Plasmon Induced Decomposition Kinetics of Brominated Nucleobases on Silver Nanoparticle Surface

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The class of halogenated nucleobases that are potential radio sensitizer in cancer therapy are also highly sensitive to low energy electrons.[1-2] Therefore, brominated nucleobases which can be incorporated into DNA sequences can easily induce damage to DNA below the ionization threshold by undergoing strong interaction with low energy electrons via dissociative electron attachment resulting in cleavage of carbon bromide bond. [2] Additionally, it has been reported that the hot electrons that are generated during the decay of plasmons can also induce the decomposition reaction of the brominated nucleobases incorporated in an arbitrary DNA sequence.[3] Surface enhanced Raman scattering (SERS) technique in that regard, has been a well-established method to study plasmon mediated reactions of molecules on nanoparticle surfaces which allows one to simultaneously trigger and track the reaction in a confocal Raman microscope setup by using particular laser wavelength and monitoring the change in vibrational fingerprint of the molecules involved respectively.[4] Further, study of halogenated nucleobases with noble metal nanoparticles is of special interest as both are effective as radio sensitizers in cancer therapy.[2]

Therefore, we present a study on hot electron induced decomposition of four brominated nucleobases viz., 8-Bromoadenine, 8-bromoadenine (8-BrA), 8-bromoguanine, 5-bromocytosine and 5-bromouracil on silver nanoparticles (Ag NPs) surfaces as substrate. The decomposition reaction is monitored by following the cleavage of carbon bromide bond in SERS spectrum which proceeds via dissociative hot electron transfer from the AgNPs to the brominated analogues of nucleobases.[3] A quantitative analysis of the decomposition behavior of all the brominated analogues has been attempted based on the reaction rate and hence reaction constant obtained from the SERS measurements of bromonucleobases. Further, the role of laser wavelength (488 nm, 532 nm, 633nm and 785 nm) and laser power on the dissociative kinetics have been examined to supplement the kinetic data. Interestingly, all four brominated nucleobases underwent decomposition under different laser illumination time, wavelength and power; however defined reaction kinetic data could be extracted successfully in case of 8-bromoadenine and 8-bromoguanine only. The decomposition reaction of 8-BrA and 8-BrG followed a power law kinetics which on the other hand exhibited a linearly dependency on the laser wavelength and laser power employed.

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