Raman Scattering Spectroscopy for Historical Incandescent Lamps with a Carbon Filament, Hg-free HID Lamps and OLEDs

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ABSTRACT
We have observed three kinds of Raman scattering spectra for the following materials: (1) the bamboo-based carbon filaments inside historical incandescent lamps fabricated by Ichisuke Fujioka and Thomas A. Edison, whose results were compared with those of a bamboo-based carbon filament annealed in our laboratory and a broken filament extracted from the incandescent lamp, which has been preserved for over a hundred years by our company; (2) iodine deposited inside a Hg-free high-intensity discharge (HID) lamp after arc discharge in a xenon (Xe) atmosphere, and (3) the variation in the spectra for PEDOT (poly(3,4-ethylenedioxythiophene)) doped with PSS (polystyrene sulfonate) and the PEDOT:PSS electrochemically dedoped. A shift in the D-band owing to defects was found to be $52 \text{ cm}^{-1}/\text{eV}$ for the bamboo-based carbon filament extracted from the incandescent lamp. The spectrum of iodine deposited inside the Hg-free HID lamp exhibited an erratic intensity progression with an overtone of more than 20, and this behavior was considered to be due to the resonance fluorescence of the gaseous iodine sublimated after the irradiation of laser light.

KEYWORDS: Raman scattering, carbon filament, iodine, HID lamp, PEDOT, OLED

1. Introduction
1.1 Raman scattering spectroscopy in light sources
Raman spectroscopy has the advantage of producing in-situ and/or nondestructive measurements, and has been extensively applied to various light sources such as a halogen lamp, an HID lamp containing mercury, and a fluorescent lamp. We have reported the Raman spectra for bamboo-based carbon filaments inside incandescent lamps fabricated by Ichisuke Fujioka in Japan and Thomas A. Edison, and the spectra were compared with those of raw bamboo, bamboo-based carbon materials, and a carbon filament inside a replica incandescent lamp produced in 1979. The historical background has been extensively reported for the atmosphere around the incandescent filament and for the dissociation behavior of iodide by coherent anti-Stokes Raman scattering (CARS).

1.2 Characterization of carbon filament in incandescent lamp by Raman scattering spectroscopy
Carbon possesses various allotropes such as graphite, fullerenes, carbon nanotubes, amorphous carbons, diamond, and diamond-like carbons. The Raman scattering spectrum of diamond was measured in 1930 using a mercury (Hg) lamp after the discovery of the Raman effect in 1928, but the feebly scattered light from graphite hindered the analysis of the Raman scattering spectrum before the advent of a laser as the excitation source. The first Raman spectrum of graphite was reported in 1970 using an argon (Ar) ion laser. The incandescent lamps with a carbon filament ceased to be manufactured by the end of the 1910s; thus, the characterization of the carbon filament has not been carried out using sophisticated analytical tools including Raman scattering spectroscopy. We now report the Raman scattering spectra for bamboo-based carbon filaments, and believe the results to be valuable from the viewpoint of light source history since the literature written at that time mainly describes the manufacturing process.

1.3 Raman scattering spectroscopy for organic light-emitting diodes (OLEDs)
Poly(3,4-ethylenedioxythiophene) (PEDOT) doped with PSS (polystyrene sulfonate) has been employed as a hole injection layer in OLEDs, and the doping state has been analyzed by Raman scattering spectroscopy. A failure analysis has been carried out using Raman spectroscopy, by which technique a dark spot was found to be produced by the dedoped state of the PEDOT:PSS brought about by the electrochemical reduction between the cathode metal of aluminum and the
PEDOT:PSS\textsuperscript{13}. The temperature estimation for OLEDs has also been reported, in which the intensity ratio of the Stokes to anti-Stokes Raman bands was measured by a temperature calibration method\textsuperscript{14}, and this technique has an advantage of the Raman scattering spectroscopy as an in-situ evaluation technique for estimating the temperature during the driving state of OLEDs.

2. Experimental procedure

The Raman microscope (Renishaw plc, inVia Raman microscope, U.K.) has a grating spectrometer with 1800 and 2400 grooves/mm for an Ar ion laser (514.5 nm) and a He–Cd laser (325 nm), respectively, and the dispersed signal is detected by a charge-coupled device (CCD) array. The excitation wavelengths at 457.9 and 532 nm were also employed for examining the dependence of the D-band on the excitation wavelength for the bamboo-based carbonized filament. The Fujioka incandescent lamp examined in this study, whose year of manufacture is estimated to be in the 1890s, has been preserved in Toshiba Lighting and Technology Corporation. The Edison incandescent lamp examined in this study has been preserved at the Rikadai Museum of Modern Science of the Tokyo University of Science (Kagurazaka, Tokyo). It was estimated to be the product manufactured in or about 1890 by comparing the form of the glass bulb and the connecting base with that in a reference picture\textsuperscript{12}. The rigorous resonance Raman spectra were measured at 514.5 nm for reagent-grade solid iodine through a glass ampoule and for the iodine deposited inside the HID lamps through a silica envelope. The HID lamps were fabricated with two tungsten electrodes and filled with Xe gas at 60.8 kPa. NaI and ZnI\textsubscript{2} were adopted as the emission sources. The aqueous PEDOT:PSS solution was spun onto an indium oxide doped with a tin (ITO) layer covered on a glass substrate, then dried at 473 K in nitrogen atmosphere. The PEDOT:PSS layer was electrochemically dedoped in an acetonitrile solution containing tetraethyl ammonium tetrafluoroborate as the supporting electrolyte at $-1.42$ V versus a platinum wire electrode as the quasi-reference electrode. The PEDOT:PSS layer dedoped electrochemically was extracted from the solution and rinsed with acetonitrile without a supporting electrolyte several times and dried in air. During the post-electrochemical treatments, oxygen seems to penetrate into the PEDOT:PSS layer. Polyfluorene was spun on the PEDOT:PSS layer, and the cathode materials were successively deposited by vacuum evaporation in the order of CsF as a buffer for the electron injection, then Mg and Al.

3. Results and discussion

3.1 Historical incandescent lamps

Figure 1 shows the Raman spectra measured at
514.5 nm for three carbon filaments at which the G-band at around 1585 cm$^{-1}$ and the D-band at around 1350 cm$^{-1}$ were observed. The spectra were shown after subtracting the background fluorescence due to a glass bulb from the raw spectra. The D-band originates from defects in the graphene layer of the graphitic carbon materials. Spectra (a) and (b) correspond to the original carbon filaments fabricated by Fujioka and Edison. Spectrum (c) was obtained from the bamboo-based carbon filament, which was prepared by Yuge and his group in 1979 as the celebration of the first electrical lighting by Edison in 1879. Judging from the relative ratio of the D-band to G-band intensities, these three carbon filaments are considered to have the same defect density in the carbon filaments.

Figure 2 indicates the Raman spectra for carbon specimens with various thermal histories: (a) the spectrum corresponds to the carbon filament inside the Fujioka lamp, (b) the bamboo-based carbon was annealed at 1273 K, (c) the commercial glassy carbon, and (d) the vapor deposited carbon on a cathode during arc discharge in He atmosphere. The G$^\parallel$-band at around 2700 cm$^{-1}$ was found to appear in the spectra for the carbon filament inside the Fujioka lamp, but not in that of the bamboo-based carbon annealed at 1273 K. The intensity of the G$^\parallel$-band has been reported to be related to the degree of graphitization, and no band is found for the poorly ordered and nongraphitized carbons such as
petroleum- and pitch-based carbons, and carbon blacks, and chars. The disappearance of the $G'$-band is considered to be due to the insufficient growth of graphene layer in the poorly ordered graphite structure for the bamboo-based carbon annealed at 1273 K. The intensity of the $G'$ band has been known to increase with increasing annealing temperature for the carbon prepared from polyfurfuryl alcohol with the decrease in intensity at around 1350 cm$^{-1}$, describing the presence of defects. The bamboo-based carbon filament is, therefore, speculated to be annealed at more than 1273 K for the Fujioka lamp in the production process. The crystallinities of the four carbons are discussed on the basis of the full-width at half maximum of the $G$-band, and the values of which were 36 cm$^{-1}$, 62 cm$^{-1}$, 59 cm$^{-1}$, and 26 cm$^{-1}$ for the carbons specified (a) to (d) in Fig. 2, respectively. The crystallinity of the carbon filament is considered to be superior to those of the bamboo-based carbon annealed at 1273 K and glassy carbon.

The $G'$-band has been considered to be due to the overtone of the D-band, but the origin has been assigned to the double resonance Raman scattering process on the basis of the graphite structure irrespective of the defects. The poorly ordered carbon, which has a lot of defects and does not attain the graphite structure, does not show the $G'$-band.

Graphite has a hexagonal structure and the reciprocal space is also given by a hexagonal one, in which $\Gamma$ and two $K$ and $K'$ points are assigned for the origin and individual edges of the hexagon, respectively. The Brillouin zone is given by an angular frequency ($\omega$) and a momentum ($\hbar$), and the $G$ band appears owing to the transition of electrons at the $\Gamma$ point. The Raman scattering process is treated as a non-resonance Raman process since the energy gap at the $\Gamma$ point is more than 15 eV and no absorption occurs using visible wavelength lasers. The Fermi plane intersects at the $K$ and $K'$ points, and the light is absorbed up to the ultraviolet region of around 4 eV near these points.

The trajectories of the excited electrons are depicted in Fig. 3(a), which shows a diagram for describing the appearance of the D-band.

An electron with the momentum $k$ is excited from $i$ to the upper level at $A$ by the incident laser in an electron-hole creation process. The electron is scattered by emitting a phonon with the momentum $q$ to state $B$. 

Figure 6 SIM image (a), TEM image (b) and the electron diffraction pattern of the bamboo-based carbon filament extracted from preserved incandescent lamp (b). The distance between the graphene layers was determined to be 0.34 nm along the c-axis. Three diffracted rings were confirmed from (002), (101) and (110).
with the momentum \( k+q \), and then scattered again back to C to recombine with a hole. The difference in \( \omega_{ph} \) corresponds to the Raman shift for the D-band, and the double resonance processes occur at the transition from \( i \) to A and A to B. The latter is called inelastic scattering, while the electron scattering from B to C is due to an elastic one without any change in energy, as shown by the dotted line. The absorption \( i \) to A occurs at a more distant \( k \) point from the K point in the Brillouin zone of graphite by increasing the incident energy of the laser, and the shift in the wavenumber of the D-band, \( \omega_{ph} \), is explained by the change in photon energy from A to B. Figure 3(b) explains the appearance of the G’ band as the second-order double resonance Raman scattering process, in which the inelastic scattering process occurs between B and C in the Brillouin zone of graphite, and gives the difference in 2\( \omega_{ph} \) as the two photon emission processes. To maintain the conservation of momentum, the transition of electrons must be satisfied at a vertical transition at the \( \Gamma \) point before and after the scattering between photons and phonons. At the \( \Gamma \) point, this condition is fulfilled by the summation of \( +q \) and \( -q \).

Figure 4 shows the dependence of Raman spectra on excitation wavelength for the bamboo-based carbon filament annealed at 1273 K. The raw bamboo is called “madake” in Japanese and collected in the Yawata district of Kyoto. The dispersion of the D-band with in-plane diffusion annealed at 1273 K. The raw bamboo decomposes with the release of gaseous hydrocarbons, which escape through these small pores during thermal annealing\(^{22}\). Two representative production methods have been known for the carbon filament: one is by the annealing of the bamboo, and the other by the annealing of the cellulose thread, which was squirted from cotton dissolved in zinc chloride solution\(^{22}\).

Figure 6(b) shows the evolution of a herringbone structure of the graphene layer in the transmission electron microscopy (TEM) image, and the space between graphene layers was found to be about 0.34 nm, which was larger than the value of 0.335 nm of a perfect graphite crystal for the (002) plane along the \( c \)-axis\(^{23}\). In order to more quantitatively evaluate the space, the analysis of the electron diffraction pattern was performed on the basis of Figure 6(c), and the calculated value for the (002) plane was derived to be in the range from 0.32 to 0.38 nm. The ordered structure was found to be present on the basis of the ring patterns from (002), (101), and (110) in the electron diffraction, as shown in Figure 6(c). This means a state of disordered arrangement of each graphene layer along the \( a \) - and \( b \) -axes of a graphite crystal and the state is called a turbostratic graphite in the polycrystalline state.

3.2 Hg-free HID lamps

Figure 7 shows emission spectra obtained when the laser is focused on the surface of the solid reagent-grade iodine encapsulated in a glass ampoule filled with argon gas at 101.3 kPa and the solid iodine deposited inside the Hg-free HID lamp filled with xenon gas at 60.8 kPa and metal halides. The erratic intensity distributions can be seen, and the peak at 212 cm\(^{-1}\) corresponds to the fundamental vibration and the following peaks being the overtone progression of the iodine molecule. The intensity distribution can be explained by considering the potential energy of the iodine molecule.

The potential energy curves in the iodine molecule are represented by \( X \left( ^3\Sigma_u^+ \right) \) as a ground state and the excited curve of \( B \left( ^3\Pi_u \right) \) with a potential minimum due to the molecule being bound in nature\(^{24}\). The excitation of an iodine molecule in the \( X \)-state reaches the discrete vibrational level of \( v' = 43 \) in the \( B \)-state when the excitation wavelength of 514.5 nm is employed\(^{25}\), and the discrete level corresponds to the intermediate state in the resonance Raman scattering process. This process has also been called resonance fluorescence\(^{26}(n)\). Iodine molecules dissociate when the excitation wavelength less than 496 nm is employed, in which the intermediate level locates in the continuum state, and the process has...
been called a continuum resonance Raman scattering process\textsuperscript{26(27)}. Apparently, owing to strong absorption, the laser beam heated up the solid iodine leading to the evaporation of gaseous molecular iodine. The erratic intensity distributions of the overtone progression with increasing vibrational quantum numbers are calculated by the transition dipole moment, $M$, and the Franck–Condon factors combining the vibrational level of $v' = 43$ in the B-state with the odd and even vibrational levels of the X-ground state\textsuperscript{26).}

The Raman scattering intensity is proportional to the square of the transition polarizability tensor, $\alpha$, the content of which has been written by the Kramers–Heisenberg equation\textsuperscript{28).} The equation is simplified by the Born–Oppenheimer approximation to indicate the vibronic wavefunctions at ground, excited, and final states as the product of the vibrational and electronic wavefunctions. In addition, the electronic transition moment, $M$, can be expanded into the Taylor series at the equilibrium position of the nuclear coordinate by the Albrecht treatment.

$$a_A = \frac{M_{0e}^g M_{0e}^{ie}}{\hbar \omega_i - \hbar \omega_0 - j \Gamma_e} \sum_{\nu_e} \nu_e \langle \nu_e | \nu_e | \nu_i \rangle$$

$M_{0e}^g$ and $M_{0e}^{ie}$ are the pure electronic transition moments between the ground and the excited states at the equilibrium position of the nuclear coordinate in the iodine molecule, and the excited and final states, respectively. $\omega_i$ and $\omega_0$ are the angular frequencies for the transition between the initial electronic ground state and the excited intermediate electronic state, and the excitation of laser, respectively. $\hbar$ is defined by $\hbar / 2\pi$, where $\hbar$ is the Planck constant. $\Gamma_e$ and $j$ are the damping constant at the excited intermediate level and the imaginary num-

Figure 7  Resonance fluorescence spectra for gaseous iodine excited at 514.5 nm originating from reagent grade iodine in Ar gas (a), and deposited inside Hg-free HID lamp in Xe gas atmosphere (b), and the normalized intensities for fundamental ($v' = 1$) and overtones ($v' = 2$ to 22) calculated on the basis of the individual Franck–Condon factors and transition dipole moments\textsuperscript{25) (c), respectively.}
The vibrational wavefunctions for the initial, excited, and final levels are represented by the bra and ket vectors proposed by Dirac as follows: \( |v_i\rangle, |v_e\rangle, |v_f\rangle \). The erratic intensities are calculated by the square of \( \alpha \) for each overtone. Since the denominator in Eq. (1) is constant to have a value of \( \Gamma_{ee}^2 \) at the resonance absorption from the initial vibrational state, \( i \), to the excited intermediate state of \( v_e=43 \), owing to the term \( \hbar \omega_{i}-\hbar \omega_{0} \) to be zero, the erratic overtone intensities are estimated by the product of \( \text{meg} \cdot \text{me}_\text{f} \langle v_f | v_e \rangle \langle v_e | v_i \rangle \). The square of \( \langle v_f | v_e \rangle \langle v_e | v_i \rangle \) corresponds to the Franck–Condon factor (FCF). The calculated values are exhibited in Figure 7(c) on the basis of the values of the FCF and the corresponding electronic transition moments. The intensity of overtone progression is determined by the Franck–Condon factors, and these physical values do not vary according to the experimental conditions. The difference in the Raman spectra between the two iodine molecules is considered to be due to the difference in the concentration of iodine molecules in the excited state. The higher concentration of iodine molecules is favorable for absorbing the irradiation light of the Ar ion laser, and this condition is applied to the case of iodine vaporized in the small space between the silica wall and the solid iodine pellet. Lastly, the excited potential curve for the iodine molecule is discussed. Although one bound excited state denoted as \( B^1(\Pi_{1u}) \) was taken into account in the discussion, the nonbound excited potential state \( B^1(\Pi_{1u}) \) has been reported, and both excited potential curves have been pointed out to crossover at the vibrational level of \( v=43 \). The probability for selecting the two excited states is considered to be influenced by the heat produced during the Raman spectroscopy according to the absorption of the light from the Ar ion laser. The potential energy curve is approximated by a harmonic oscillation for diatomic molecules under the conditions of a lower vibrational quantum number, \( v \). The anharmonicity increases apart from the equilibrium in-
ternuclear distance for the diatomic molecule at the higher vibrational quantum number \( v \), and the molecules finally dissociate. The theoretical relationship between the Morse function to describe the anharmonicity and the Birge–Sponer plot has been reported for the iodine molecule\(^{30}\) and is briefly shown here. The vibrational energy, \( E \), at the ground state is given by substituting the Morse function to express the anharmonicity into the Schroedinger equation:

\[
E(v) = G(v) + \frac{1}{2} \hbar \omega_e \chi_e v^2
\]

where \( G(v) \) is the vibrational term value represented by the vibrational quantum number, \( v \), at the ground state, \( \omega_e \) is the harmonic wavenumber in \( \text{cm}^{-1} \), \( \chi_e \) is the molecular nondimensional constant related to the anharmonicity, \( \hbar \) is the Planck constant, and \( c \) is the velocity of light. The zero point energy at \( v = 0 \) is shown as the value of 1/2. The difference between \( v \) and \( v + 1 \) is given as

\[
\Delta G(v) = G(v+1) - G(v) = \omega_e \chi_e v^2
\]

Figure 10 Raman spectra for the PEDOT layer electrochemically dedoped and measured through polyfluorene layer without (a) and with Al cathode (b). The spectrum (c) is the PEDOT/polyfluorene reference device. The excitation wavelength is 514.5 nm. The inserted figure explains the arrangement of the anode and cathode for driving the OLED to obtain the Raman spectra.

Figure 11 Molecular structure of PEDOT backbone with five monomer units and the monomer unit. \( \alpha \) and \( \beta \) carbon atoms are shown in the monomer unit.
molecular iodine produced from the two solid iodine specimens. The value of $\omega eXe$, has been reported to be 0.61 for the gaseous iodine at a pressure of 12 kPa, and the values greater than that of the gaseous state have been known for iodine dissolved in organic solvents. The harmonic wavenumber, $\omega e$, was derived to be 215 cm$^{-1}$ by adding the value of $\omega eXe$ to the y-axis intersection according to Eq. (4).

The Birge–Sponer plot was also applied to obtain the dissociation energy of the iodine molecules, as shown in Figure 8(b). The surrounded area for the value intersecting on the x-axis and the value intersecting on the y-axis and the line corresponds to the dissociation energy, $D_0$, for the iodine molecules. The surrounded area was approximated as a triangle and the dissociation energy, $D_0$, was estimated to be 15225 cm$^{-1}$ by the principal band at 1443 cm$^{-1}$, which was obtained by the multiplication of the value of 217.5 cm$^{-1}$ intersecting on the y-axis and the vibrational quantum number n of 140 intersecting on the x-axis, and divided by 2. The reference value of $D_0$ has been reported to be 12440.2 cm$^{-1}$, but the value of $D_0$ obtained from the Birge–Sponer plot has been pointed out to be overestimated since the linear extrapolation was employed, although the deviation can be recognized at a higher vibrational quantum number, $v''$.

Free iodine is evidence for the decomposition of the doped metal iodides inside the Hg-free HID lamp. For the HID lamp containing Hg, the high vapor pressure due to Hg is effective for capturing free iodine produced during the discharge in the HID lamp. The Hg-free HID lamp does not have any Hg to scavenge free iodine, and free iodine deposits inside the wall of the HID lamp envelope. After the deposition of free iodine, the ignition is influenced by the presence of free iodine because of its capability of capturing electrons.

3.3 Organic light-emitting diodes (OLEDs)

Figure 9 shows the Raman spectra of the PEDOT layer measured through a glass substrate of an encapsulated OLED device at 514.5 nm.

The measured area (a) shows a broad band at 1435 cm$^{-1}$ due to the electrochemically dedoped PEDOT layer, and the intense peak at 1605 cm$^{-1}$ is due to the polyfluorene as the emission layer. Area (a) is not biased with the driving voltage owing to the lack of a cathode electrode, and the dedoped state of the PEDOT layer is maintained without injection of holes from the anode. The measured area (b) indicates the disappearance of the broad band indicating the dedoped state since the carrier injections are available from the cathode and anode electrodes. The PEDOT is in the doped state with PSS molecules, and the two-valent positive charges have been pointed out to be produced in the PEDOT, the state of which is called a bipolaron. The polaronic state of the PEDOT is reduced to the neutral state doped by the injection of an electron during cathodic reduction. The Raman spectrum of area (b) denotes the disappearance of the dedoped state, and the reversible redoping was observed to proceed for the PEDOT once dedoped. The Raman spectrum in Figure 9(c) indicates the reference OLED device without electrochemical treatment of the PEDOT:PSS layer before fabrication of the OLED.

The top spectrum in Figure 10 shows the Raman spectrum after subtracting (b) from (a) in Figure 9.

The middle and bottom spectra correspond to the doped PEDOT:PSS and dedoped PEDOT:PSS, respectively. The differences between the doped and dedoped PEDOT:PSS layers are observed by the broadness of the principal band at 1443 cm$^{-1}$ and 1435 cm$^{-1}$, and the bands are due to the $C\alpha=C\beta$ ($\pi$) double bond for the symmetrical vibration in the 5-member thiophene ring, as shown in Figure 11.

The weak bands observed at more than 1500 cm$^{-1}$ are also influenced by the magnitude of the doping. The band at 1503 cm$^{-1}$ for the doped PEDOT shifts to 1519 cm$^{-1}$ after dedoping, and is ascribed to the asymmetric stretching vibration of the $C\alpha=C\beta$ double bond. The subtracted band is considered to indicate the presence of the dedoped state on the basis of the above assignments, and the partially dedoped state seems to be due to oxygen doping during the handling of the PEDOT:PSS specimen after the electrochemical cathodic reduction and the stray injection of carriers around the area.

4. Concluding remarks

Raman spectroscopy is a versatile method to obtain more information about the carbon filaments inside historical incandescent lamps from the viewpoint of the history of light sources. By Raman scattering spectroscopy, the discrimination between graphite and non-graphite structures is possible by examining the presence of the G'-band, which appears at around 2700 cm$^{-1}$, although the appearance of the G- and D-bands has been employed to characterize carbon materials. The bamboo-based carbon filament was found to possess the polycrystalline state, and turbostratic graphite structure on the basis of the evolution of the G'-band and the TEM and electron diffraction techniques. Free iodine has been reported to deteriorate the ignition characteristics of the HID lamp since the iodine molecule can capture an electron to be produced upon the ignition of discharge, and the presence of an isolated iodine deposit was confirmed inside the Hg-free HID lamp after discharge without breaking the HID lamp envelope by Raman scattering spectroscopy. Raman scattering spectroscopy is expected to be applied to the examination of dose materials and reaction products in the HID lamp.
which have high vapor pressure and are apt to react with air. The doping state of the PEDOT:PSS has been evaluated by Raman scattering spectroscopy for the hole injection layer in the OLED device.

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