

Polyiodide Production Triggered by Acidic Phase of Aqueous Solution Confined in Carbon Nanospace

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1 Polyiodide species were synthesized by the
2 acceleration of an acidic environment in the nanospace of
3 single-walled carbon nanotube (SWCNT) with a light
4 irradiation. Raman and EXAFS results strongly support the
5 production of polyiodide species after the adsorption of CsI
6 on SWCNT from aqueous solution. Interestingly, the
7 reaction was initiated by the nano-confined acidic phase
8 formed in a basic environment. The acidic phase plays an
9 essential role as an oxidant for the production of the
10 diiodine that is a source of polyiodide.

11 **Keywords:** Single-wall carbon nanotube, Adsorption,
12 Polyiodide

13 Porous materials have been crucial for molecular and
14 ionic adsorption, separation, and purification. For instance,
15 zeolites and porous carbons are representative materials in
16 various fields. However, these adsorbents have been used
17 not only in application fields but just in fundamental
18 researches although they are sometimes regarded as old
19 materials. Such situation evidently reflects that we do not
20 perfectly understand the adsorbents, adsorption phenomena,
21 or adsorbed phases. Especially, a confinement effect in
22 nanospaces is the most essential for the better understanding
23 of the adsorbents and, therefore, is one of the research topics
24 in fundamental chemistry.

25 A restriction effect in nanospaces cannot be negligible
26 for adsorption of molecules and ions. Actually, the strong
27 potential well provided by the nanospaces can obviously
28 distort or solidify the structure of molecular assembly of
29 adsorbed species.¹⁻⁵ For example, Urita et al. has reported
30 that the nano-restricted potassium iodide (KI) in tubular
31 spaces of carbon nanohorn forms the high-pressure phase
32 crystalline structure even under the ambient and evacuated
33 conditions.⁶ The nano-restricted structure of KI is the same
34 as the bulk crystalline structure under 9 GPa. Thus, the
35 phenomena called quasi-high pressure effect in nanospaces
36 have been elucidated with various experimental and
37 theoretical methods.^{7,8} On the other hand, we have revealed
38 structural anomalies of hydration around ions such as
39 rubidium,^{9,10} zinc,^{11,12} and cobalt¹³ ions as well as specific
40 photoreduction reaction of the copper acetate confined in
41 the carbon nanospace.¹⁴ In addition, we have confirmed that
42 the adsorbed amount of Br ion on porous carbons exceeds
43 that of Rb ion when the carbons are immersed in the
44 aqueous RbBr solution.¹⁵ We have proposed a possibility
45 that the surplus adsorption of Br ion was enhanced by the
46 acidic-phase formation in the pore. However, there was little
47 evidence to indicate such a specific phase formed in the
48 pore. After the previous work, we came up with the
49 hypothesis that if a kind of acidic atmosphere were

50 produced by the pore, some chemical reactions that need
51 acidic condition would be specifically initiated.

52 Iodine (I) is another candidate for halogen species and
53 can form polyiodides, I_n^- , under some different conditions.¹⁶
54 Typically, triiodide, I_3^- , species can be synthesized in
55 aqueous I^- solution under a UV-light irradiated condition.¹⁷
56 The photochemical reaction is known to be accelerated by
57 the existence of proton. Therefore, it is confident that we
58 could evidently describe the acidic phase in the pore of
59 carbon if we studied the properties of iodine species
60 confined in the pore. This manuscript discusses chemical
61 states of iodine species restricted in the pore of single-
62 walled carbon nanotube (SWCNT).

63 We used a SWCNT (EC1.5) purchased from Meijo
64 Nano Carbon Co. Ltd. The EC-type SWCNT is synthesized
65 by an enhanced direct injection pyrolytic synthesis (called
66 eDIPS) method.¹⁸ Since the pristine SWCNT does not have
67 enough pore windows that enables to use the inner pore, we
68 oxidized pristine SWCNT at 673 K for 1 hour under the air
69 condition followed by the treatment in conc. HCl (Nacalai
70 Tesque, Inc.; special grade reagent) for 24 hours. After
71 filtration, washing in distilled water, drying in a desiccator,
72 and heating at 1173 K in Ar flow condition, open-ended
73 SWCNT with less surface functional groups was obtained.
74 In the following part, we denote the open-ended SWCNT as
75 "SWCNT". CsI (99.9%) purchased from Fujifilm Wako
76 Pure Chemical Co. was used for electrolytes without any
77 further purification. In the typical preparation, SWCNT (50
78 mg) was stirred at 303 K in the aqueous CsI solution over
79 24 hours under a room light irradiated condition to
80 impregnate the electrolyte into the nanospace. Other
81 information is provided in the Supporting Information.

82 As shown in Figure S1, the nitrogen adsorbed amount
83 on SWCNT was obviously larger than pristine (i.e. close-
84 ended) SWCNT. The result indicates the end of each
85 SWCNT was successfully opened enabling the use of the
86 inner space of the cylindrical pore. The pore parameters
87 obtained by the analysis of nitrogen adsorption isotherms
88 are collected in Table 1. The average pore size of SWCNT
89 was able to be estimated as 1.2 nm from the analysis of the
90 isotherm.¹⁹

91 **Table 1.** Parameters of the pore structure for pristine SWCNT
92 and SWCNT from the analysis of N_2 adsorption isotherms

Sample	Micropore		Mesopore	
	$a / m^2 g^{-1}$	$W / ml g^{-1}$	$a / m^2 g^{-1}$	$W / ml g^{-1}$
Pristine SWCNT	50	0.01	317	0.66
SWCNT	591	0.18	358	0.71

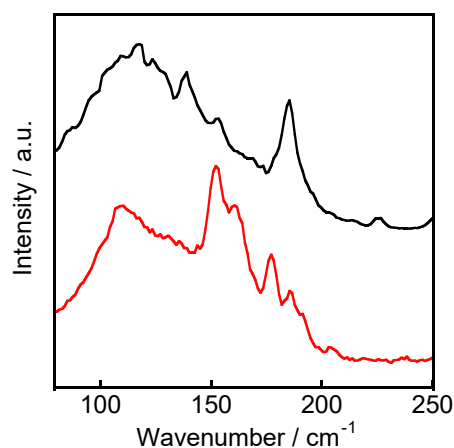
93 a : Specific surface area, W : Pore volume

1 The adsorption experiment showed the change in pH of
 2 aqueous CsI solution from 6.6 to 10.1. The pH variations
 3 between initial and final (i.e. after adsorption equilibria)
 4 states of the aqueous solutions were also observed and
 5 reported elsewhere by use of aqueous RbBr solutions.¹⁵ In
 6 addition to the literature results, the pH variations of
 7 aqueous RbBr solution could be observed only when the
 8 aqueous solution was adsorbed in the carbon nanospace as
 9 shown in Table S1. From these results, we have concluded
 10 that protons can be condensed in the carbon nanospace to
 11 compensate the charge balance in the pore. Basically, the
 12 adsorbed amount of anion species such as halogen ions is
 13 larger than that of cation species.¹⁵ In fact, the adsorbed
 14 amount of iodine species was also larger than that of Cs⁺ as
 15 shown in Figure S2. Hence, the aqueous solution confined
 16 in the carbon nanospace should be acidic even though the
 17 pH value in the bulk phase is around 10. However, there is
 18 no evidence other than the pH variation of the aqueous
 19 solution dispersed by carbon materials. Hence, we applied
 20 CsI as not only an electrolyte but also a kind of indicator for
 21 the acidic condition formed in the nanospace of SWCNT.

22 At first, we investigated the structure of CsI-adsorbed
 23 SWCNT by Raman spectroscopy. Raman spectrum of CsI-
 24 adsorbed SWCNT is shown in Figure 1 with the spectrum of
 25 SWCNT. Some bands assigned to the radial breathing mode
 26 (RBM) were observed in the spectrum of SWCNT. For
 27 example, a clear sharp band was observed around 185 cm⁻¹
 28 whose tube diameter can be calculated as 1.3 nm.²⁰ Another
 29 large and broad band was also detected below 150 cm⁻¹
 30 suggesting the existence of larger-diameter tubes.
 31 Comparing the RBM result with the average pore size
 32 obtained by the nitrogen adsorption isotherm (i.e. 1.2 nm),
 33 we concluded that not so many tubes having larger diameter
 34 is contained in the present SWCNT. On the other hand,
 35 clear bands around 152 and 160 cm⁻¹ were detected in
 36 addition to RBM bands in the spectrum of CsI-adsorbed
 37 SWCNT. The characteristic bands in the spectrum of the
 38 CsI-adsorbed SWCNT can be regarded as any modes of CsI.
 39 Here, Yoshida et al. studied the Raman spectra of iodine
 40 species restricted in various kinds of SWCNTs and
 41 concluded that polyiodide anions such as I₃⁻, I₅⁻, and I₇⁻
 42 show their Raman bands in between 100 and 200 cm⁻¹.²¹
 43 According to their conclusion, the bands observed around
 44 152 and 160 cm⁻¹ are assignable to I₅⁻ species, indicating the
 45 production of polyiodide species even just after the
 46 adsorption of CsI. Especially, the band around 160 cm⁻¹ can
 47 be assigned to a symmetrical vibration mode of I₅⁻.²² On top
 48 of that, the bands less than the 140 cm⁻¹ region varied its
 49 shape after the adsorption of CsI. Actually, Yoshida et al.
 50 denoted that the band assigned to I₃⁻ species can be
 51 observed around 110 cm⁻¹. Hence, I₃⁻ species might
 52 contribute to the change in the band shape after the CsI
 53 adsorption. In fact, the intensities of any RBM bands are
 54 quite smaller than that of the bands assigned to polyiodide
 55 species.²³ In any case, polyiodide species were synthesized
 56 only by the adsorption of CsI to SWCNT from its aqueous
 57 solution.

58 Figure 2 shows the Fourier-transformed I *K*-edge
 59 extended X-ray absorption fine structure (EXAFS) spectrum

60 of CsI adsorbed on SWCNT. The spectrum of aqueous CsI
 61 solution used for the impregnation of the electrolyte into the
 62 nanospace of SWCNT was also shown in comparison. Here,
 63 we have to clearly note that both spectra were collected
 64 without any light shielding. Since an appropriate light
 65 irradiation is an important condition to synthesize
 66 polyiodide species, we discuss the effect of light irradiation
 67 in the last part of this manuscript. In the CsI-adsorbed
 68 SWCNT spectrum, the largest profile that is assignable to
 69 neighboring I atoms was detected around 0.27 nm.^{24, 25} The
 70 assignment is reasonable because the reverse Fourier-
 71 transformed experimental spectrum between 0.141 and
 72 0.328 nm shown in Figure 2 was able to be described by the
 73 linear combination of theoretical EXAFS functions of both
 74 I-O and I-I structures as shown in Figure 3. Here, the
 75 theoretical function of the I-O shell structure was included
 76 in the analysis because the typical distance between I⁻ and
 77 the oxygen atom of H₂O is in the range of 0.355 and 0.370
 78 nm and, therefore, the largest profile had the possibility to
 79 involve the structural information of the hydrated water
 80 molecules.²⁶ From the analysis after the phase shift
 81 correction, the interatomic distance between two I atoms
 82 was estimated as 0.289 nm. The distance is very close to the
 83 literature value of I₃⁻ (0.290 nm).¹⁶ Therefore, the result
 84 support the production of I_n⁻ species from CsI adsorbed on
 85 SWCNT that initially contains only I⁻ species. However, the
 86 similar band assigned to neighboring I structure was
 87 observed in the spectrum of aqueous CsI solution shown in
 88 Figure 2 although the peak intensity is smaller than that of
 89 CsI adsorbed on SWCNT. The result cannot perfectly
 90 exclude the possibility that I_n⁻ species synthesized in the
 91 bulk aqueous solution adsorbs into the SWCNT nanospace.
 92 As we mentioned, production of I_n⁻ species is normally
 93 initiated by both acidic and light-irradiated conditions. Next,
 94 we conducted the experiment for the production of I_n⁻
 95 species by using dark and light-irradiated conditions to
 96 study whether I_n⁻ species can be synthesized in the
 97 nanospace.



98
 99 **Figure 1.** Raman spectra of CsI-adsorbed SWCNT (red) and
 100 SWCNT (black) measured with 532 nm excitation laser.

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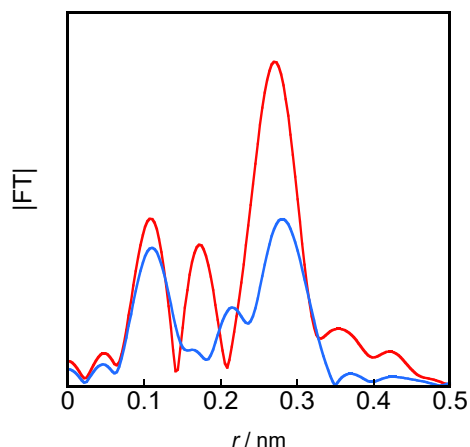


Figure 2. I K -edge Fourier-transformed EXAFS spectra of CsI adsorbed on SWCNT (red) and aqueous CsI solution (blue).

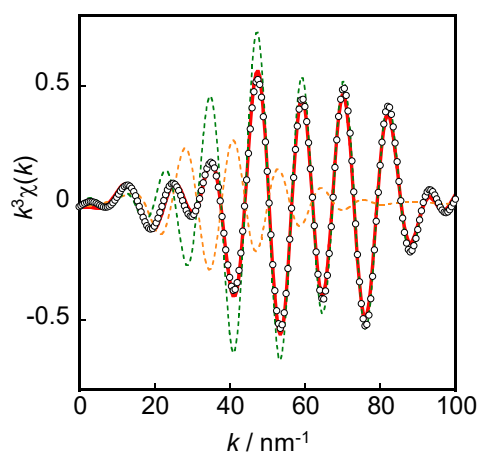


Figure 3. Reverse Fourier-transformed EXAFS spectrum (between 0.141 and 0.328 nm) of CsI adsorbed on SWCNT (red), calculated spectra of I-O (orange dot), I-I (green dot), and the best fit with the linear combination of the theoretical spectra (circle).

Figure 4 shows X-ray absorption near edge structure (XANES) spectra around I L_1 edge for various species. Here, the CsI-adsorbed SWCNT giving the spectrum of Figure 4(a) was prepared by impregnation of CsI by the aqueous solution, filtration, wash with distilled water, and dried in a desiccator. Whole these processes were done under a dark condition. The spectrum of CsI-adsorbed SWCNT that was prepared and measured under a dark condition is quite similar to that of aqueous CsI solution, indicating the formation of hydrated Γ^- species similar to that in the bulk phase. On the other hand, the spectrum of CsI-adsorbed SWCNT becomes similar to that of the CsI_3 crystal after the light irradiation to the sample used for the measurement of Figure 4(a) with Xe lamp for 1 hour. The result strongly supports that I_3^- was synthesized even though the hydrated Γ^- species was adsorbed before the light irradiation. Although I_n^- species can be obtained by several methods,

some reports indicate the necessity of H^+ through photochemical processes.^{17, 27-29} For example, Jortner et al. reported that the initial quantum yield of I_2 in the photochemical reaction strongly depends on its solution pH; the yield is quite low for pH = 3 or higher and increases drastically in the acidic condition.²⁹ Of course, I_2 species in the SWCNT pore is insufficient to synthesize I_n^- ,³⁰ both I_2 and $\text{I}_{(n-2)}^-$ species are indispensable. In fact, a G-band shift to a higher wavenumber region was observed after the CsI adsorption under a room-light irradiated condition as shown in Figure S3. Such a G-band shift is a clear evidence of the existence of I_2 molecules.^{21, 31} Therefore, Γ^- adsorption followed by the oxidation under the acidic condition in the pore are both key steps for the production of I_n^- . Interestingly, as indicated by the pH variation, aqueous CsI solution dispersed by SWCNT is in a basic condition at the equilibrium state, but an acidic phase is abnormally formed in the nanospace of SWCNT leading to the production of I_n^- species.

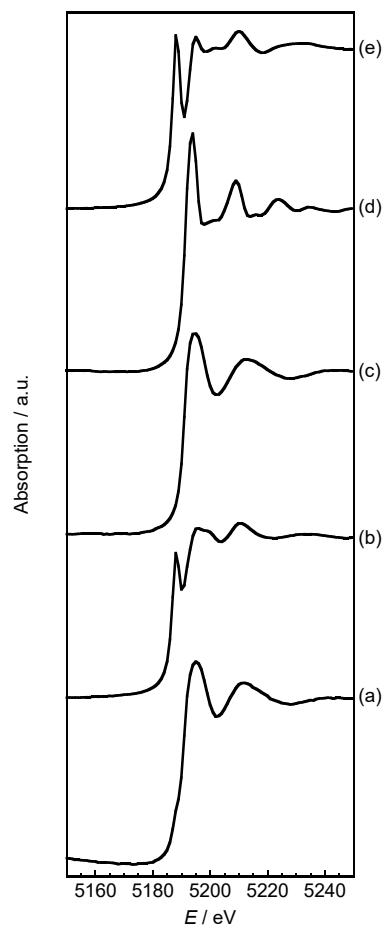


Figure 4. I L_1 -edge XANES spectra of (a) CsI adsorbed on SWCNT under a dark condition, (b) CsI adsorbed on SWCNT after a light irradiation for 1 h, (c) aqueous CsI solution, (d) CsI powder crystal, and (e) CsI_3 powder crystal.

In summary, the acidic-phase formation of aqueous CsI solution restricted in SWCNT nanospace was investigated.

1 Since the bulk aqueous solution dispersed by SWCNT is
 2 basic at the CsI adsorption equilibria, proton species
 3 confined in the nanospace would strongly interact with the
 4 surface of SWCNT and condensed in the pore. Such acidic
 5 phase in the pore can initiate the photochemical reaction that
 6 oxidizes I^- species to I_2 leading to I_2 production. I_2 can be a
 7 source of I_n^- species. Hence, an acidic adsorbed phase is
 8 obviously formed in the SWCNT nanospace that is
 9 produced in basic aqueous environment.

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