

Supporting Information

Water-dispersible “carbon nanpods” with controllable graphene orientation

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1. Experimental Details

Two kinds of polymeric nanospheres, whose acrylonitrile (AN) unit contents were 90 mol % (AN90) or 75 mol % (AN75), were prepared by emulsion polymerization. AN90 was synthesized by polymerizing 12.7 g AN, 1.8 g methylacrylate, 0.5 g methacrylic acid, and 0.3 g *n*-butyl mercaptane in 150 g deionized water containing 0.3 g sodium dodecyl sulfate using 0.1 g potassium persulfate as an initiator. In case of AN75, 26.0 g AN 13.8 g methylacrylate, and 0.3 g methacrylic acid were polymerized in 120 g deionized water containing 0.4 g sodium dodecyl sulfate. The polymerizations were continued at 70 °C until the conversion exceeded 98 %. In order to comparison, AN unit contents of 80 mol %, which is between 90 mol % and 75 mol %, was also synthesized, which named as AN80.

Monodisperse ellipsoidal polymer particles were prepared by a method similar to that described by Ho *et al.*^{S-1} AN75 or AN90 nanospheres were dispersed in the aqueous solution of polyvinyl alcohol (PVA, 89 mol % hydrolyzed with a molecular weight of ca. 66,000) and the mixture was then cast on a shallow circular Teflon tray. The resulting thin PVA film containing the polymer particles was elongated 6 times in the air at 140 °C. The polymer particles were liberated from the

elongated film by dissolving the PVA in water at 25 °C and centrifuged. The particles were washed with deionized water and centrifuged again, and repeated this sequence 3 times. As the spindle-shaped nanoparticles keep their original hydrophilicity, they were able to be mixed uniformly with silica sol. A silica sol was prepared by stirring a mixture of TEOS, ethyl alcohol, deionized water, and HCl at 50 °C for 2 h in a manner similar to the method described by Kawashima *et al.*^{S-2}. The mole ratio of TEOS, ethyl alcohol, and water was 1:4:2. The reaction pH value was 2.5 for AN75 and 4.0 for AN90, respectively. After the mixtures were cooled in an ice bath, the polymer particles dispersed in water (2 wt %) was added to the silica sol with a weight ratio of the polymer-containing water to the sol of 1:3. These mixtures were poured into shallow circular Teflon trays and then dried for 5 h at 40 °C. To prepare the parallel-type CNPs, oxidization was carried out in dry air at 220 °C for 16 h within the silica gel. Then, the polymer particles/silica gel composite film was heat-treated at a rate of 5 °C min⁻¹ to 1000 °C under a N₂ flow and held for 30 min to carbonize the polymer in the gel. The silica matrix was dissolved by 1 M NaOH at 130 °C for 16 h and the liberated carbon particles were purified by several cycles of centrifugation, decantation, and rewashing with 1 M aqueous NaOH solution.

The microscopic features of the samples were examined with SEM (HITACHI, S4500) and TEM (HITACHI, H9000, 300 kV). For testing CNPs as ink, a Drop-on-Demand bubble jet printer (Canon, iP4100) was used. The ink contains 3 wt % perpendicular-type CNPs, 7 wt % glycerin and 7 wt % 3-methyl-1,3-butanediol in water. The ink was placed in a standard ink cartridge and printed onto A4-sized glossy papers.

2. Elemental analysis

As shown in the results of elemental analyses for the two types of CNPs (Table S1), these carbons contain large amounts of nitrogen and oxygen atoms. The nitrogen content of perpendicular type CNPs is larger than that of parallel type CNPs, but this is the opposite in the case of oxygen content. Oxygen atoms may be introduced during the alkaline treatment to dissolve the silica matrix, because the oxygen contents in both types of CNPs tend to increase by increasing the severity of the treatment conditions.

Table S1. Results of elemental analysis for two types of CNPs (wt %).

Type of CNPs	C	H	N	O (diff.)
Perpendicular	84.5	0.3	9.2	6.0
Parallel	85.3	0.3	6.5	7.9

Note: For the two samples, about 1.5 wt% of ash remained unremoved. The weight percentage of each element in the columns was thus calculated on ash-free basis. The oxygen contents were determined from the difference between the whole sample weight (ash-free basis) and the total amounts of C, H and N.

3. TEM observation

As shown in Fig.S1, the resulting carbons can not keep the spindle shape and aggregated together when AN75 are carbonized in the loose silica matrix, however, the orientation of graphene layer of the walls is still perpendicular to the long axis as that AN75 are carbonized in the dense silica matrix. Because the carbonization of AN75 take place in liquid phase, the flow of liquid in the loose silica matrix is easy to result in the aggregation of carbons during the carbonization, therefore, to obtain the carbons with a spindle shape when the carbonization take place in liquid phase the dense

The TEM images of CNPs from carbonization of AN90 in the loose silica matrix are shown in Fig.S2. The resulting CNPs look as if they are burst and broken, and there is no preferential orientation of graphene layer. It is probably that the inner pressure induced by decomposed gas damages the CNP and disrupts the alignment of graphene layer.

Fig.S3 shows the TEM image of carbonization of AN80 in the dense silica matrix. The formed CNPs have a similar morphology with that from AN75, but the walls of CNPs are not perfect. The orientation of graphene layer is perpendicular to the long axis.

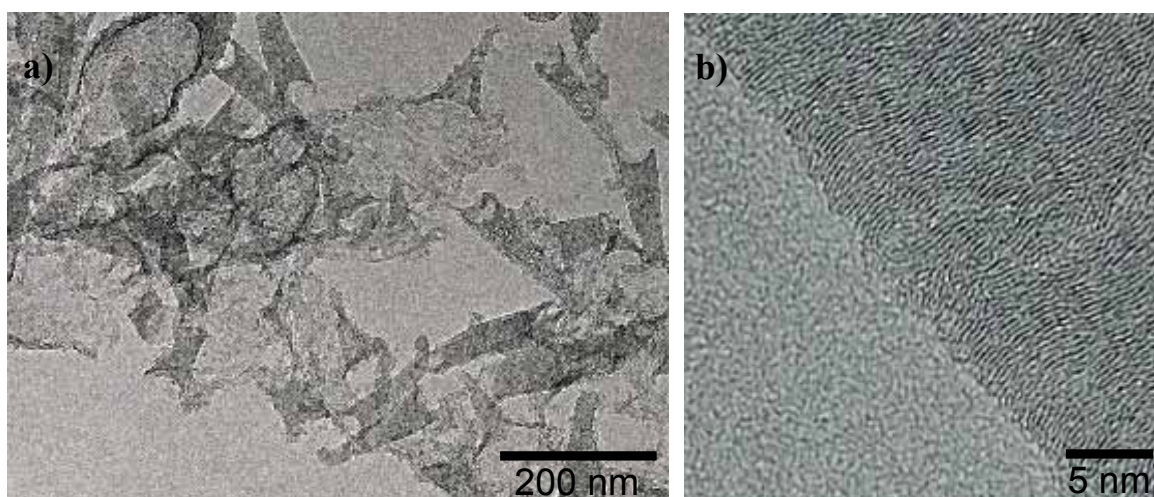


Fig.S1. TEM images of the resulting carbons by carbonization of AN75 in the loose silica matrix. (a) low magnification image and (b) high resolution image of walls in the resulting carbons.

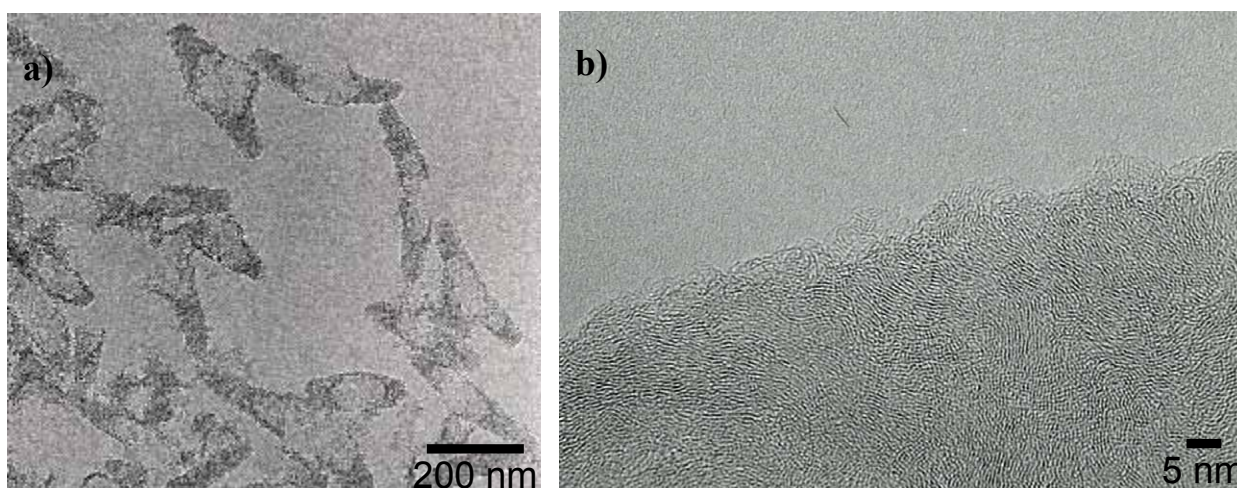


Fig.S2. TEM images of the resulting carbons by carbonization of AN90 in the dense silica matrix.

(a) low magnification image and (b) high resolution image of walls in the resulting carbons.

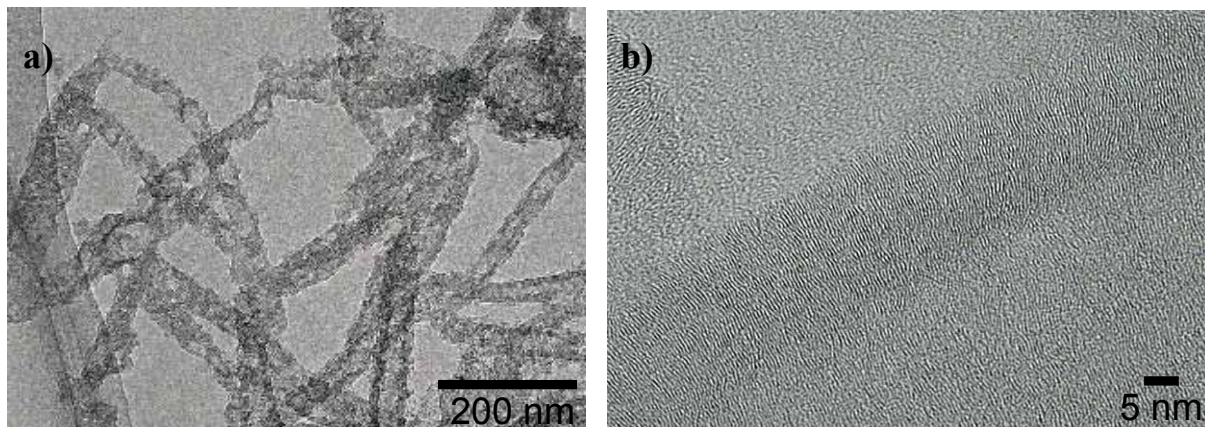


Fig.S3. TEM images of the resulting carbons by carbonization of AN80 in the dense silica matrix.

(a) low magnification image and (b) high resolution image of walls in the resulting carbons.

References

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