On the feasibility of the Radiochromic film dosimetry using Raman-spectroscopy based on the change of carbon triple bonds concentration

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1. Introduction

High-atomic-number(Z) contrast agents such as gold nanoparticles(AuNPs) are proven to enhance radiation effects in kilovoltage x-ray radiation therapy beams[1]. Photoelectric interaction has the most cross section in terms of kilovoltage x-rays. Therefore, high-Z gold nanoparticles provide localized does enhancement with very short range within tumors.

Supposing that aqueous solution of gold nanoparticles irradiated by kilovoltage x-ray produce dose enhancement by gold, dose enhancement comes from mainly photoelectrons, setting aside the auger electrons and characteristic x-rays. Enhanced energy by photoelectrons depends on the probability of photoelectrons and the number density of materials.

Based on the database of National Institute of Standards and Technology, the cross section of photoelectrons per each energy and material can be acquired. For example, the gold cross section by photo electric effect of 30 kV photon is almost 3000 times higher than water and the totally enhanced energy will be estimated approximately as much as 3% when the gold molar concentration is about 0.55 milimole which means the number density ratio is about 10^{-5}. The slowing down range of low energy electrons would be at most several decades micro meters.

Although Monte Carlo simulation provides the calculated deposit energy of the region of interest, the measurement of such low energy electrons is a matter of concern if it is possible.

The dose distribution in subcellular size could be required to track out where the low electrons deposit their energies. Since recent Raman spectrometers provide the focal volume of micro meter scales, this feature will be applicable to an appropriate measurement at the micro meters scale. Note that the spatial dose distribution analysis is available through two dimensional scans.
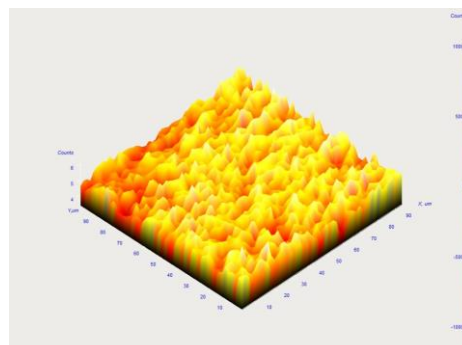

Fig. 1. Raman data scan is available for spatial analysis. This map shows the $1437 cm^{-1}$ peak intensity for EBT3 unlaminated radiochromic film scanned for one hundred micrometers by one hundred micrometers with spatial resolution of one micrometer. Data acquisition by courtesy of Lambda Ray Co., Ltd. Nanofinder FLEX G model was used for this measurement.

Raman spectroscopy usually provides fingerprints of chemical component species and molecular motion. In order to apply to a dosimetry, the raman peak intensity should be quantified as dose changes. Since Raman peak intensity is proportional to the electric field intensity of incidence beam and the concentration of compounds, the radiation dose would have the linearity in terms of the concentration of radio-active compounds, which would reflect the Raman peak intensity.

As belows, the radio-active compound of Lithium pentacoasa-10,12-dyionoic acid(LiPCDA) has the polymerization feature in that the concentration of carbon triple bonds will decrease as the cross-linking process goes on.
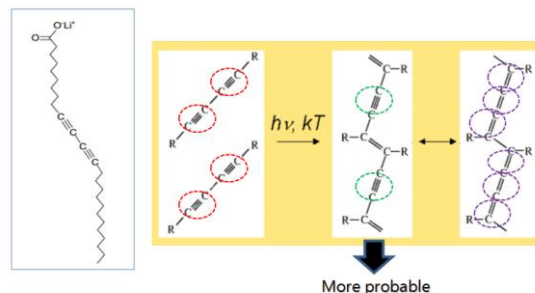
Fig 2. When photon gives the energy above activation energy for polymerization, the number of carbon triple bonds changes with more probabilities. The polymerization schematic is by courtesy of D.F. Lewis, Ph.D ,Ashland Co. Analysis based on optical density is common and popular for radiochromic films.

Carbon triple bonds are known for strong Raman active and the required energy for changing the triple bonds into double bonds or single bond is comparatively low. It features as a sensitive dosimetry since dosimetry ultimately concerns the radiation ionization.

Raman spectroscopy has been tested as a common dose analysis based on the chemical polymerization even though it has not yet distinguished small dose difference due to ambiguous uncertainties[2]. However, Raman has the best sensitivity when compared with other spectrometers, there seems to be still chances that Raman spectroscopy would be used for a reliable micro dosimeter in a relative manner.

As a fundamental study for the reliable future micro-dosimetry measurement, this research aims for elucidating inherent uncertainties of Raman spectroscopy. Once we are aware of the issues for Raman dose analysis, it would be possible to find out the reliable methodology using Raman spectroscopy for the actual measurement with respect to the micro-dosimetry in the future.

2. Methods and Results

2.1. Raman Spectrometer

Four separate raman facilities were used for this experiment. Seoul National University National Center for inter-University Research Facilities, Lamda Ray Co.,Ltd, Uninanotech Co.,Ltd, and Seoul National University Graduate school of Convergence Science and Technology(GSCST) provided the courtesy for Raman Spectrometers. Mainly, the Raman Spectrometer from DongWoo Optron Co.,Ltd. belongs to GSCST and the spectroscopy analysis software of Andor Solis were in use for this study.

2.2. Unlaminated Radiochromic film with LiPCDA

With the purpose of Raman analysis, special orders as Gafchromic unlaminated EBT3 films were performed through Ph.D. Lewis of Ashland Co.. Raman scattering portion is almost 1% among the whole scattered light which is extremely weak to detect. Therefore, protect layers of radiochromic films had better to be removed for more sensitive measurement. Active layer has the depth as much as 30 micrometers. In order to the maximum intensity, adjusting the laser focal point onto this active layer is very crucial for every measurement.

2.3. Radiation Source with MV potential

Photon irradiation of 6MV energy provided by therapeutic linear accelerator belongs to radiation oncology department in Seoul National University Hospital. In order to see the dose linearity with Raman peak intensity, each of 100MU,200MU,300MU, and 400MU was delivered respectively. MU stands for monitor unit. 1MU corresponds to the dose in the reference condition of radiation therapy linear accelerator. We must calibrate using ion chambers in order to get the absolute dose.

2.4. Laser power effect

The laser power of most frequently used setup was 18mW. The activation energy of the polymerization is known as about 50kJ/mol and ultra violet light of the wavelength of 266nm is recommended to keep from the films[3].

Although laser beam has the wavelength of visible light below UV light, it has such a high intensity by amplification that focused photons with same phase would definitely affect the polymerization of radio-active components.

Fig 3. shows the drastic change of Raman peak intensity influenced by the laser exposure. Judging from the peak trends by time, it seemed to be obvious that the laser affects the polymerization process. On the other hand this trend by laser effect seems to provide an expecting dose map based on the carbon triple bonds for more radiation exposure.

Decreasing the incidence intensity of laser by additional filters would be required and more sensitive CCD cameras should be developed for better detection in the future. However, Raman scattered signal is relatively very weak and it would be very crucial to compromise the minimally required incidence laser intensity and the Raman cross section in order to get the data free from the laser effect. Moreover, appropriate laser exposure would be essential to acquire proper spectral changes for micro-dosimetry.

2.5. Carbon Triple Bonds Concentration

There exists different wave shift values of carbon triple bonds depending on where the bond is attached. Triple bonds of cross-linked polymers would have higher wave shift than monomers since cross-linking results in more heavier components combined, which causes more atomic binding energy.

Fig. 3. shows the Raman peak change by time affected by laser. The first peak intensity of 2070 cm^{-1} and the second peak intensity of 2110 cm^{-1} changes rapidly.
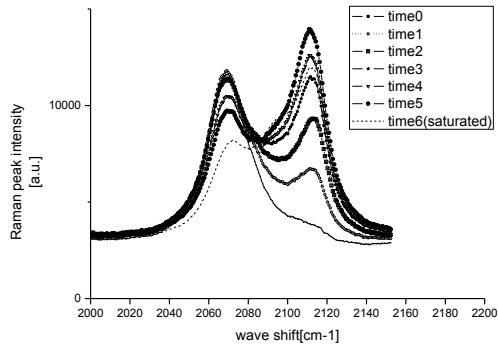
Fig. 3. 50MU delivered film analyzed as time changes. Raman peak intensity drastically changes as seconds go on by laser output power. This data was acquired within five minutes. The concentration of triple bond for cross-linked polymers increases. Time0=5 seconds exposure, time1=15 seconds exposure, time2=30 seconds exposure, time3=40 secodns exposure, time4=50 seconds exposure, time5=1minute exposure, time6=3minutes exposure(peak intensity was almost saturated)

Removing the baseline affected by fluorescence and additional multipeak fitting process (Fig.4.) gives the distinct intensity difference. Revision process provides the data belows such as table 1 and Fig.5. The generation of carbon triple bonds belong to polymers was more rapid than the vanishment of bonds belong to monomers.
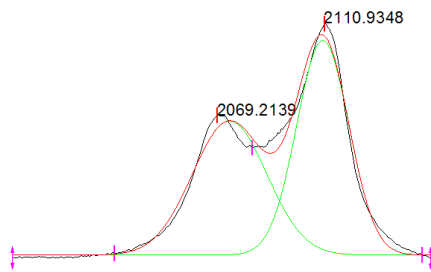

Fig.4. baseline removal and multi peak fitting process is required to get the distinct Raman peak intensity

Table I: Raman peak values for carbon triple bonds concentration affected by laser exposure on time

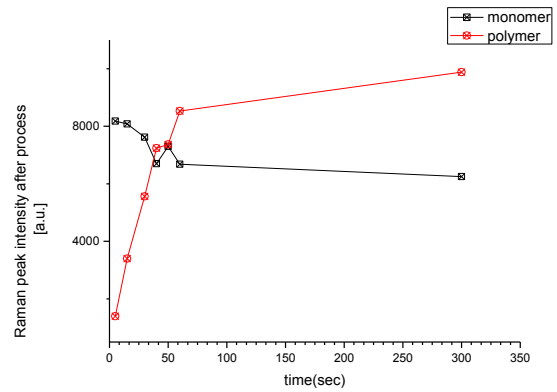| Exposing Time	Momomer peak(a.u.) for 2070cm^{-1}	Polymer Peak(a.u.) for 2110 cm^{-1}
Time 0	8180	1400
Time 1	8080	3400
Time 2	7620	5560
Time 3	6700	7240
Time 4	7300	7370
Time 5	6680	8530
Tiem 6	6250	9880

Fig. 5. The decreasing trend of monomers and increasing trend of polymers by laser exposure time. Exposure by laser undergoes faster generation of polymers than vanishment of monomers

2.6. Dose Linearity with a decreasing trend for monomer

In order to see the linearity with the dose being free from laser effect as much as possible, the very early spectroscopy acquisition should be performed. Therefore, the digital stage moved on to next irradiation spots in order that the laser focuses an undamaged point right after the z-axis is determined by adjustment so as to get the maximum Raman intensity. Inherent errors by laser power would be expected in this process and repetitive measurements were required to minimize the errors.

Fig.6. result doesn't show directly the trend by the increase of the carbon triple bonds generated by cross-linking process. The main reason is such that delivered MU would not be enough to show the increased concentration of the polymerized component. In other words, the wave shift between monomers and polymers is not so large that the existing peak intensity of monomers hides the early generation of polymers. Actually, monomer peaks close to polymer peaks grow rapidly during the early laser irradiation, which is affected by the polymer peak's early growing, not by the monomer peak's own growing.
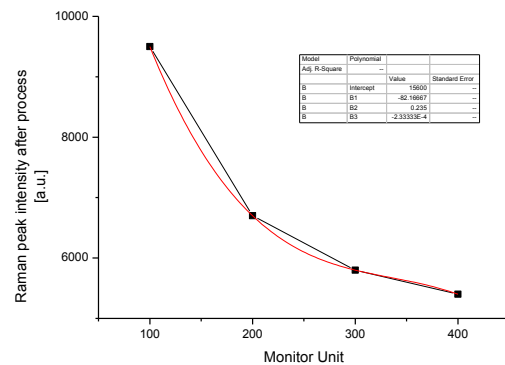

Fig.6. This shows the dose linearity for Raman signal. As the monomer concentration decreases during with more irradiation, the Raman intensity of momomers shows the decreasing trend.

2.7. Carbon double bonds trend for polymer

We found out that the Raman peak around 1500 cm^{-1} also increased drastically as laser exposure goes on. Polymerization is also expected to generate the carbon double bonds belong to polymers and this feature can be used as the dosimeter.

3. Conclusions

Polymerization process of radiochromic films were used to apply to the dosimetry based on the concentration change of carbon triple bonds or double bonds. Laser was a major influence generating the polymerization concentration for Raman analysis. The rapid trend by laser effect seems to provide an expecting dose map based on the carbon triple bonds for more radiation exposure. In order to get a robust and reliable micro-dosimetry with spatial analysis based on Raman spectroscopy, trade-off between the laser intensity not to generate too much polymerization and enough sensitivity of Raman cross-section would be necessary.

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