



INDIAN INSTITUTE OF TECHNOLOGY GUWAHATI  
SHORT ABSTRACT OF THESIS

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Thesis Title: "Raman Spectroscopic Probe of Chemical Reactions at the Surfaces of Gold Nanostructures"

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SHORT ABSTRACT

This PhD thesis illustrates the potential applications of Au nanostructures in plasmon induced photochemical reactions, in catalyzing the synthesis of amorphous bridged polynuclear peroxo-complex and to detect H<sub>2</sub>O, D<sub>2</sub>O and HOD simultaneously. Chapter 1 gives a general overview of the metal nanostructures and their implications in chemical reactions. Chapter 2 displays the formation of end-to-end assembled Au nanorods exploiting selective binding nature of 4-aminothiophenol (4-ATP) at the longitudinal end of Au nanorods. Illumination of laser converted 4-ATP molecules situated at the hot-spots of Au nanorods into dimercaptoazobenzene (DMAB). The kinetic rate of this plasmon driven photochemical reaction at the hot spot was faster than that at the longitudinal end surface of non-assembled Au nanorods. Chapter 3 shows that the presence of transition metal cations can significantly increase the yield of DMAB. During the oxidation of 4-ATP into DMAB, the oxidation states of metal cations plausibly were changed, leading to the formation of metal oxides, which augmented the surface enhanced Raman scattering (SERS) signal. Chapter 4 describes the synthesis of amorphous bridged polynuclear peroxo complex, when 2-picolyamine (2-PA) molecules react with Co(II) in aqueous alkaline medium. 2-PA molecules were adsorbed on Au nanospheres following Langmuir adsorption isotherm and following formation of the complex surface enhanced resonance Raman scattering (SERRS) conditions were met. That helped in deciphering the structure and bonding of the complex product. The product formation also catalyzed by the Au nanospheres. Chapter 5 illustrates the application of the complex polynuclear species in detecting H<sub>2</sub>O, D<sub>2</sub>O and HOD simultaneously in their mixture using peroxo vibrations. H<sub>2</sub>O, D<sub>2</sub>O and HOD formed different nature of hydrogen bonded structures with peroxide of the complex. The combined effect of adding extra mass to the peroxo "oscillator" and the coupling between the O-O and adjoining O••D/O••H hydrogen bonds resulted in significant vibrational frequency shift of the peroxide bond. The nature of hydrogen bonding with three different species (based on H or D being bonded to the peroxide) provided an estimation of the content of H<sub>2</sub>O or D<sub>2</sub>O in the mixture. Chapter 6 includes summary and future prospects of the thesis.