The Influence of γ-Irradiation on Nitrogen Configuration in Nitrogen-Doped Single-Walled Carbon Nanotubes

Theerapol Thurakitseree[a,*], Christian Kramberger[b], Narong Chanlek[c], Ratchadaporn Supruangnet[c], Anurat Wisitsorraat[d], Hideki Nakajima[c], Shigeo Maruyama[e,f]

[a]*Program in Applied Physics, Maejo University, Chiang Mai, 50290 Thailand*
[b]*Faculty of Physics, Universität Wien, A1090 Vienna, Austria*
[c]*Synchrotron Light Research Institute (Public Organization), 111 University Avenue, Muang District, Nakhon Ratchasima 30000, Thailand*
[d]*Nanoelectronics and MEMS laboratory, National Electronics and Computer Technology Center (NECTEC), 112 Paholyothin Rd., Klong 1, Klong Luang, Pathumthani, 12120 Thailand.*
[e]*Department of Mechanical Engineering, University of Tokyo, Tokyo, 113-8656 Japan*
[f]*National Institute of Advanced Industrial Science and Technology, Tsukuba, 305-8564 Japan*

Abstract

Electronic properties of nitrogen-doped single-walled carbon nanotubes (N-doped SWCNTs) depend on carbon and nitrogen configuration. Depending on the intrinsic nitrogen structure, it can be either intrinsic p- or n- doping. Here, we have investigated the influence of soft gamma (γ)-irradiation on the nitrogen configuration in vertically aligned N-doped SWCNT arrays. As the irradiation dose increased, pyridinic and graphitic nitrogens become more predominant. In general, the presence of holes refer to p-doping. However, XPS spectra show n-doping features, whereas the slight downshift in

*Corresponding author
Email address:* `theerapol@mju.ac.th` (Theerapol Thurakitseree)

the G line position is from compensating the ambient p-doping. The local transition of π^* nitrogen was also revealed by X-ray absorption spectroscopy.

Keywords:

Single-walled carbon nanotube, Nitrogen-doped SWCNTs, Nitrogen configuration, Reforming, Gamma irradiation

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1. Introduction

The modification of the properties of single-walled carbon nanotubes (SWCNTs) after growth can be performed with many different approaches. Direct post-treatment by chemical doping [1–3] has been used to modify the charge transfer state in which chemical reactions would lead to the functionalization of the nanotubes. The reaction requires a wet process that makes surface modifications more complicated. Plasma treatment is another choice that employs incident particle striking on nanotube surfaces and replacing carbon atoms to alter the nanotube electronic properties [4–7]. The mechanical properties of SWCNTs have, however, not been improved for specific applications. Conceptually akin approaches have been reported earlier in CNTs [8–13], few-layered graphene [14] and and graphite [12, 13]. The gamma (γ)-irradiation has been used to improve the nanotube surface [9–11, 13] or mechanical strength [8]. V. Skákalová *et al.* [8] have reported on γ-irradiation-dependent mechanical improvement of CNT paper. They identified the presence of air molecules as a prerequisite for structural improvement. At an irradiation doses of $170\,\mathrm{kGy}$, the Young's modulus and electrical conductivity could reach the maximum values due to covalent cross linking between the nanotubes. On the other hand, increasing defect con-

centration has been observed with high irradiation dose [9, 10, 13]. The γ-irradiation is, therefore, one of the key parameters to alter the nanotube properties and promote the formation of bonding environment.

Due to great promising properties of nitrogen (N)-doped SWCNTs, there have been many attempts to modify their electronic transition. Reorganization of nitrogen configuration is one crucial method that enables the property modifications of the nanotubes. By introducing N as heteroatom in the sp^2 carbon framework, the N dopant can serve as p- or n- type dopants depending on the bonding environment [15]. Incorporation of N into sp^2 carbon wall can turn the nanotube into many different configurations during synthesis, resulting in different intrinsic properties. They may occur as pyridinic, graphitic (substitution, sp^2 N) and pyrrolic nitrogen structures. While sp^2 N introduces electrons to the conduction band, other N configurations provide holes in the valence band.

To our knowledge, there are no reports on the influence of γ-irradiation on structure changes of N configurations in N-doped SWCNTs. In this work, γ-irradiation was used to alter the nitrogen configuration in vertically aligned N-doped SWCNT arrays synthesized from no-flow chemical vapor deposition (CVD) process. The influence of various irradiation doses of γ-ray on nitrogen bonding environment was investigated. The N1s transition spectra as measured by X-ray photoemission and X-ray absorption reveal a clear effect of gamma irradiation on specific nitrogen configurations. As the irradiation dose increased, pyridinic and graphitic nitrogens became more predominant. These transformations were accompanied by increasing n-doping.

2. Experimental

N-doped SWCNTs were synthesized by no-flow CVD [16, 17]. The catalyst solution was prepared from 0.1 wt.% each of cobalt (Co) and molybdenum (Mo) acetate dissolved in ethanol. The Co/Mo catalyst particles were deposited on silicon substrate by a liquid dip-coating method. [18] To synthesize N-doped SWCNTs, a 10% acetonitrile mixture in ethanol was used as mixed C/N feedstock. Prior to the CVD reaction, the Co/Mo catalyst was reduced under 3% H_2 in Ar atmosphere. When the growth temperature reached 800°C, the reducing gas was evacuated before injecting the C/N feedstock mixture into the CVD chamber. The reaction was kept for 10 min at a pressure of about 1.3-2.5 kPa. The atmosphere was finally replaced by Ar and the CVD setup was cooled down to room temperature.

The morphology of resulting N-doped SWCNT arrays was imaged by scanning electron spectroscopy (SEM, 1 kV acceleration voltage, S-4800, Hitachi Co., Ltd.). To investigate the influence of the γ-irradiation on C/N formation, five identical nanotube samples were prepared from the same batch. Each sample was inserted into one closed-end glass tube. The glass tube was then evacuated to vacuum level before the other end was sealed. The nanotube samples stored inside the glass tube under vacuum were exposed to soft γ-irradiation at irradiation doses of 0-50 Gy. All nanotube samples were characterized by resonance Raman spectroscopy (Renishaw, inVia Qontor Raman microscope) at an excitation wavelength of 633 nm with 1800 mm^{-1} grating. The incident laser with less than 2.5 mW power was focused by a ×50 objective lens. The local chemical shifts of carbon and nitrogen were analyzed by X-ray photoelectron spectroscopy (XPS) measured with a PHI 5000

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VersaProbe II, ULVAC-PHI set up. The monochromatic $Al\,K_\alpha$ radiation with the energy of 1486.6 eV was used as an excitation source. The X-ray absorption spectroscopy (XAS) was also measured to identify localized substructure of nitrogen. The X-ray electric field vector is parallel to the nanotube axis with an incident angle of 70° from normal surface for all measurements. The XPS and XAS measurements were, respectively, conducted at BL5.3 and BL3.2 at the Synchrotron Light Research Institute, Thailand.

3. Results and Discussion

The morphology of as-grown N-doped SWCNTs synthesized from $10\,\%$ acetonitrile mixture in ethanol is shown in Fig. 1. The vertically aligned growth of the nanotube array could be observed with the thickness of about $10\,\mu$m. Note that this homogeneous nanotube film on silicon was cut into five identical samples for further study of the γ-irradiation effect.
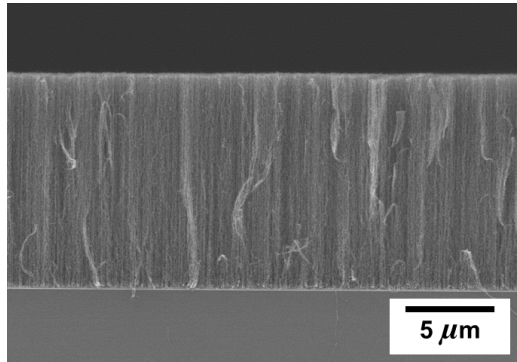

Fig. 1: SEM micrograph of as-grown N-doped SWCNTs film synthesized fom 10% acetonitrile mixture in ethanol.

Fig. 2 shows resonance Raman spectra of N-doped SWCNTs exposed to different γ-irradiation levels. All spectra were obtained with $633\,$nm excita-

tion wavelength. The high D-band intensity is a common feature for N-doped SWCNTs [17] due to the presence of stress in carbon walls, whereas weak Breit-Wigner-Fano (BWF) lineshape is observed in semiconducting window. The radial breathing mode (RBM) was used to characterize the nanotube diameters that are in resonance with the excitation wavelength of 633 nm. The empirical relation [19] was used to evaluate the nanotube diameter. The resonance of the observed small-diameter RBM peaks stem from the second semiconducting transition (E_{22}^S) as seen in weak BWF lineshape. The smaller-diameter RBM peaks (more than 250 cm^{-1}) could be observed for all nanotubes samples. The reduction of these peaks with increasing irradiation dose implies that specifically the high curvature of carbon network of small-diameter SWCNTs was decomposed during irradiation. Similarly, the prominent irradiation-induced lattic distortion can be clearly seen with higher irradiation doses. Note that there is a slight shift toward lower frequency observed in the tangential G-band feature. This could be caused by a doping effect [20].

Resonance Raman spectra of the 2D-band (G') were obtained using 633 nm excitation wavelength (Fig. 3). The G' peak was decomposed and fitted with Voigtian peaks with a constant full-width at half maximum (FWHM) of 13.6 cm^{-1}. All spectra were fitted with five constant Voigtian peaks at 2421.6, 2500.1, 2641.3, 2826.4 and 2891.7 cm^{-1} with one additional main peaks at 2603.1, 2590.8, 2590.5, 2589.8 and 2597.8 cm^{-1} for 0, 5, 10, 25 and 50 kGy of irradiation dose, respectively. Fig. 3 shows the identical G' linesshapes of N-doped SWCNTs exposed to different irradiation doses. With γ exposure, the G' shows a slight downshift, which is consistent with a slight shift observed
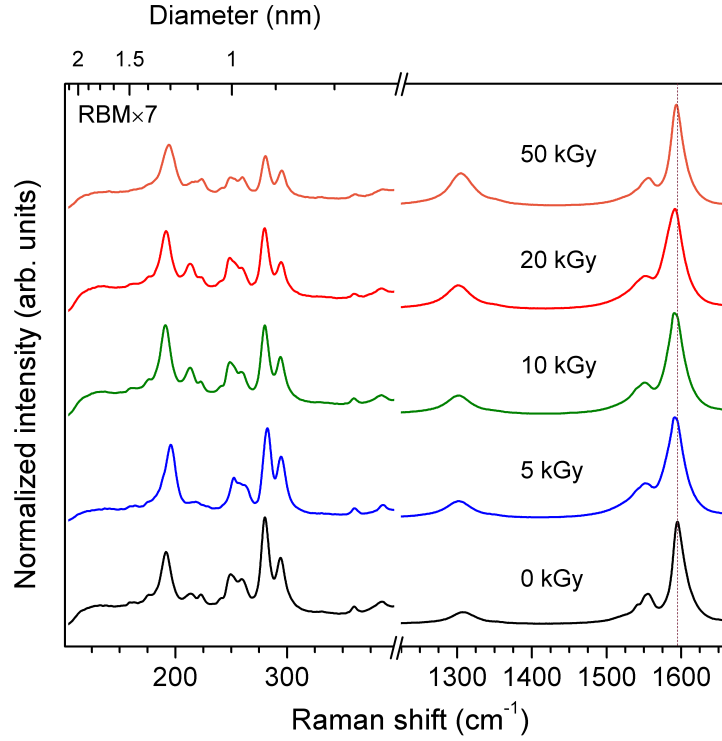
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Fig. 2: Resonance Raman spectra of N-doped SWCNTs excited with 633 nm excitation wavelength show a selective decrease in small-diameter RBM peaks and higher defect concentration with increasing γ-irradiation doses.

in the G-band position.

The electronic configuration of nitrogen was directly detected by XPS measurement. Fig. 4 shows a comparison of XPS spectra of N-doped SWCNT arrays exposed to different levels of γ-irradiation. After annealing the SWCNT films, only neglibile oxygen content was observed for all samples. A narrow asymmetric Doniach-Šunjić lineshape in the binding energy range of 279 eV to 298 eV was assigned to the sp^2 C1s of N-doped SWCNTs, whereas the binding energy and lineshape of the N1s were shown in the range of 391 eV
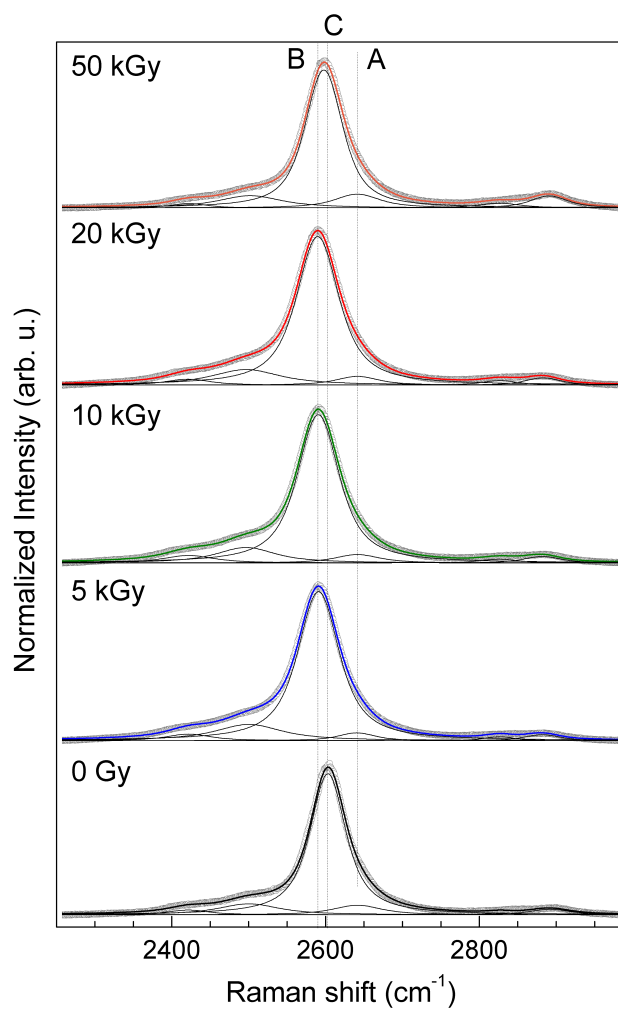
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Fig. 3: Resonance Raman spectra of the 2D band of N-doped SWCNTs exposed with different γ-irradiation doses at $633\,\mathrm{nm}$ excitation wavelength.

to $411\,\mathrm{eV}$. The well-defined C1s peaks was found to be at $284.4\,\mathrm{eV}$ as seen in previous reports, the $\pi - \pi^*$ electron shake up is also resolved [21–23]. The binding energy at about $404\,\mathrm{eV}$ indentifies the $\mathrm{N_2}$ molecules encapsulated inside the nanotube hosts [24], while signals from both substitutional and pyridinic N configurations are well expected in the range of 398-400 eV [25].
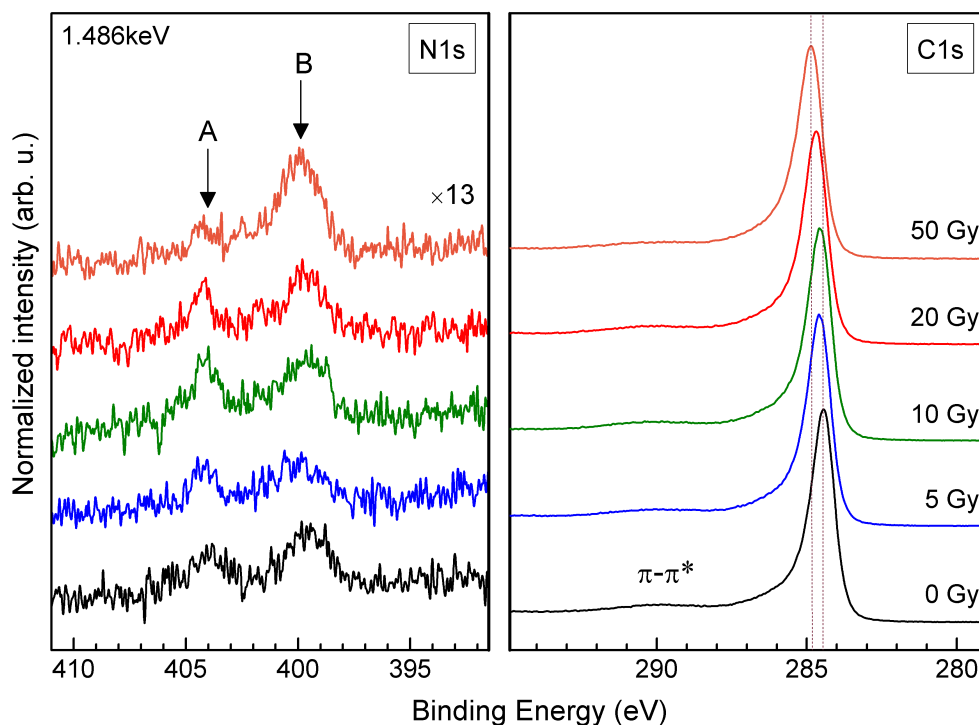
Fig. 4: XPS spectra of N-doped SWCNTs reveal a refomation of nitrogen configuration from trapped N_2 molecules to incorporated N with increasing γ-irradiation doses.

After high dose exposure, there is a predominance of substitutional and pyridinic N incorporation (peak B), whereas there is a seizable contribution of trapped N_2 molecules even after lower dose exposures (peak A). The change in nitrogen configuration by the radiated energy implies that the γ-irradation, when adequate energy is present, could induce the local transformation of N configurations. The concomitant decrease in N_2 and increase in incorporated nitrogen does suggest that the SWCNT walls can also react with the encapsulated N_2 molecules. Interestingly, there is also a slight shift toward higher binding energy observed in the C1s binding energy, which is consistent with the shifts observed in resonance Raman spectra (Fig. 2 and 3). This

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slight shift can be attributed to n-doping by covalently incorporated nitrogen atoms as reported earlier [22, 26].

The XPS spectra also reveal the formation of nitrogen configuration into pyridinic and graphitic nitrogens, whereas the interconnection between tube-to-tube would then result in different chemical shifts, unlike the peaks observed at $399.2\,eV$ in XAS spectra (see Fig. 5). The appearance of the absorption peak at $403\,eV$ also suggests that there may be two contributions from either N doping from activated N_2 molecules or reformation of N configurations occurring in sp^2 carbon networks as observed in the higher D-band intensity (Fig.2).

The local structure of nitrogen configuration was characterized by XAS measurement. All samples were baked at $400°C$ in vacuum before the measurement, to remove any atmospheric absorbants. The spectra were recorded in drain current mode at room temperature as seen in Fig. 5. The C1s spectra are not distiguishable for all samples. The identical feature of C1s$\rightarrow \pi^*$ of sp^2 carbon occurs at $285.2\,eV$ with the C1s$\rightarrow \sigma^*$ transition at $289.9\,eV$ as shown in Fig. 5(left panel). All spectra were normalized to the C1s$\rightarrow \pi^*$. The two features emerging at the photon energy of about $287\,eV$ and $288\,eV$ are essentially attributed to bonding environment of sp^2 carbon in the direct neigborhood of nitrogen sites. While the transition at $287\,eV$ is generally attributed to isolated nitrogen atoms involved in C=N and C≡N bonds, the transition at $288\,eV$ corresponds to single bond configuration, $i.e.$ N−C−N and N≡C−N bonds [27].

The N1s spectra of N-doped SWCNTs exposed to different irradiation doses as shown in Fig. 5(right panel) indicate the possibe chemical shifts
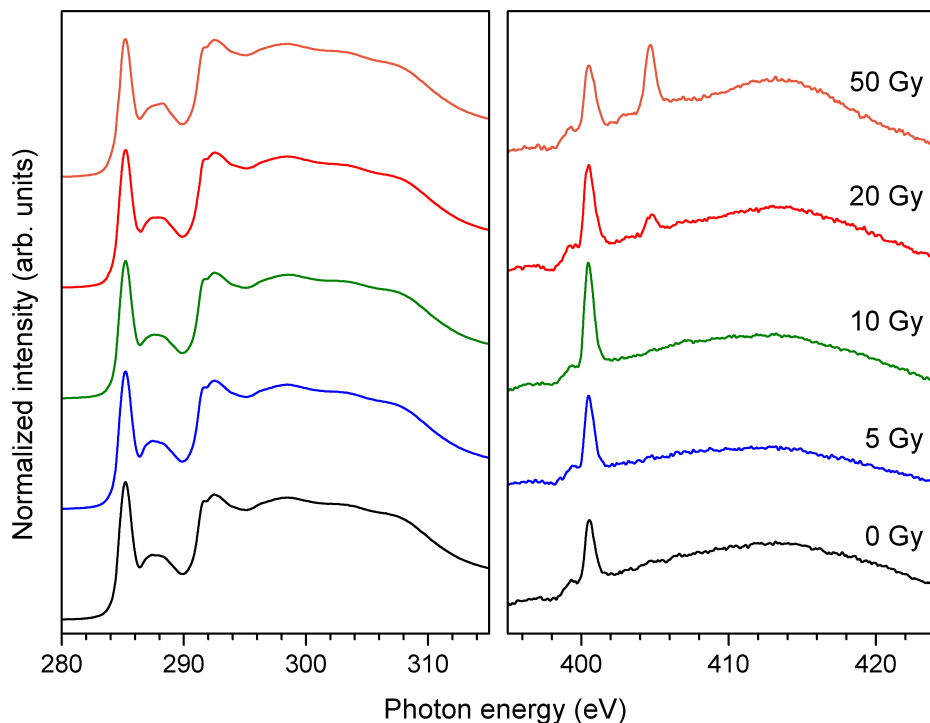
Fig. 5: XAS spectra of C1s (left panel) and N1s (right panel) of N-doped SWCNTs exposed to different γ-irradiation doses. All spectra are normalized to the maximum in the π^* resonance.

of nitrogen in the nanotube samples. The predominance chemical shift at 400.5 eV found in all samples comes from the N1s$\rightarrow \pi^*$ of encapsulated N_2 molecules, which is well expected as shown in our previous report [24]. The π^* feature of N_2 entirely covers that of graphitic nitrogen, which is supposed to occur at a binding energy of 401 eV [28, 29]. The noticeable N1s$\rightarrow \pi^*$ resonance peak at 399.2 eV is unambiguously assigned to the π^* transition of pyridinic nitrogen.

As the irradiation level increased up to 20 Gy, the unexpected additional N1s$\rightarrow \pi^*$ chemical shifts at 404.6 eV with the very weak peak at 403 eV are

clearly observed. These unexpected additional peaks strongly suggest that a seizable fraction of all nitrogens are bonded to another atomic species. Note that the contribution of oxygen molecules can be ruled out due to the lack of an oxygen atmosphere. V. Skákalová *et al.* [8] have previously reported bonding formation between the nanotubes at low irradiation doses, which could be able to lock their mutual positions. This interconnection resulted in higher Young's modulus and electrical conductivity as the bulk was much better interconnected, while the indivudual SWCNT still retained their structure. Thus, these two additional chemical environments can only be comprised of carbon and other nitrogen atoms. It stands to reason that nitrogen sites on SWCNT walls would be very reactive and that they would be prefered cross linking sites [30]. If nitrogen would then very often be simultaneously bonded to sp^2 and sp^3 carbon, this might result in a novel chemical shift nitrogen.

4. Conclusion

We have demonstrated the influence of soft γ-irradiation on nitrogen configuration in vertically aligned N-doped SWCNT arrays. Upon increasing the irradiation doses, the RBM of small-diameter SWCNTs is dampened, which is linked to the higher reactivity and the higher ability to cross link to other SWCNTs. The pyridinic and graphitic nitrogens are predominant species at higher irradiation level. Their occurence is concomitant to an increasing n-doping, evidenced by X-ray photoemission spectroscopy. At the highest irradiation levels X-ray absorption reveals local N1s$\rightarrow \pi^*$ transitions with a new chemical shift. We suppose the new chemical sites belong to nitrogen at

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cross-linked SWCNT walls. We hope to inspire further research on the new chemical shift in nitrogen, likely to be focused on nitrogenated SWCNT to SWCNT cross links.

Acknowledgements

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Captions

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