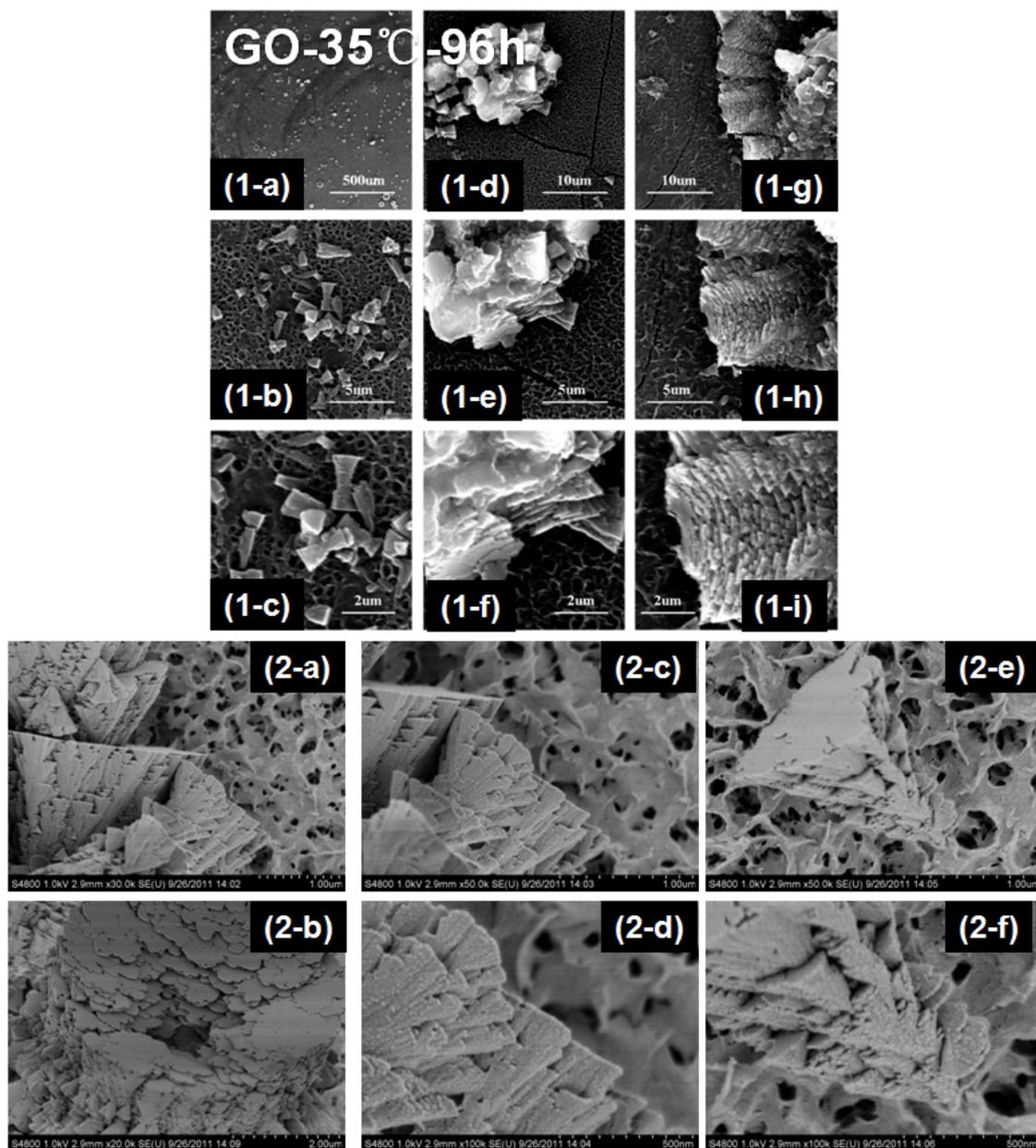


Fig. S12. More (FE-) SEM images of the self-assembled structure (GO) of the time-resolved experiment at 35 °C for 96h. (on the aluminum surface I)

12.

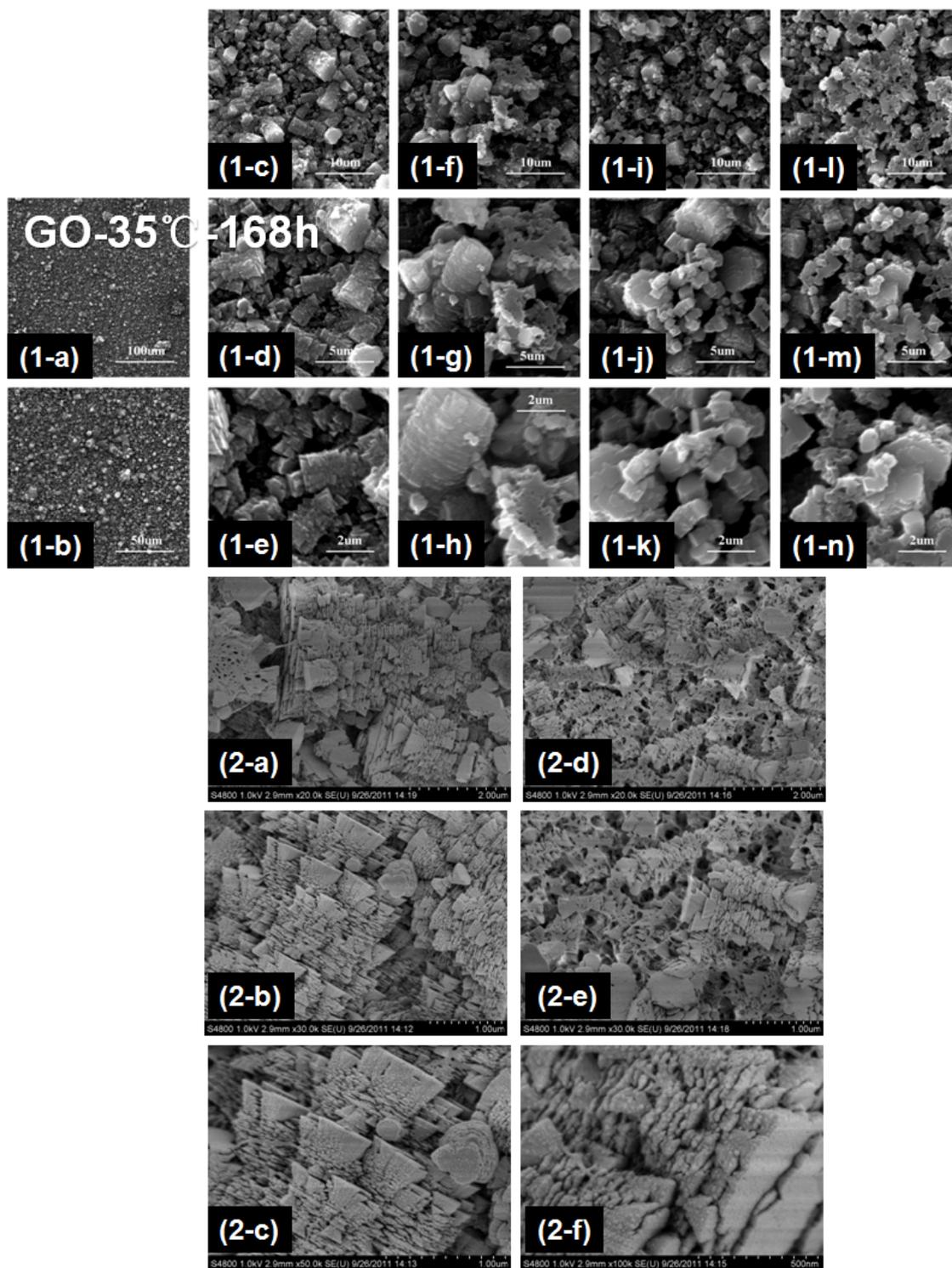


Fig. S13. More (FE-) SEM images of the self-assembled structure (GO) of the time-resolved experiment at 35 °C for 168h. (on the aluminum surface I)

13.

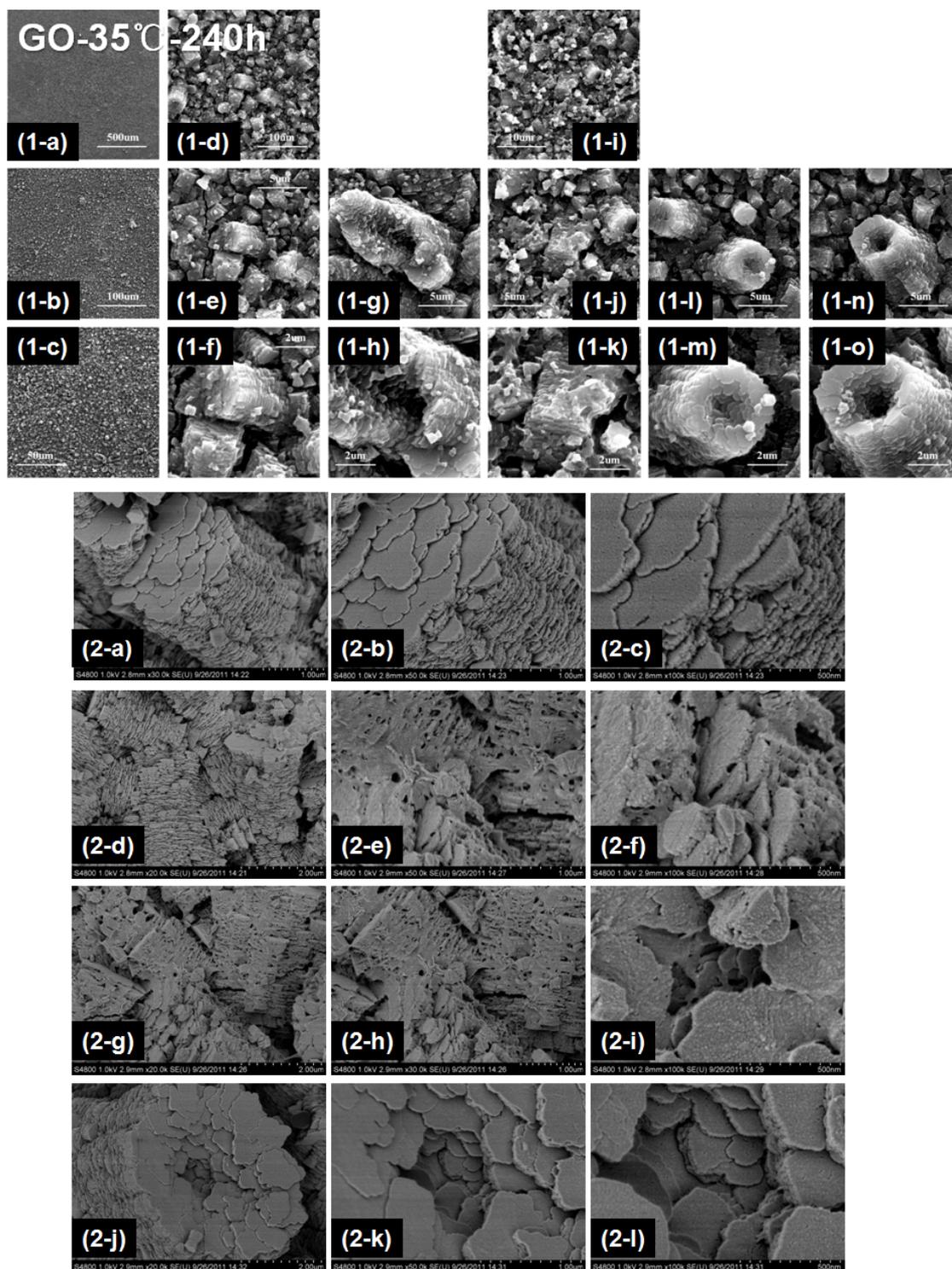


Fig. S14. More (FE-) SEM images of the self-assembled structure (GO) of the time-resolved experiment at 35 °C for 240h. (on the aluminum surface I)

14.

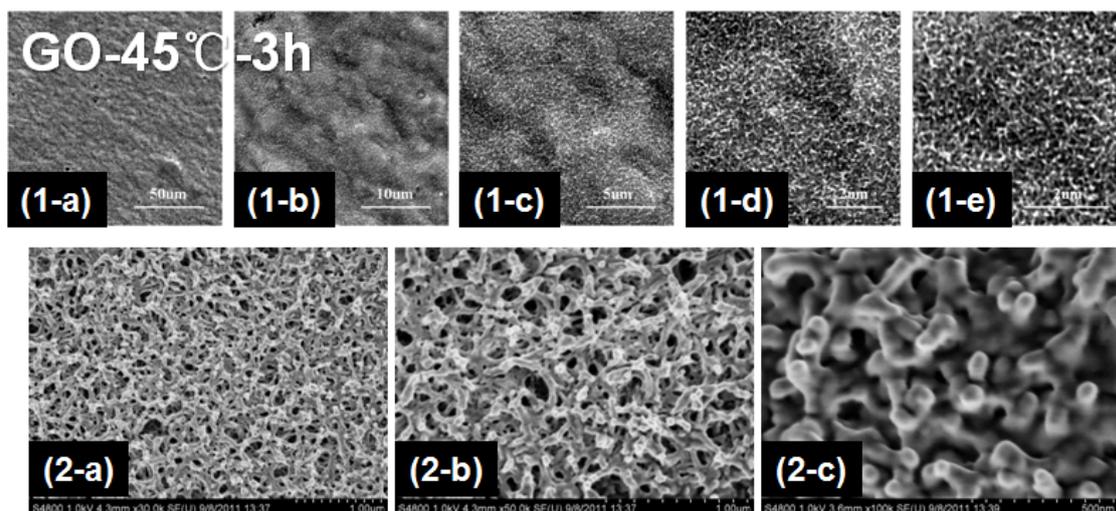


Fig. S15. More (FE-) SEM images of the self-assembled structure (GO) of the time-resolved experiment at 45 °C for 3h. (on the aluminum surface I)

15.

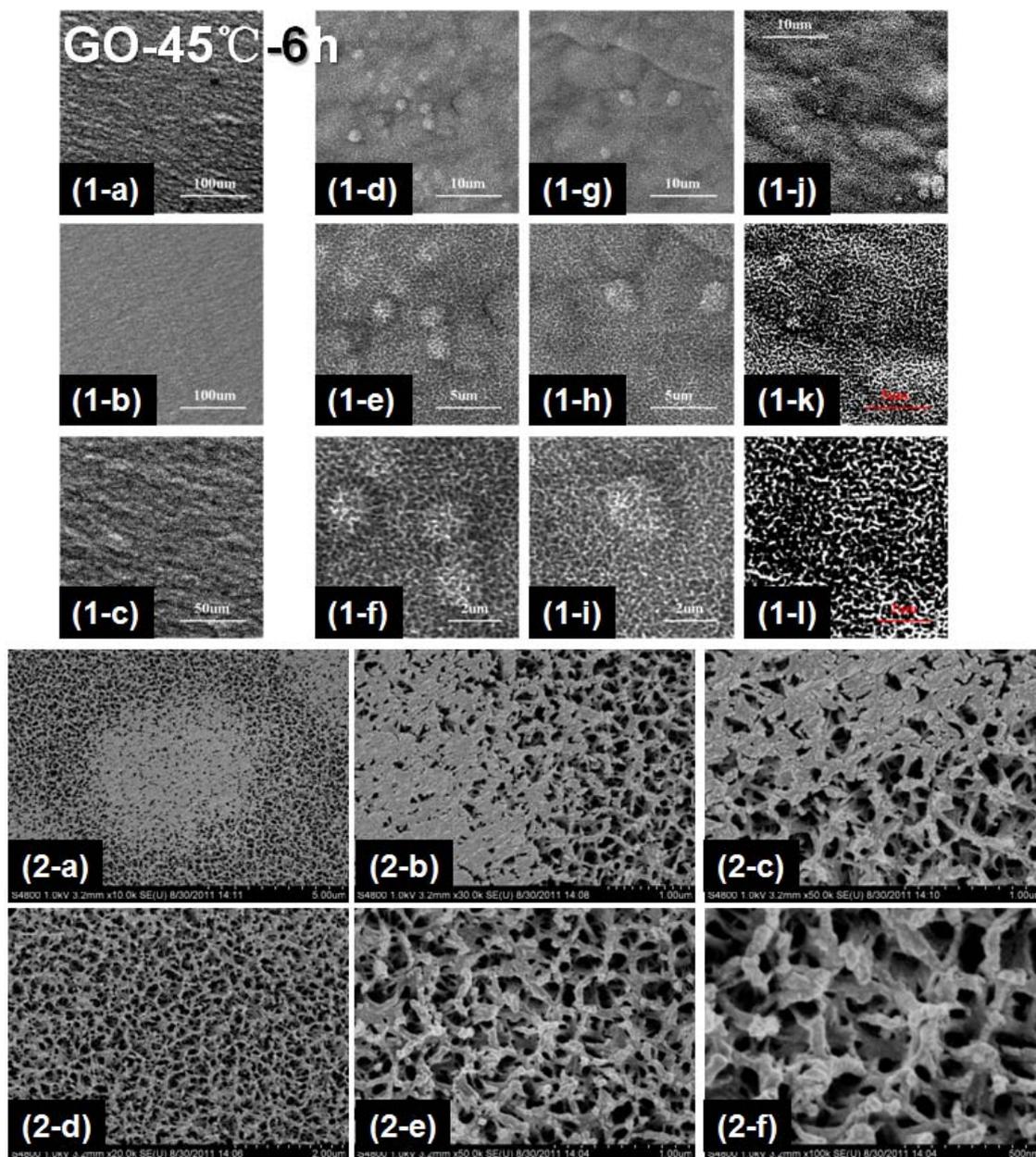


Fig. S16. More (FE-) SEM images of the self-assembled structure (GO) of the time-resolved experiment at 45 °C for 6h. (on the aluminum surface I)

16.

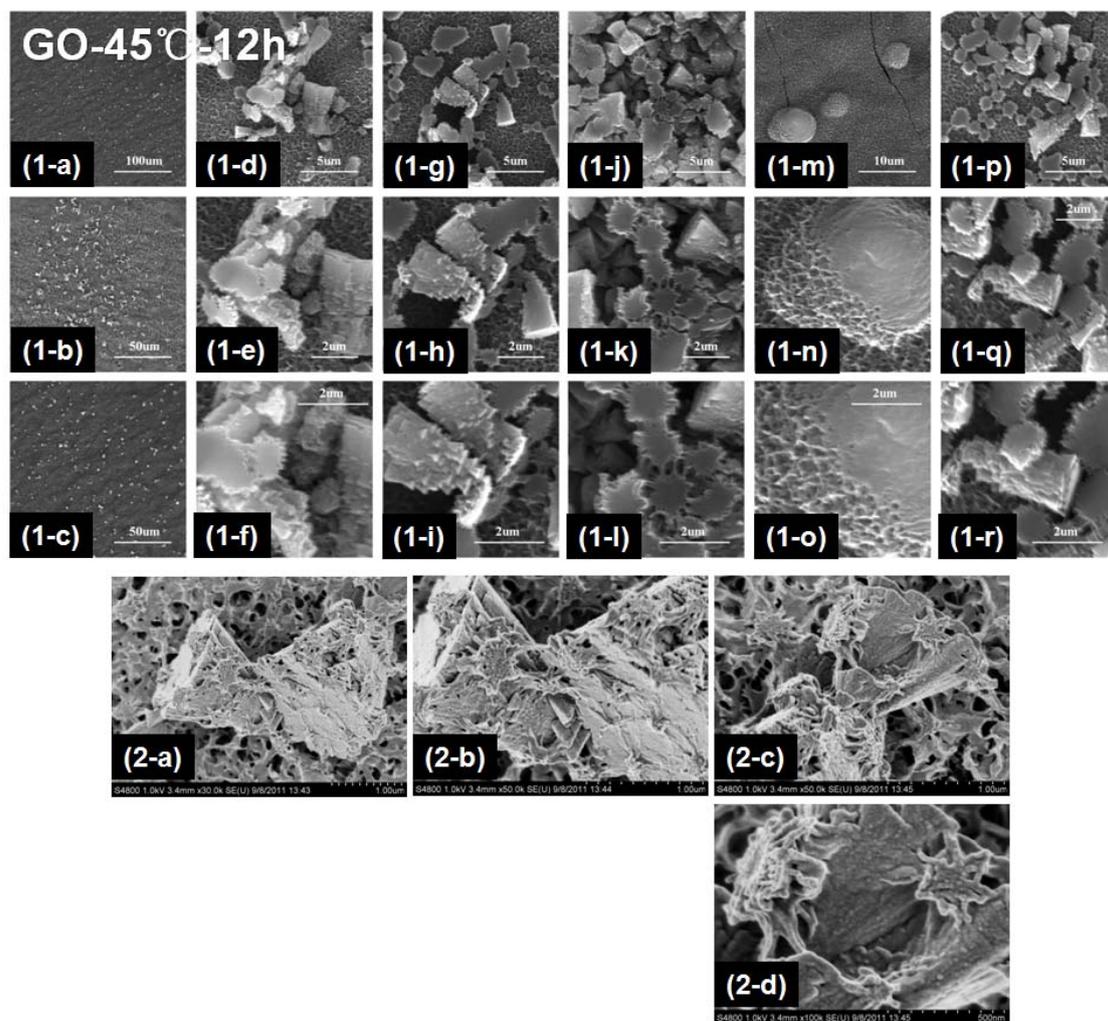


Fig. S17. More (FE-) SEM images of the self-assembled structure (GO) of the time-resolved experiment at 45 °C for 12h. (on the aluminum surface I)

17.

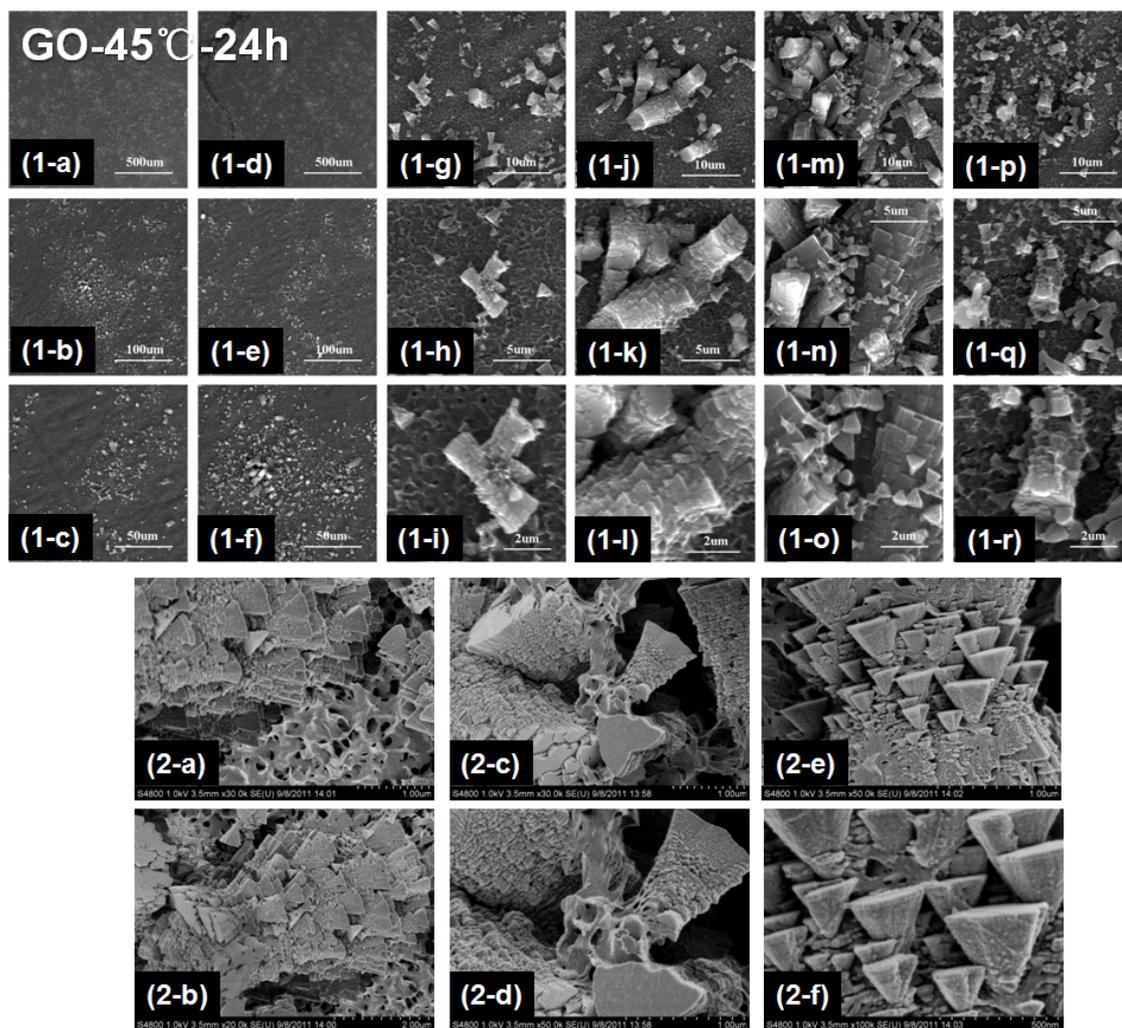


Fig. S18. More (FE-) SEM images of the self-assembled structure (GO) of the time-resolved experiment at 45 °C for 24h. (on the aluminum surface I)

18. The fresh aluminum foil surface II, whose SEM images are shown in Fig. S19, was used for the deposit of GO as the SEM images shown in Fig. S20-S24.

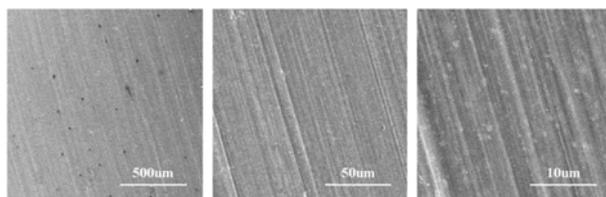


Fig. S19. The SEM images of the fresh aluminum foil surface II.

19.

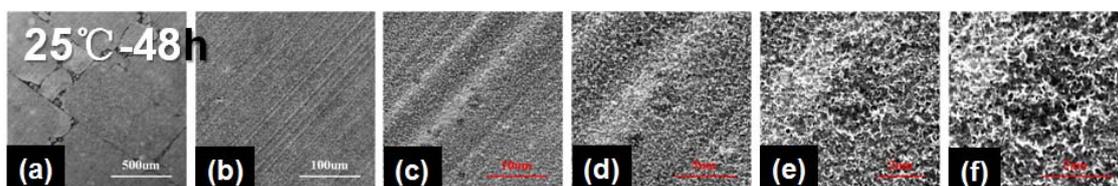


Fig. S20. The SEM images of the self-assembled structure (GO) on the aluminum surface II at 25 °C for 48h.

20.

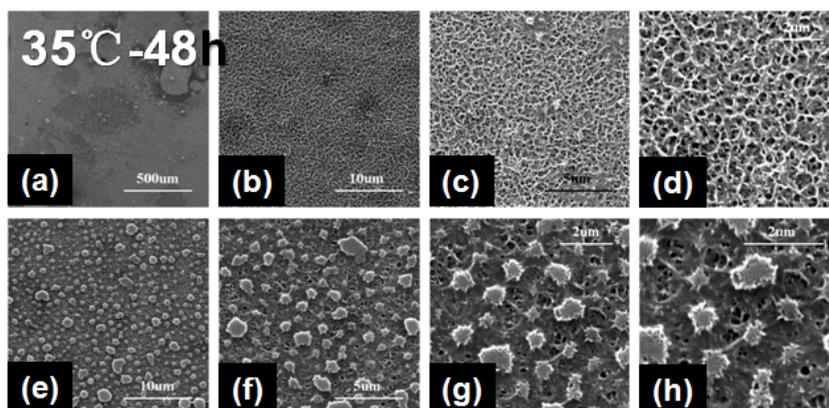


Fig. S21. The SEM images of the self-assembled structure (GO) on the aluminum surface II at 35 °C for 48h.

21.

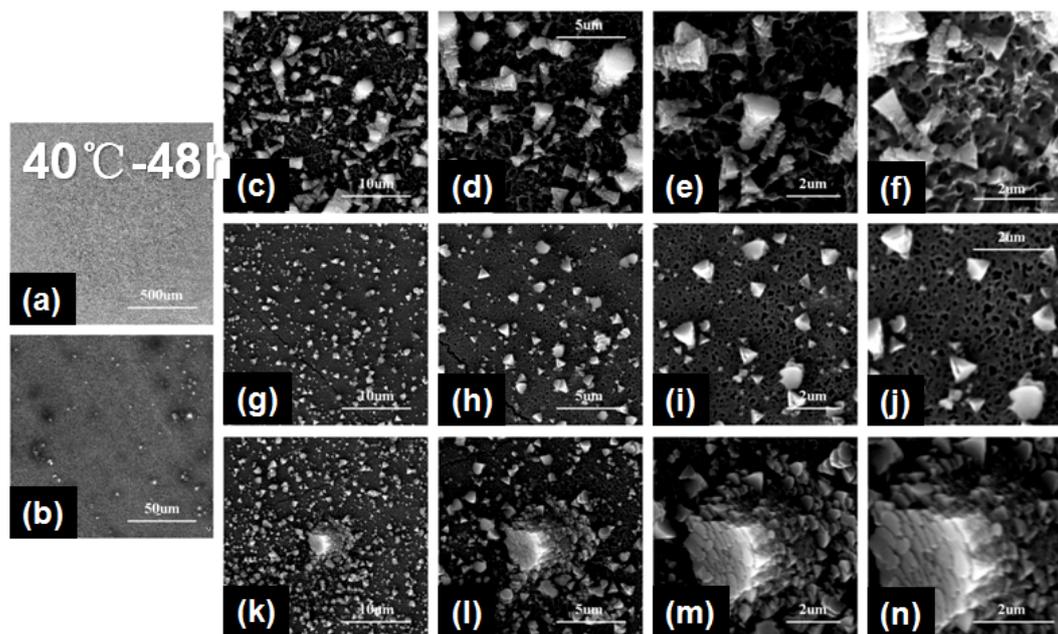


Fig. S22. The SEM images of the self-assembled structure (GO) on the aluminum surface II at 40 °C for 48h.

22.

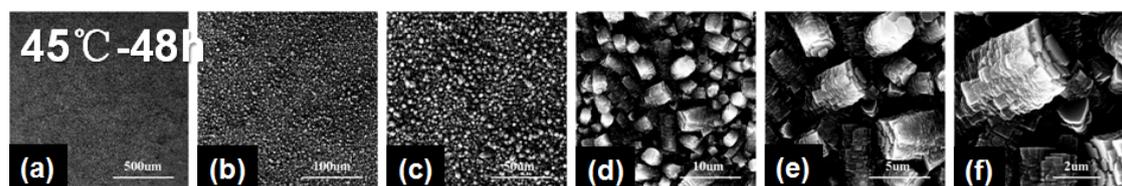


Fig. S23. The SEM images of the self-assembled structure (GO) on the aluminum surface II at 45 °C for 48h.

23.

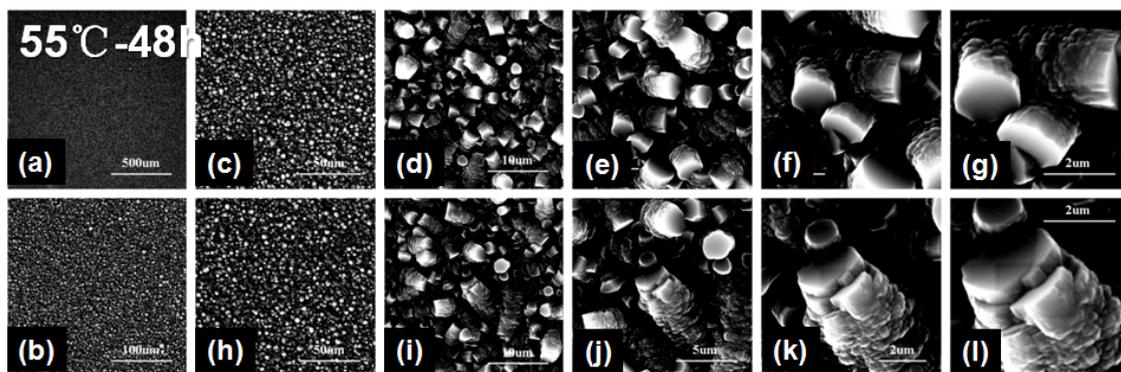


Fig. S24. The SEM images of the self-assembled structure (GO) on the aluminum surface II at 55 °C for 48h.

24. The 50nm Al₂O₃ coated silicon slice (named as “aluminum surface III”), whose SEM images are shown in Fig. S25, was used for the deposit of GO as the SEM images shown in Fig. S26.

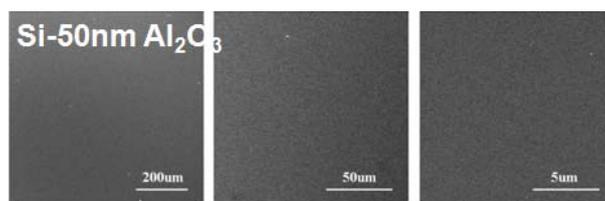


Fig. S25. The SEM images of 50nm Al₂O₃ coated silicon slice (aluminum surface III).

25.

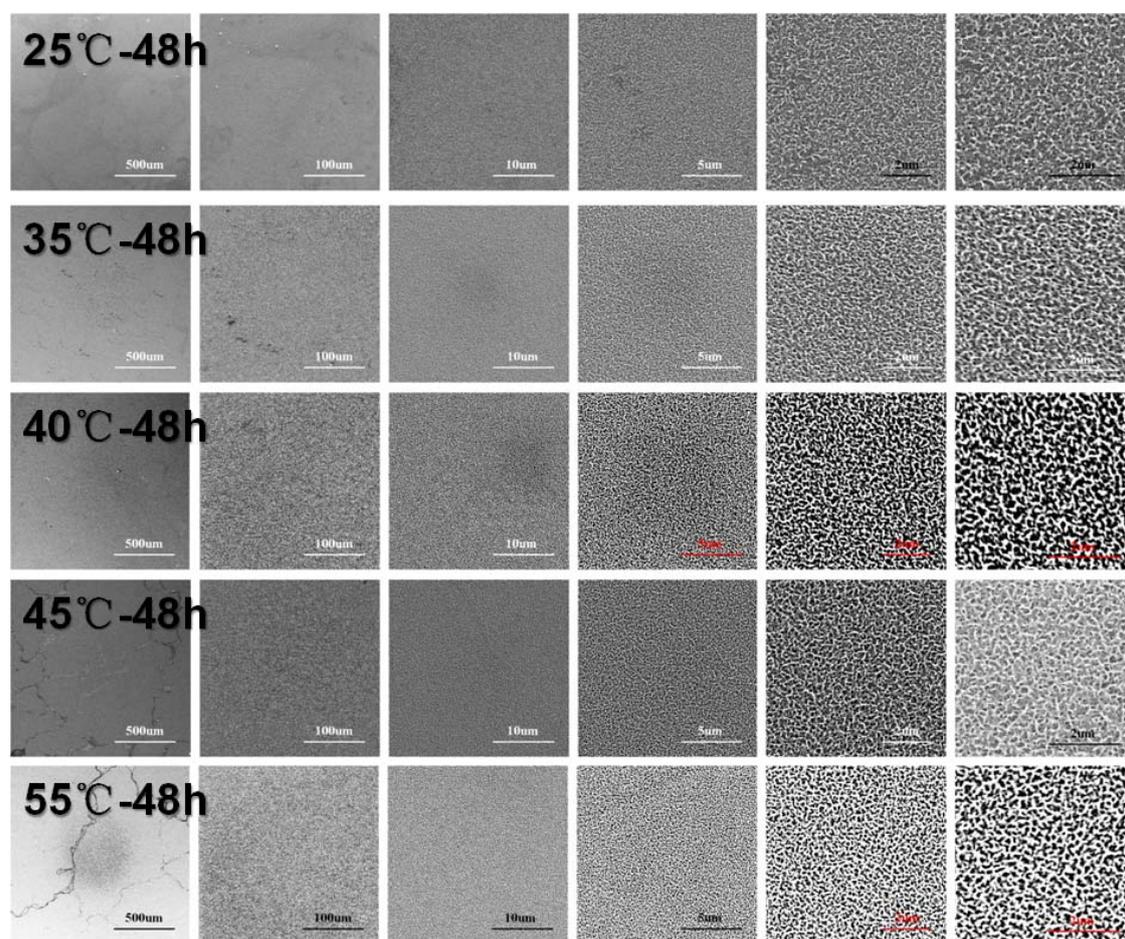


Fig. S26. The SEM images of the self-assembled structure (GO) of the temperature-resolved experiment on the aluminum surface III.

26. The 50nm Al₂O₃ coated glass (named as “aluminum surface IV”), whose SEM images are shown in Fig. S27, was used for the deposit of GO as the SEM images shown in Fig. S28.

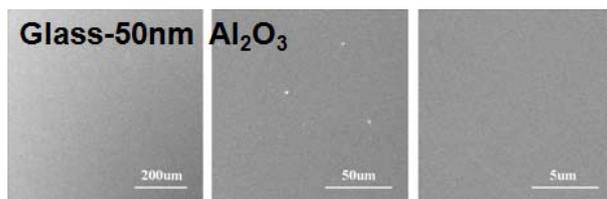


Fig. S27. The SEM images of 50nm Al₂O₃ coated glass (aluminum surface IV).

27.

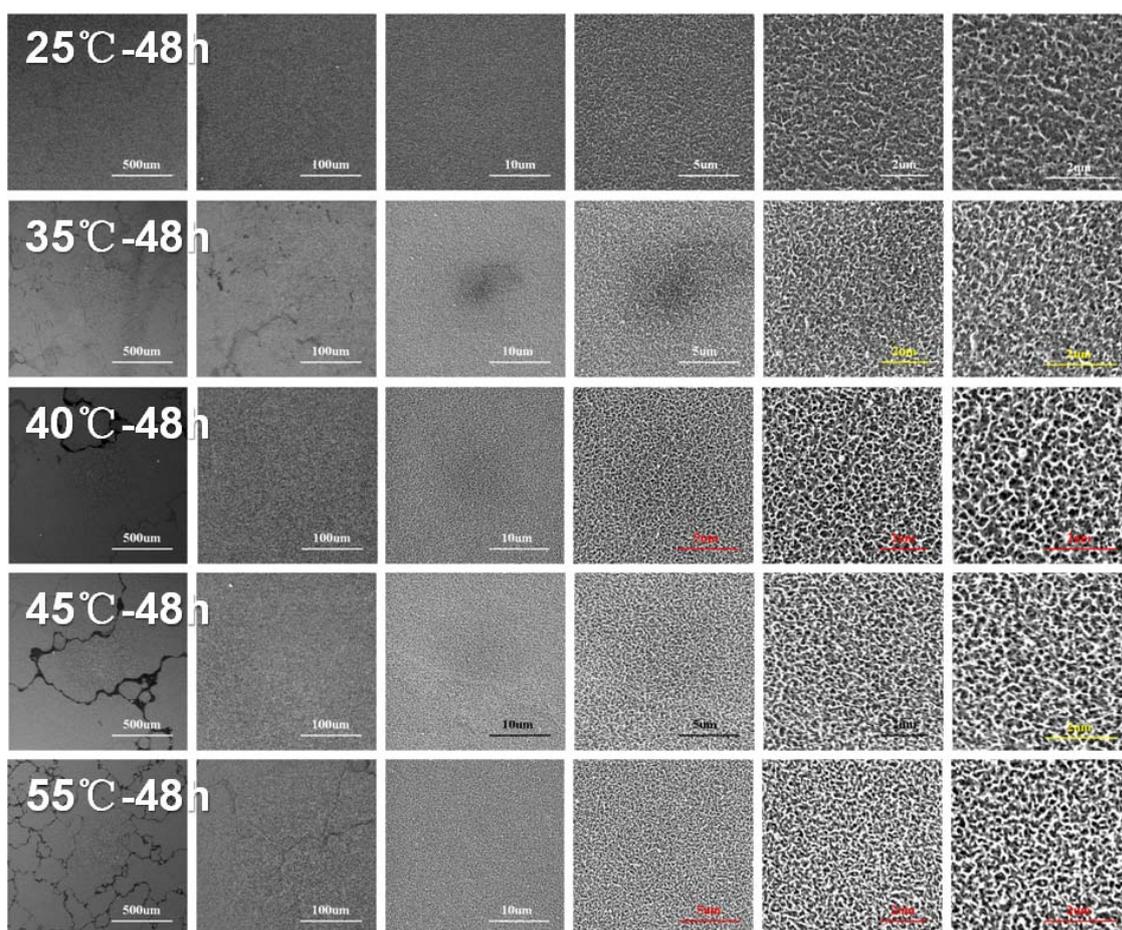


Fig. S28. The SEM images of the self-assembled structure (GO) of the temperature-resolved experiment on the aluminum surface IV.

28.

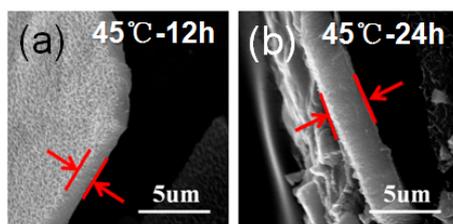


Fig. S29. The sectional SEM views of the GO deposit layers on the aluminum surface I of the time-resolved experiment at 45 °C.

29.

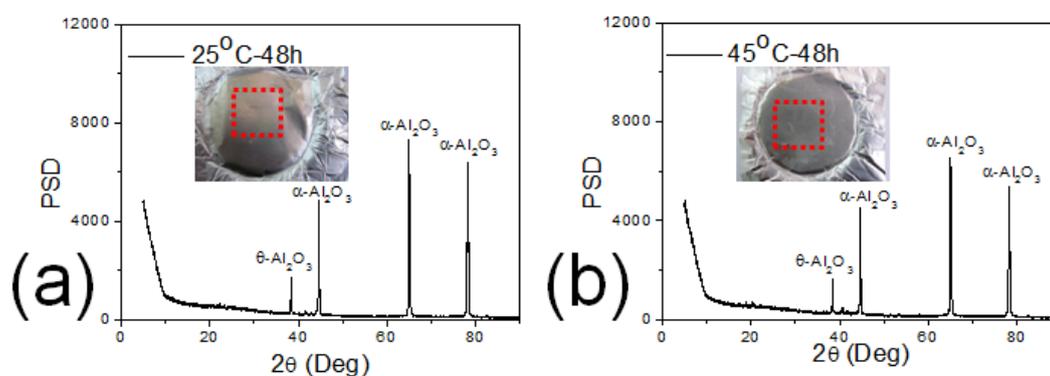


Fig. S30. The XRD patterns of the GOSs deposit layer on the aluminum surface I .

30.

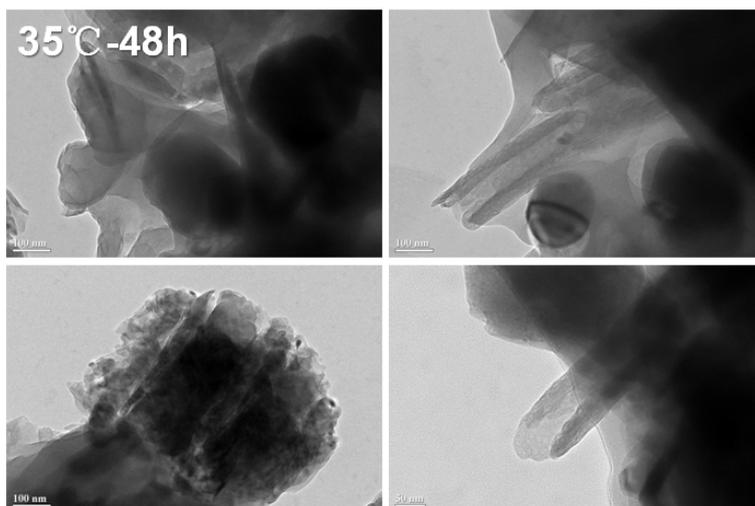


Fig. S31. More TEM images of the “evaporated” GOSs which deposited on the aluminum surface I at 35⁰C for 48h.

31.

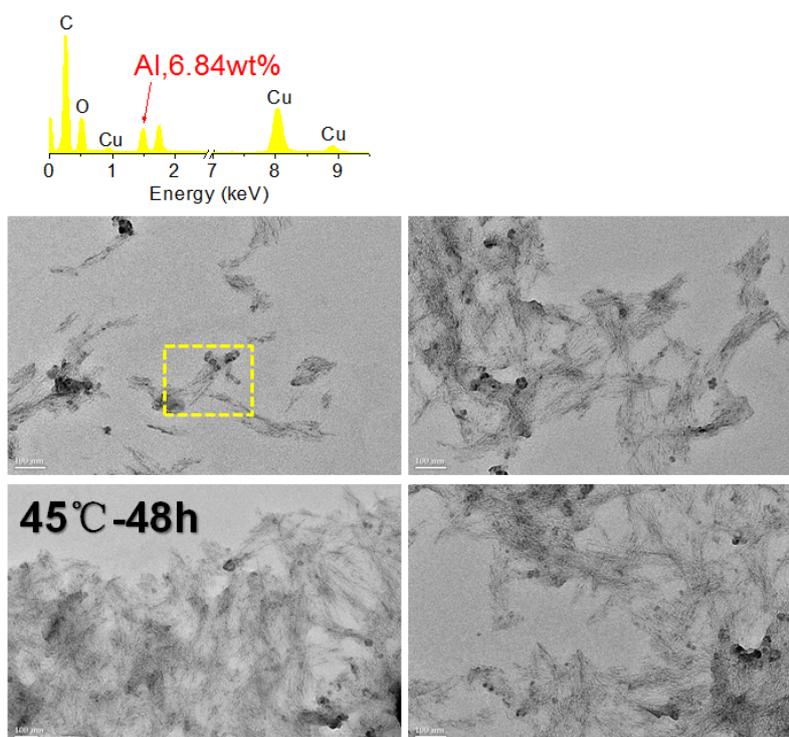


Fig. S32. More TEM images and EDS analysis (indicated by the yellow box) of the “evaporated” GOSs which deposited on the aluminum surface I at 45⁰C for 48h.

32.

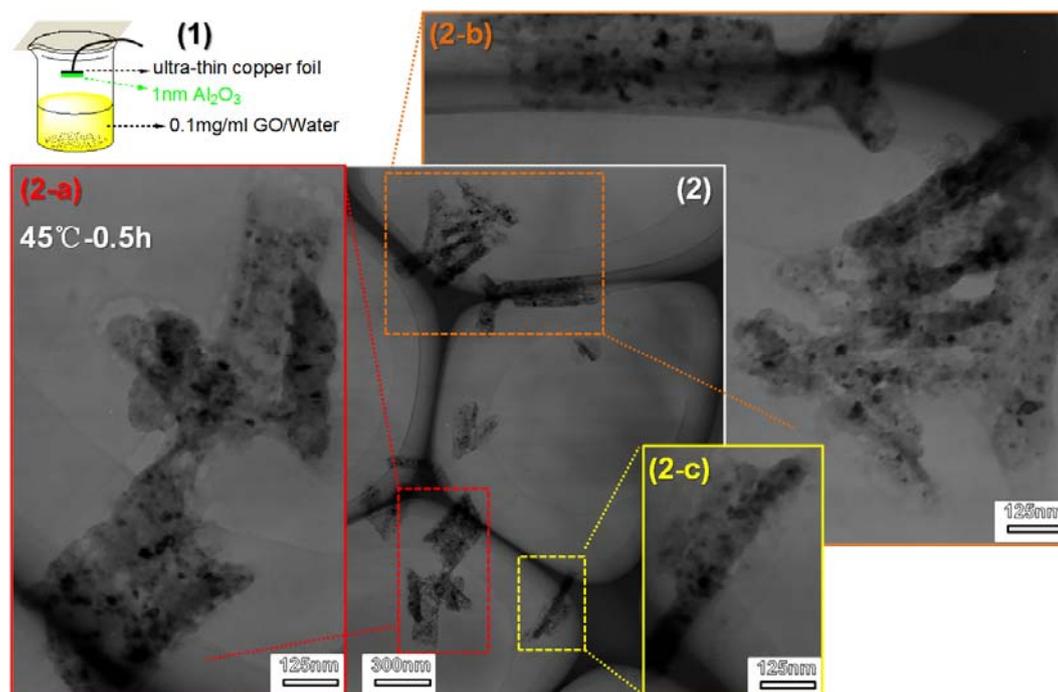


Fig. S33. Capture the “evaporated” GOSs with the aid of the 1nm Al₂O₃ coated ultra-thin copper foil directly, as schematically shown in (1); (2) In-situ TEM characterization of the captured GOSs.

33.

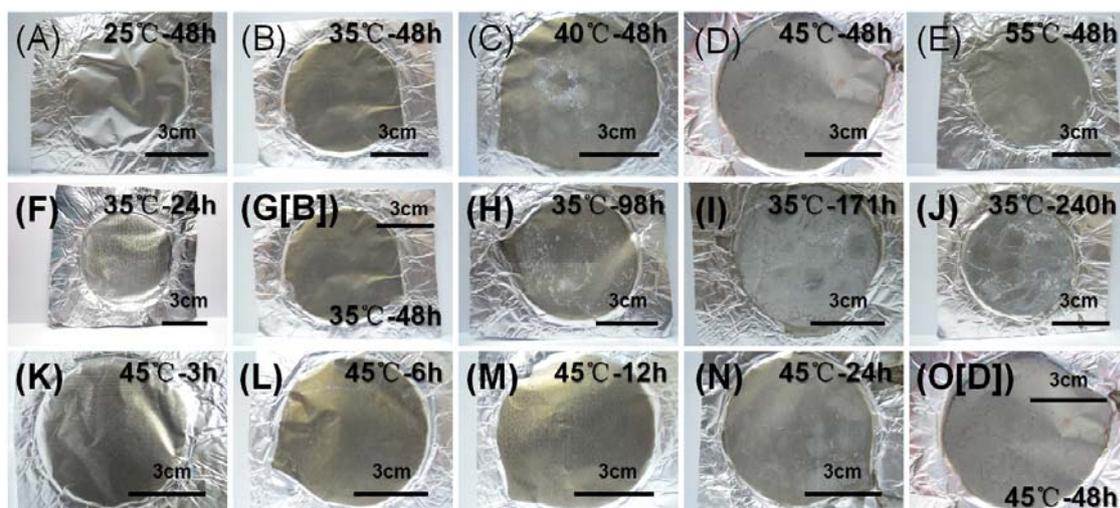


Fig. S34. The digital photos of CNT-COOH deposit layers on the aluminum surface I under different evaporation conditions. (No visible deposit of CNT-COOHs on the aluminium foil was found at 25 °C for 48h because now the evaporation time is probably not long enough for the transfer of a detectable amount of CNT-COOHs from their aqueous dispersion.)

34.

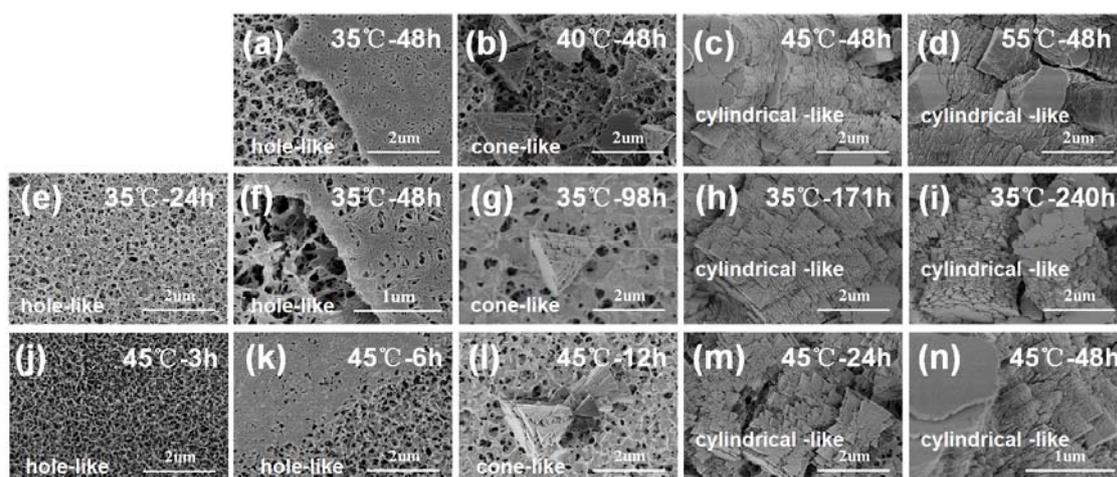


Fig. S35. The FE-SEM images of CNT-COOH deposit layers on the aluminum surface I under different evaporation conditions.

35.

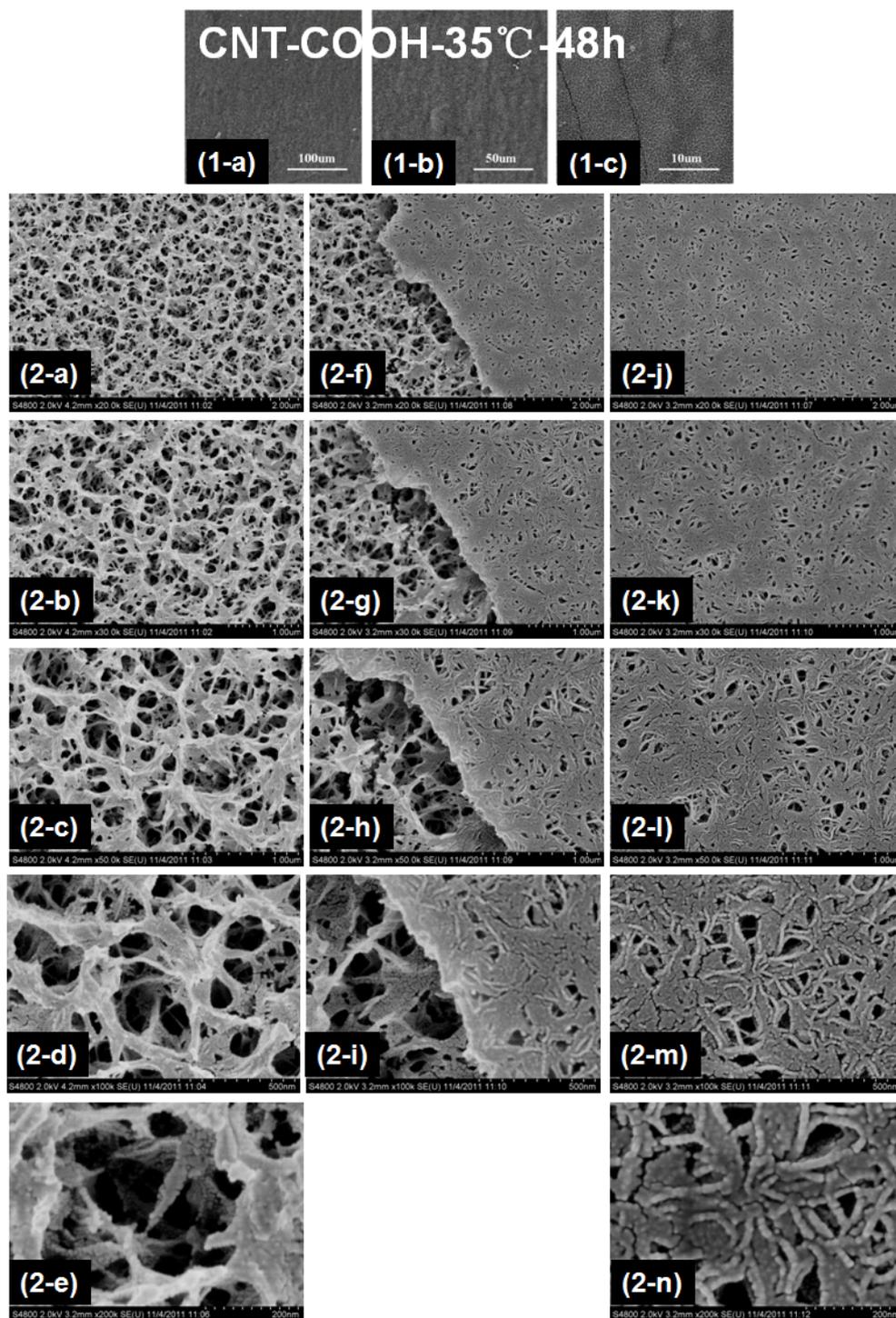


Fig. S36. More (FE-) SEM images of the self-assembled structure (CNT-COOH) of the temperature-resolved experiment at 35 °C for 48h on the aluminum surface I .

36.

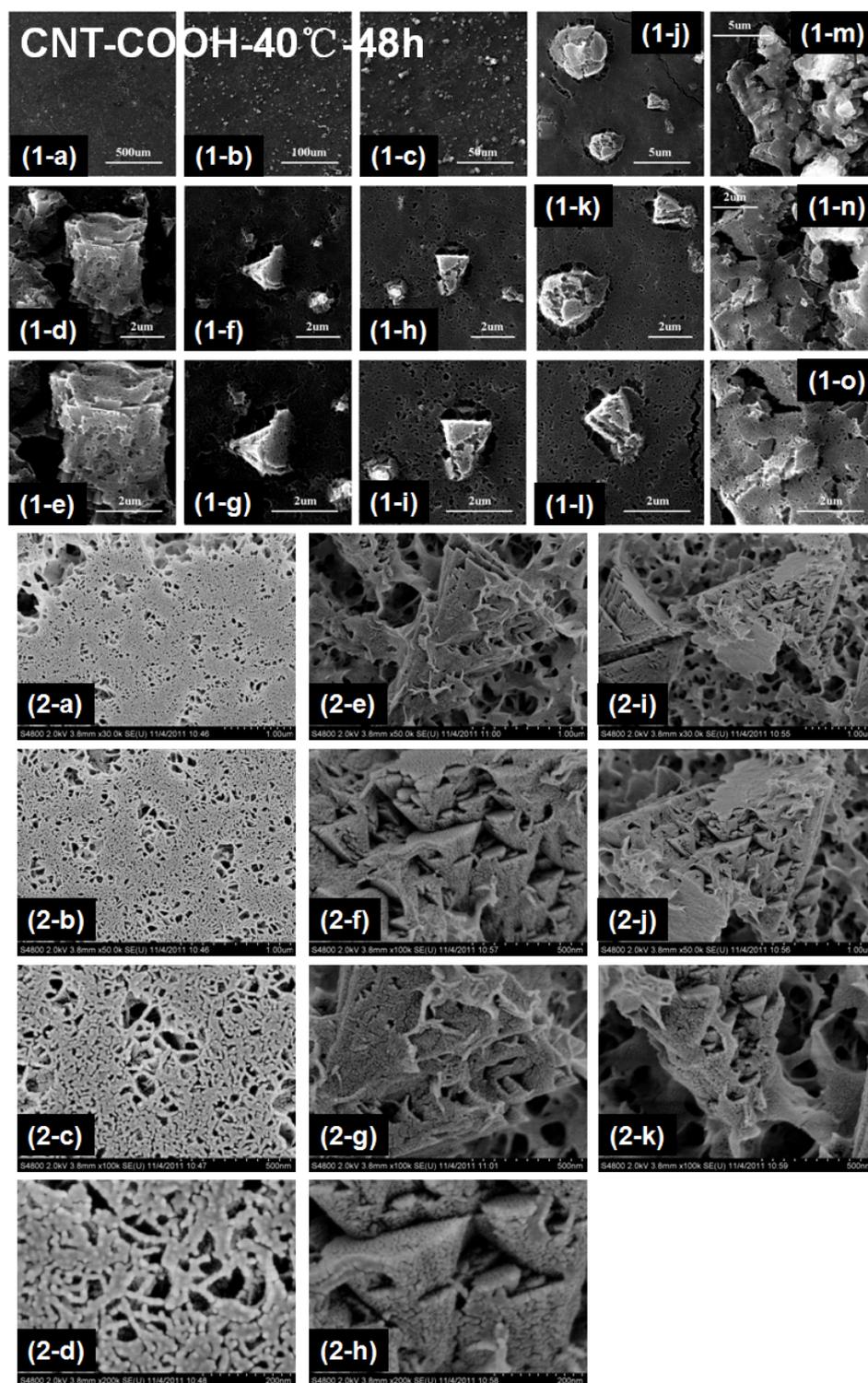


Fig. S37. More (FE-) SEM images of the self-assembled structure (CNT-COOH) of the temperature-resolved experiment at 40 °C for 48h on the aluminum surface I .

37.

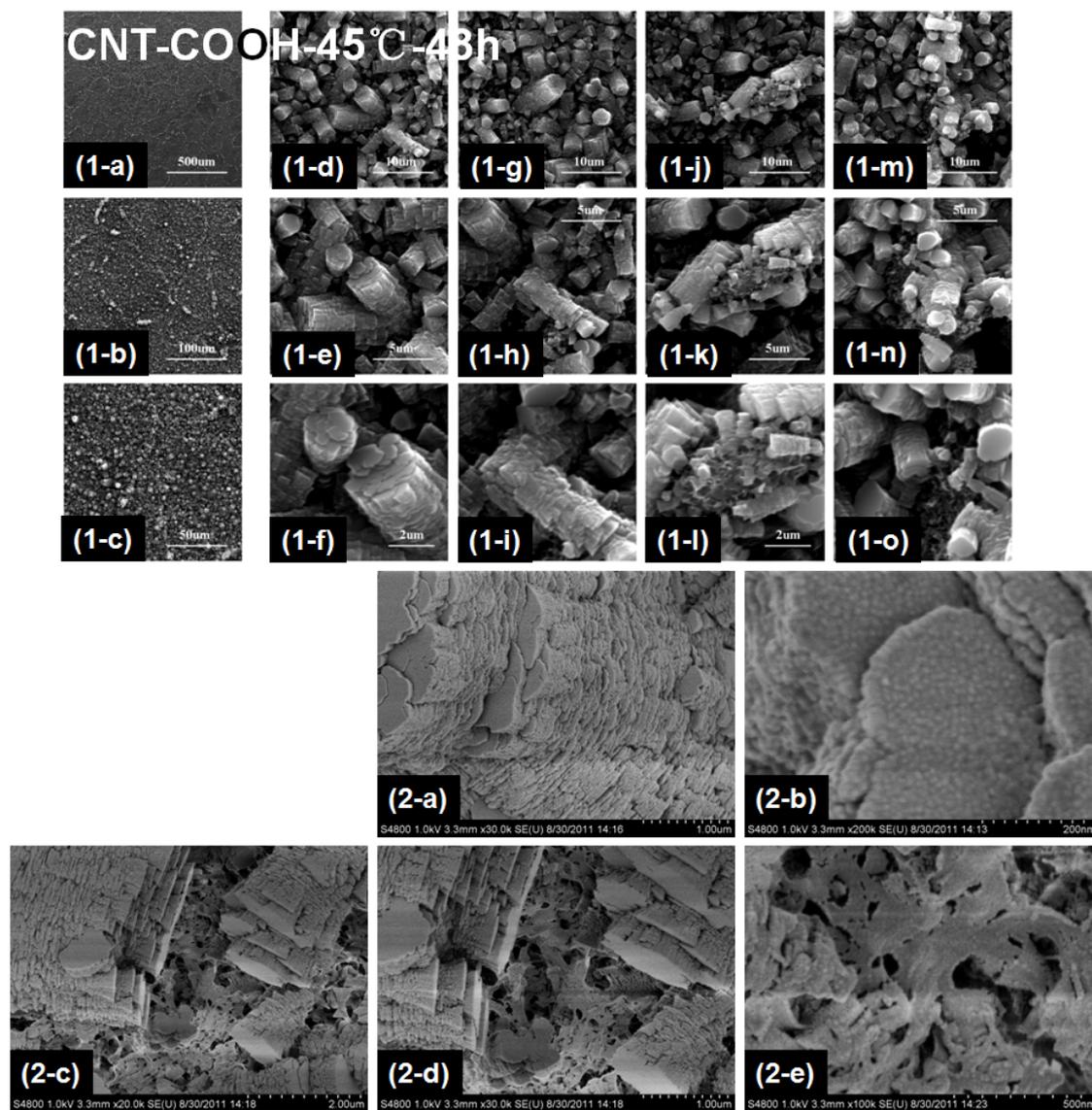


Fig. S38. More (FE-) SEM images of the self-assembled structure (CNT-COOH) of the temperature-resolved experiment at 45 °C for 48h on the aluminum surface I .

38.

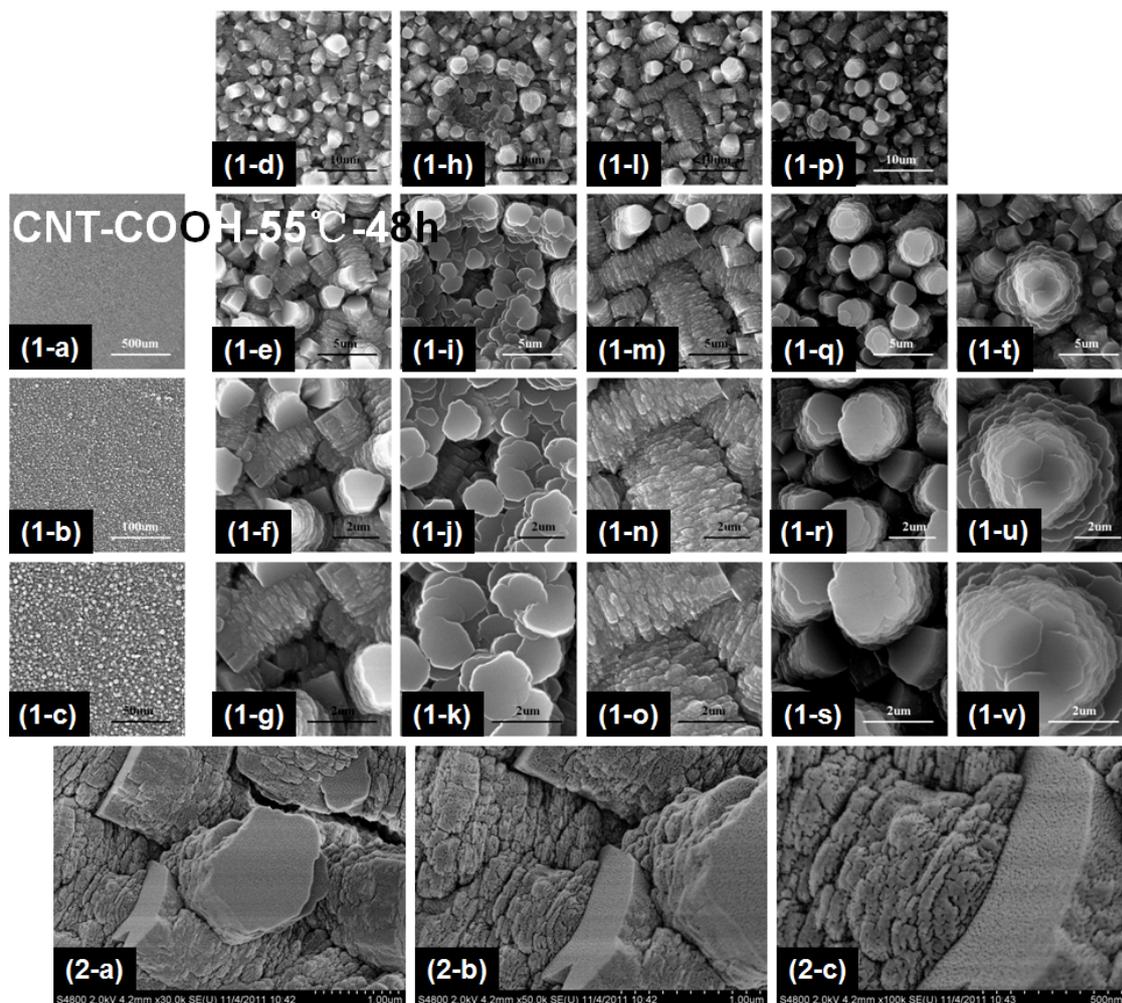


Fig. S39. More (FE-) SEM images of the self-assembled structure (CNT-COOH) of the temperature-resolved experiment at 55 °C for 48h on the aluminum surface I .

39.

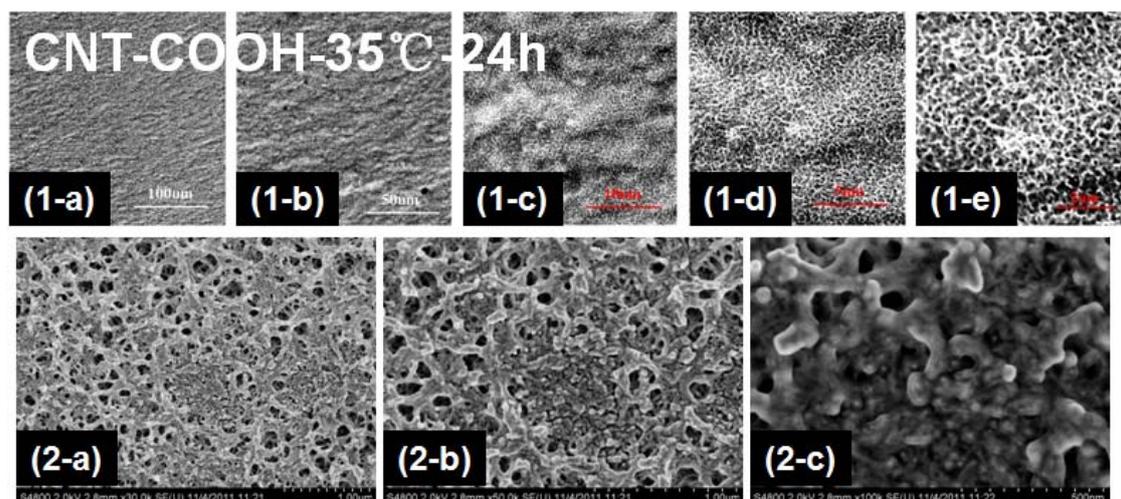


Fig. S40. More (FE-) SEM images of the self-assembled structure (CNT-COOH) of the time-resolved experiment at 35 °C for 24h on the aluminum surface I .

40.

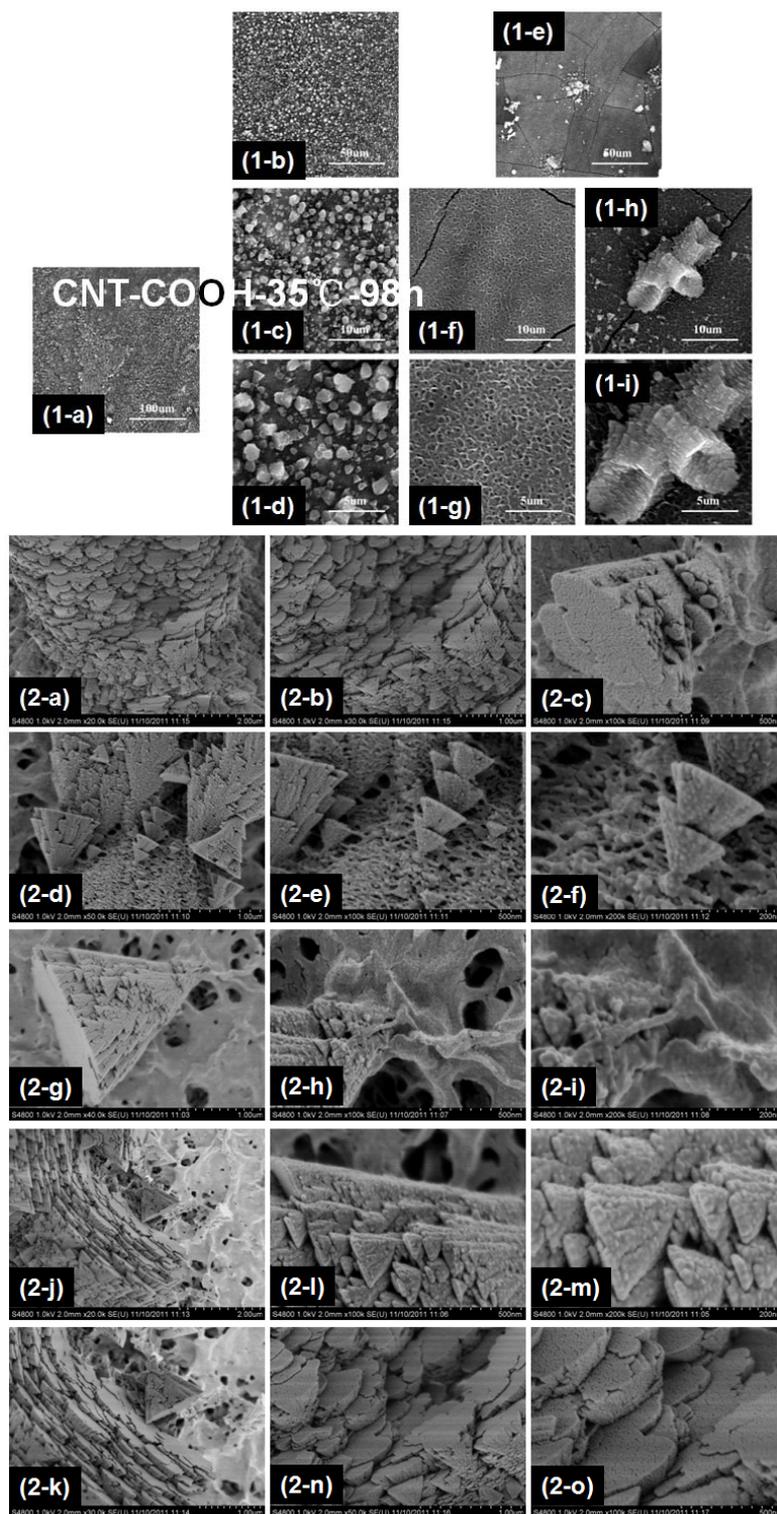


Fig. S41. More (FE-) SEM images of the self-assembled structure (CNT-COOH) of the time-resolved experiment at 35 °C for 98h on the aluminum surface I .

41.

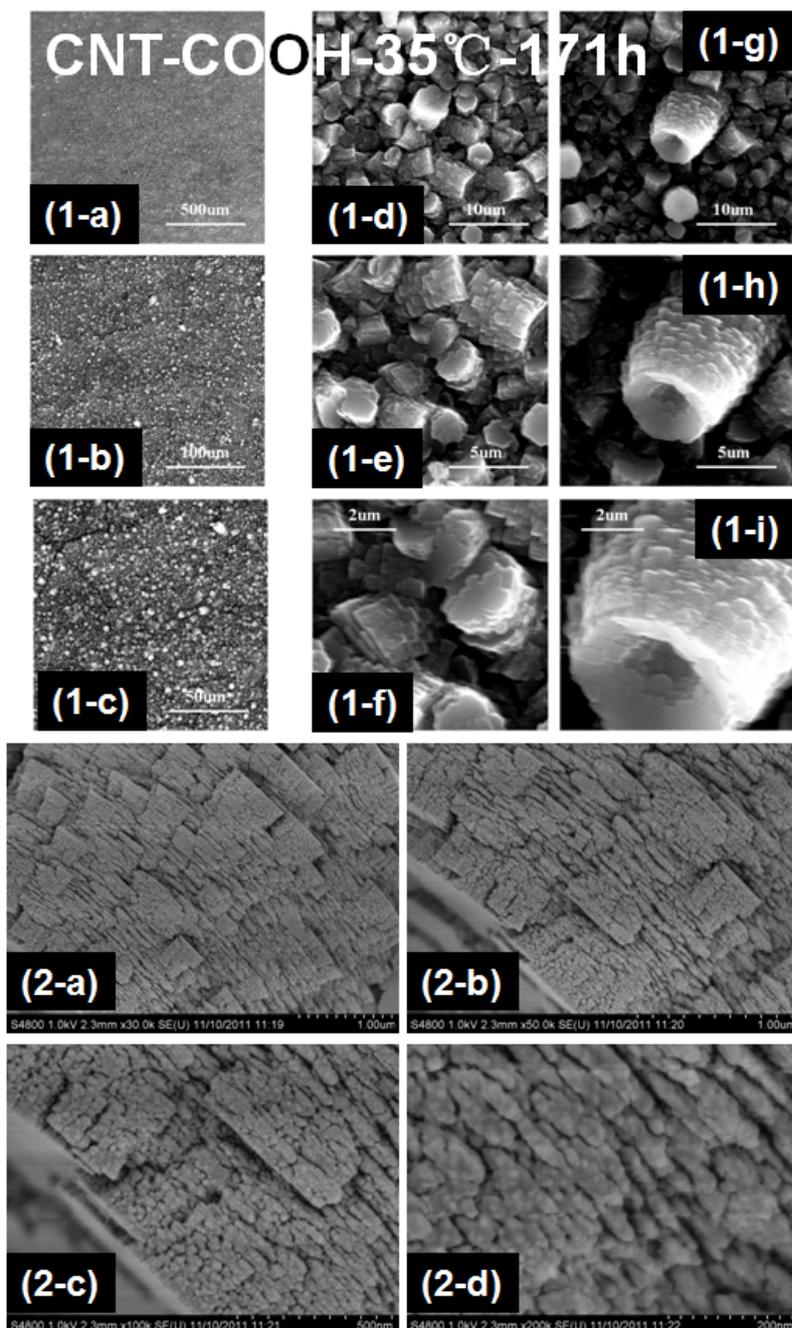


Fig. S42. More (FE-) SEM images of the self-assembled structure (CNT-COOH) of the time-resolved experiment at 35 °C for 171h on the aluminum surface I .

42.

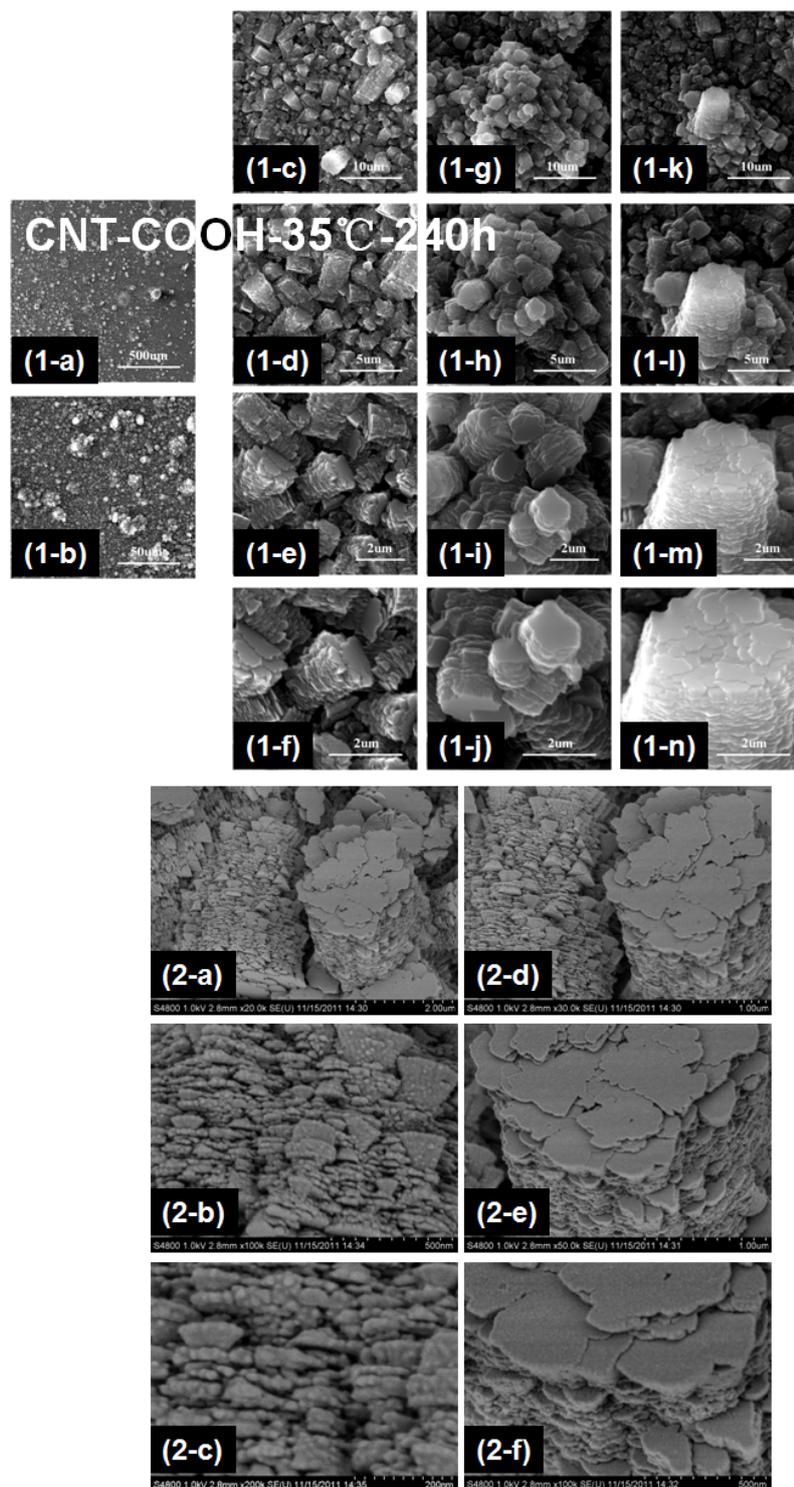


Fig. S43. More (FE-) SEM images of the self-assembled structure (CNT-COOH) of the time-resolved experiment at 35 °C for 240h on the aluminum surface I .

43.

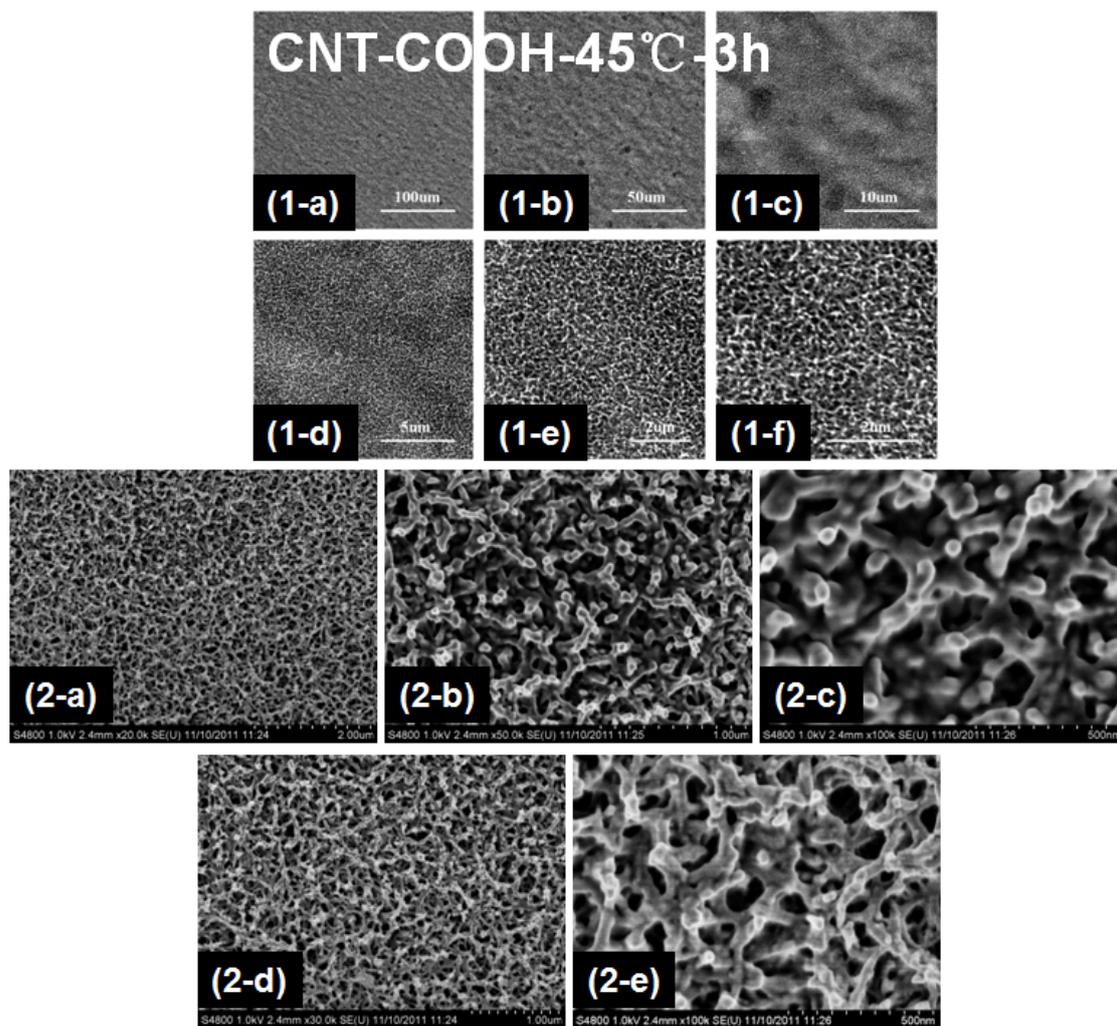


Fig. S44. More (FE-) SEM images of the self-assembled structure (CNT-COOH) of the time-resolved experiment at 45 °C for 3h on the aluminum surface I .

44.

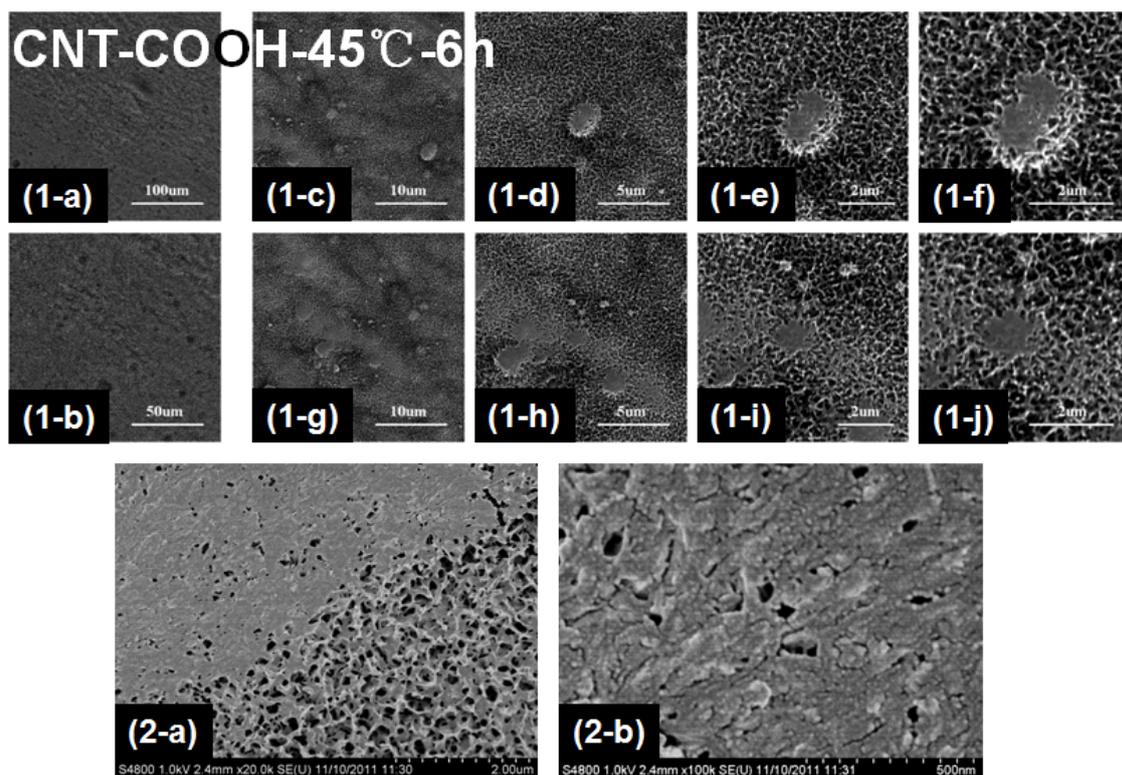


Fig. S45. More (FE-) SEM images of the self-assembled structure (CNT-COOH) of the time-resolved experiment at 45 °C for 6h on the aluminum surface I .

45.

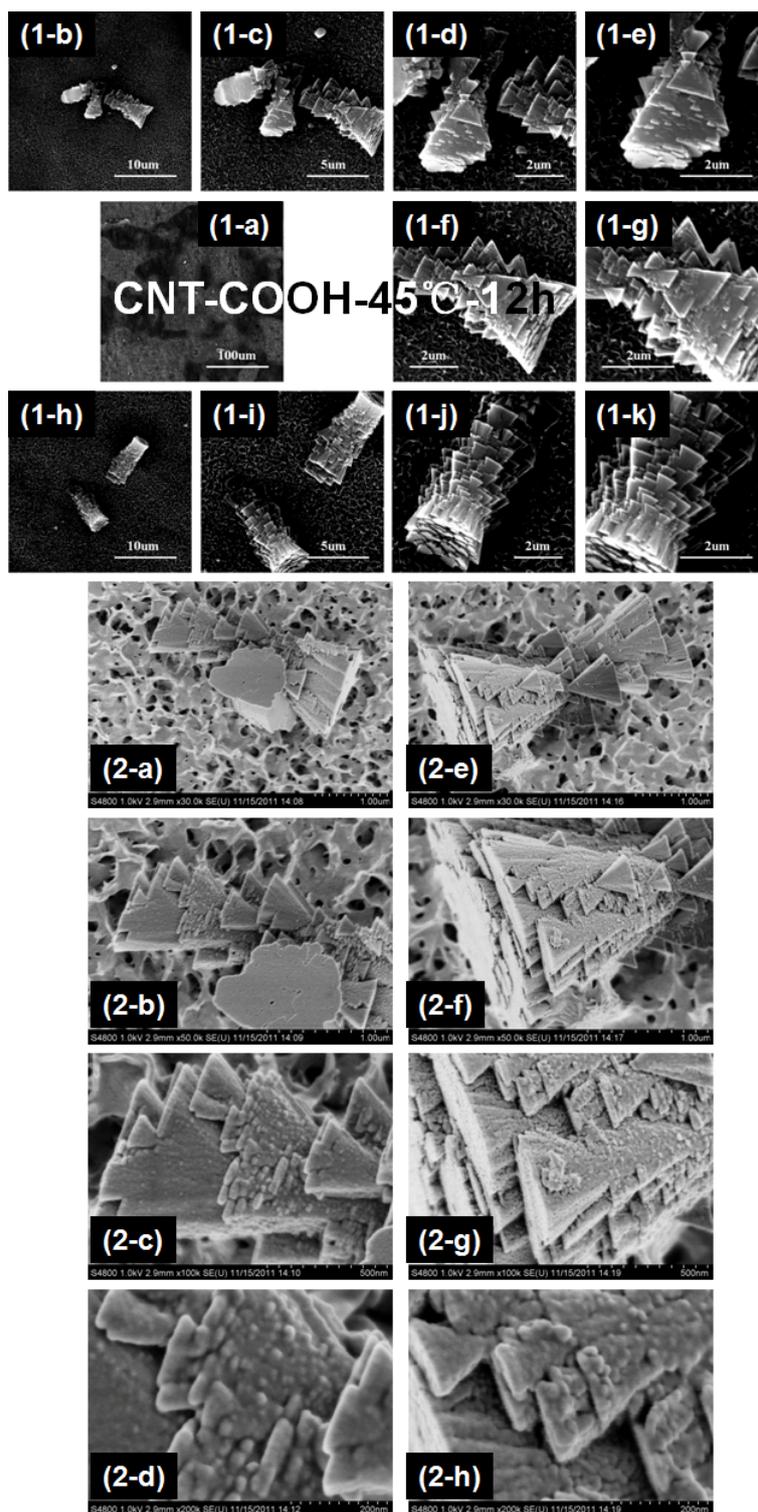


Fig. S46. More (FE-) SEM images of the self-assembled structure (CNT-COOH) of the time-resolved experiment at 45 °C for 12h on the aluminum surface I .

46.

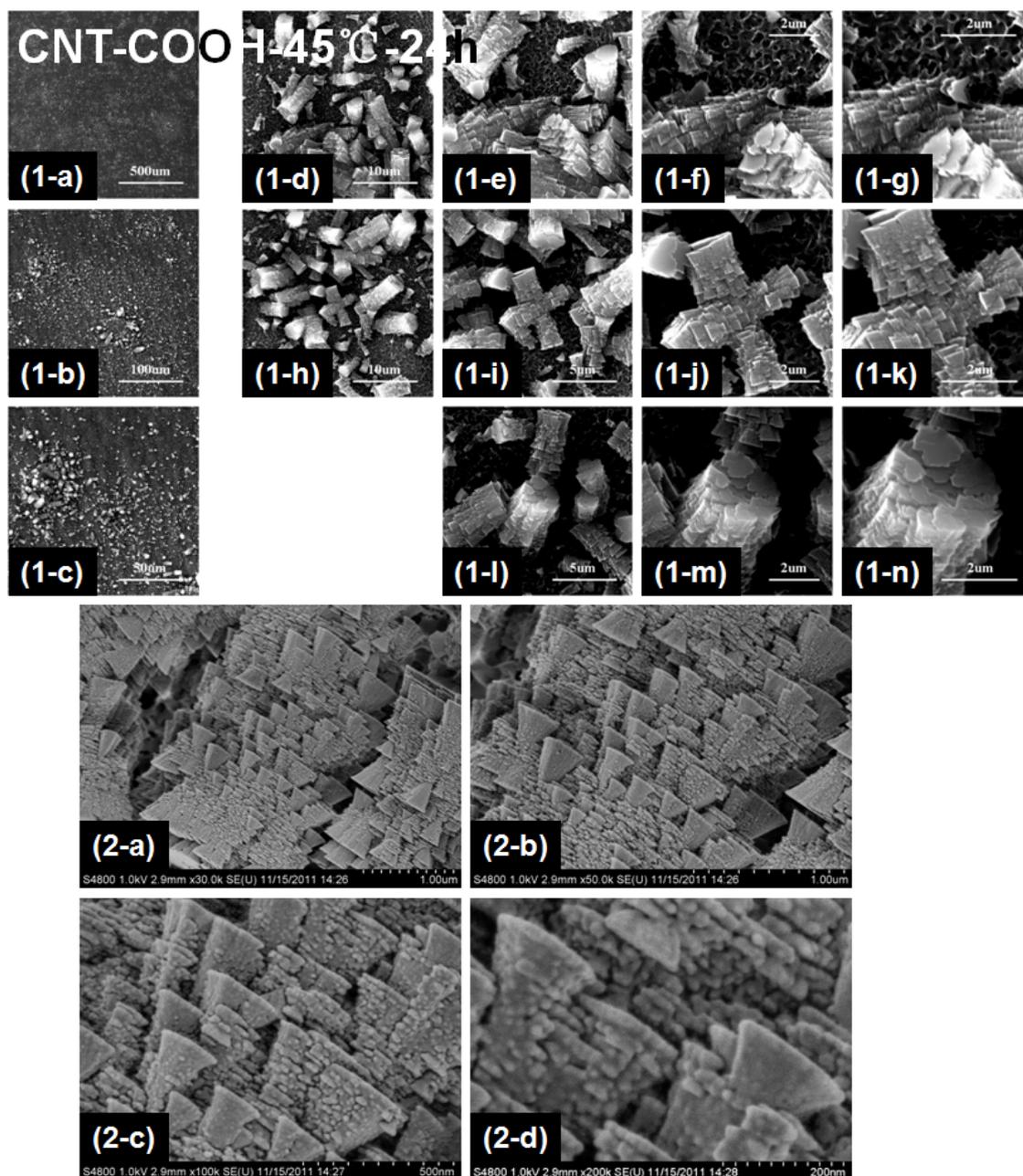


Fig. S47. More (FE-) SEM images of the self-assembled structure (CNT-COOH) of the time-resolved experiment at 45 °C for 24h on the aluminum surface I .

47. The sectional views of CNT-COOH deposit layers on the aluminum surface I shown in Fig. S48 also indicate that both longer evaporation time and higher evaporation temperature boost the transfer of more CNT-COOHs from their aqueous dispersion to the aluminum foil surfaces, similarly.

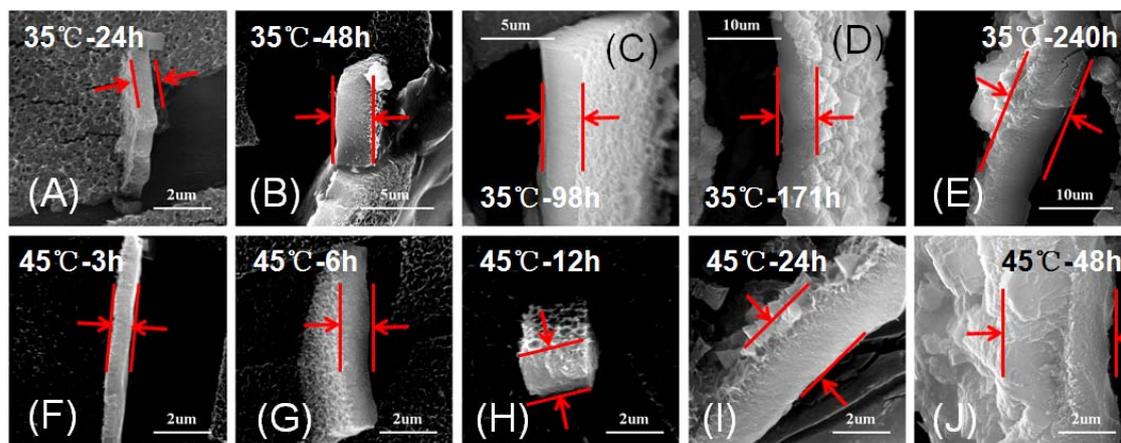


Fig. S48. The sectional SEM views of the CNT-COOH deposit layers on the aluminum surface I under different evaporation conditions.

49. The CA of the smooth Au surface (replication of silicon surface) is 101° under 10ul water droplet.

² The contact angles of the sample “GO-35°C-48h” and “GO-45°C-48h” are $54.6^\circ (\pm 3.2^\circ)$ and $10.8^\circ (\pm 4.8^\circ)$, respectively. The mean value was calculated from at least 10 individual measurements.

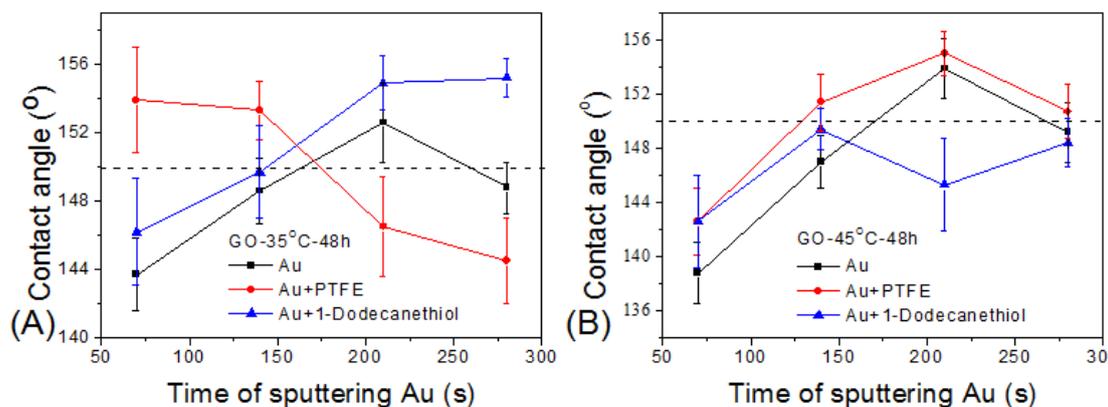


Fig. S50. Contact angle values of GO deposit layer on the aluminum foil surface before and after modification; “GO-35 /45°C-48h” correspond to the samples which were prepared by depositing GOSs on the aluminum foil surface at 35 /45 °C for 48h, respectively. (1) black lines: the samples were sputter-coated with a thin layer of gold by a SBC-12 coater (KYKY Technology Development Ltd., China; sputtering time: 70/140/210/280 s, sputtering current: 10 mA, sputtering pressure: 4 Pa); (2) red line: firstly, the samples were sputter-coated with gold via the same method as (1), then the samples were spin-coated with a PTFE solution (polytetrafluoroethylene, Teflon[®] AF 601S2, 6wt%, Dupont[™]) followed by being dried for 24h at room temperature; (3) blue line: similarly, the samples were firstly sputter-coated with gold via the same method as (1), then the samples were spin-coated with 1-Dodecanethiol and placed for 24h at room temperature before being put in an oven maintained at 75°C for 20h.

Notes and references

1. Y. W. Cao, T. Yang, J. C. Feng and P. Y. Wu, *Carbon*, 2011, **49**, 1502.
2. W. J. Zhao, L. P. Wang and Q. J. Xue, *J. Polym. Sci., Part C*, 2010, **26**, 11509.