Supporting Information

The motivation of using benzene

We have already tried applying different solvent including ethanol, propanol, sucrose/glucose/fructose solution, xylene, cyclohexane and toluene. However, the synthesis rate of all of hydrocarbon solvents excluding aromatic hydrocarbon is too low (synthesis rate was 10~50 mg/hr with a pair of electrode for 30min.) and its shape was not very uniform. In comparison, in case of aromatic carbon showed high synthesis rate (synthesis rate was more than 300 mg/hr at the same discharge condition).

Fig. 1 shows Nitrogen adsorption-desorption isotherms and Table 1 summarized the BET surface area, total pore volume, and pore diameter if the synthesized NP carbons from various aromatic hydrocarbon solutions. These data shows that benzene and toluene have excellent pore structure against other synthesized carbon materials.

Meanwhile, we want to synthesis carbon materials which have highly developed pore structure because it has an important role in many advanced application and modern science area, such as carriers of catalysts, adsorbents in separation processes, purification of water and air, gas storage materials, electrode material of battery, and electrochemical double-layer capacitors. For this reason, we choose benzene and toluene as the precursor of carbon materials.

When comparing the active species observed under optical emission spectrum in benzene and toluene, major radical generated in benzene was C_2 while H_{α} was found to be in majority in toluene. Although both liquid are aromatic hydrocarbon compounds, the dissociation process of molecules seems to be different. For benzene, the resonance of the double bond was break at first and become open ring structure. Once the ring structure is broken, carbon and hydrogen molecules are dissociated and formed the active species. In the case of toluene, the H atom is first dissociated from the C-H bond outside the benzene ring, and the unstable molecule might further react. The results showed that carbon molecules were more likely being created by the discharge in benzene. This proposal also agreed with the result of the amount of carbon nanoparticles generated from each solvent. The benzene was in higher amount compared to that from toluene. It is expected that benzene would achieving high yield and quality of carbon nanoparticles since the decomposition of liquid benzene would give the greatest number of carbons for a given volume. The corresponding OES in toluene and benzene and detail discussion of the discharge mechanism was reported in our previous study.¹²



Fig. S1 Nitrogen adsorption-desorption isotherms of various solvent with gold electrode

Solvent	Surface area (m ² /g)	Pore volume (cm^3/g)	Mean pore size (nm)	Weight (g)
Benzene	241	0.81	15.05	230~250
Toluene	234	0.79	16.43	210~230
Cyclcohexane	117	0.62	14.7	less than
xylene	75	0.32	17.0	200

Table S1. Structural parameters of NPs/Carbon.

The effect of varying the experimental parameters on the final morphology and composition of the NP/Carbon systems.

To find any effect of pH in solution we tried to control the pH of solution. The most general method is to mix with aqueous (polar) solution such as HCl, H_2SO_4 , KOH and NaOH. However, since benzene is aromatic (non-polar) solution we cannot assign any pH to benzene by using aqueous solution. To the best of our knowledge, there is one possible to control of benzene pH by using benzoic acid. However its solubility is low and hence the range of pH controllable is too narrow. In addition, above all things it was extracted as impurity after drying to get carbon powder and thus we cannot get pure carbon materials.

To try controlling of NPs size we had been tried another method which is to change discharge condition of power supply. Fig. 2 shows X-ray diffraction patterns of NPs(Au)/CNBs with various experimental parameter including voltage, frequency and pulse width. There is no change of FWHM(Full width at half maximum) which calculable NPs size and it means that NPs size cannot be controlled by these parameters. The reason is assumed as follow. Metal atoms are ejected from the solid electrodes pair's tip by the produced energetic particles and grown in the plasma zone. Along with it numerous graphite flake also synthesized from plasma surrounding benzene medium. Meanwhile, the synthesis rate of these graphite flakes is supposed much higher than the rate of sputtering metal atoms because the amount of electrode consumption is too low compare with the amount of carbon weight (Fig. 3). Therefore, the growth of metal nano particles will be interrupted by a lot of graphite flake unless its rate is higher than that of graphite flake and hence the size of metal particle can't seem to be controlled.

However, the amount of NPs loading onto carbon can be controlled. Fig. 3 shows the changing of the amount of loaded NPs onto CNB with various experimental parameters with 5min. discharge time and it was calculated by Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES, Perkin-Elmer, PE OPTIMA-3300 DV). The sputtering rate of electrode was increased with increasing frequency, pulse width, and voltage. The loading amount of NPs was increased with increasing of frequency and voltage excluding. However, in case of pulse width parameter, it was reduced with increasing of pulse width. The reason is the rate of electrode consumption is proportional the amount of sputtered metal nano particles and the rate of electrode consumption was lower than that of synthesized carbon with increasing pulse width. Meanwhile, to confirm, if NPs is exist in solution (not onto CNBs) or not, discharged solution was filtered by syringe filter unit for gas chromatography and mixed with other carbon materials (Ketjen black EC600Jd) which don't contain any metal particle. It was dried and measured by XRD. Fig. 4 shows the X-ray diffraction patterns of filtered solution of discharged solution. It didn't show any peaks of NPs. It is supposed that all of sputtered NPs from electrode were loaded on CNBs during discharging.



Fig. S2 X-ray diffraction patterns of NPs/CNBs under (a) 0.5µs, 15 kHz (b) 1.4kV, 15 kHz and (c) 0.5µs, 1.4kV



Fig. S3 changing the amount of electrode consumption, synthesized NPs/CNB and loaded NPs onto CNB with various experimental parameters



Fig. S4 X-ray diffraction patterns of discharged solution

The change of elemental composition of NPs/CNBs before and after annealing.

To determine accurate elemental composition of carbon & hydrogen in NPs/CNBs, CHN(Carbon Hydrogen Nitrogen) – Corder Elemental analyzer (YANACO MT-6) was applied as mentioned in the main manuscript. The hydrogen containing in CNBs is considerably decreased due to decomposition by annealing process. However the ratio of carbon and NPs(putative) is not changed. It is expected the composition excluding C and H is NPs. On the other hands, Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) was applied to determine the amount of NPs before and after annealing. Table 2 shows the amount of loaded NPs onto CNBs and it shows the amount of NPs is almost unchanged. It is agreed with the result observed from CHN – Corder Elemental analysis and the composition rate is also corresponding.

	Wt %
Au/CNB (before annealing)	11.3
Au/CNB (after annealing)	10.9
Pt/CNB (before annealing)	11.6
Pt/CNB (after annealing)	11.1

Table S2. Weight percent of NPS in CNBs by ICP-AES



The chemical reaction carried out by radicals in benzene solution

Fig. S5 chromatograms of the discharged solution by SPP with structural formula

Group No.	Compound name	
1	Cyclohexane, methyl-	Cyclopentane, ethyl-
	Cyclohexene, 3-methyl-	Toluene
2	Ethylbenzene	Phenylethyne
	Styrene	
3	Indene	1,4-Diethynylbenzene
	Azulene	
4	Naphthalene	1,4-Diethynylbenzene
5~6	Biphenyl	Naphthalene, 2-ethenyl-
	Biphenylene	Acenaphthene
	Acenaphthylene	Styrene
7~8	Benzene, 1,1'-(1,2-cyclobutanediyl)bis-, trans-	Benzene, 3-cyclohexen-1-yl-
	Fluorene	1H-Phenalene
	Anthracene	Phenanthrene
	Diphenylacetylene	[2.2]Paracyclophane
	Benzene, 1,1'-(1,2-cyclobutanediyl)bis-, trans-	Cyclobutane, 1,3-diphenyl- trans-
	Naphthalene, 1,2,3,4-tetrahydro-2-phenyl-	Benzene, 3-cyclohexen-1-yl-
9~11	Anthracene, 9-methyl-	Phenanthrene, 2-methyl-
	Anthracene	Benzene, 1,1'-(1,2-cyclobutanediyl)bis-, cis-
	5H-Benzocycloheptene, 6,7-dihydro-	Benzene, 1,3-hexadienyl-
	1,4-Dihydronaphthalene	Benzene, 1,1'-(1,3-butadiyne-1,4-diyl)bis-
	Fluoranthene	Pyrene
	Triphenylene	Pyrene, 4,5-dihydro-
	Annulene	Benzo[ghi]fluoranthene
	Benzo[c]phenanthrene	Cyclopenta[cd]pyrene
	Benz[a]anthracene	Chrysene
	Cyclopenta[cd]pyrene	Cyclopenta(cd)pyrene, 3,4-dihydro-

Table S3. Structural name corresponding to the chromatograms in Fig. 1.



Fig. S6 (a) Nucleation of a pentagon, (b) growth of a quasi- icosahedral shell, and (c) formation of a spiral shell carbon particle proposed by Kroto and McKay⁴ (d) Growth of a large size carbon sphere^{65–68}.



Fig. S7 (a) Hexagonal, (b) pentagonal, and (c) heptagonal carbon ring structures in graphitic flakes^{65–68}.