Optical Spectroscopy, Modification and Imaging of Nano-Objects

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Optical spectroscopy is powerful tool in investigations of properties of nanosystems. In addition to probing of energy level structure and dynamics, photons can also be used to modify their properties via various processes.

In this presentation, I will discuss results from our two recent projects:

A. Patterning and tuning of electrical and optical properties of graphene by laser induced two-photon oxidation.

Graphene has high potential for many advanced applications but many of them require band gap engineering. One of the primary goals in current graphene research is to find ways for modifying the band gap and other properties of graphene. We have found a novel method for modifying properties of graphene via two-photon induced oxidation. By using tightly focused laser beam, arbitrary features can be patterned with a line width of ~300 nm and with varying level of oxidation. Electrical measurements were performed to show that oxidation leads to opening of a band gap. The key technique for development of the patterning method was four-wave-mixing (FWM) imaging, which gives from graphene strong signal which is sensitive to the level of oxidation. I will discuss very recent AFM studies on morphology of oxidized graphene and development of fast characterization of graphene with wide-field FWM microscopy.

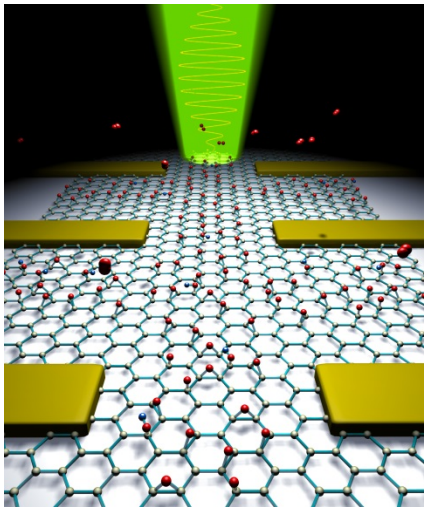

Figure 1. Cartoon of patterning of graphene by laser induced photo-oxidation.

Reference:

A1. Aumanen et al. Patterning and tuning of electrical and optical properties of graphene by laser induced two-photon oxidation. *Nanoscale*, **7**, 2851 (2015).

B. Observation of Molecular to Metallic Transition in Ligand-Protected Gold Nanoclusters by Using Ultrafast Mid-IR Transient Absorption Spectroscopy

An important fundamental question in chemistry and nanoscience concerns the behavior of systems when their size increases from atomic limit toward bulk matter. Considering metal nanoparticles a key property is the existence of a band gap or HOMO-LUMO gap. Upon closing the gap, properties change toward metallic from molecular-like. We have studied this general question via ultrafast photodynamical studies of well-defined ligand-protected gold nanoclusters having 102 – 144 gold atoms. Relaxation dynamics is very sensitive to the existence of an energy gap and thus dramatic difference in dynamics is expected to occur when the gap closes. The present study shows strikingly that the transition from molecular to metallic behavior occurs between ~130 and 144 gold atom clusters. By combining experimental and theoretical work, we are able to present a complete picture of relaxation dynamics for the studied clusters, showing several timescales for relaxation from subpicosecond to longer than nanosecond. Surprisingly, our study reveals an important role of the triplet state in the molecular clusters.

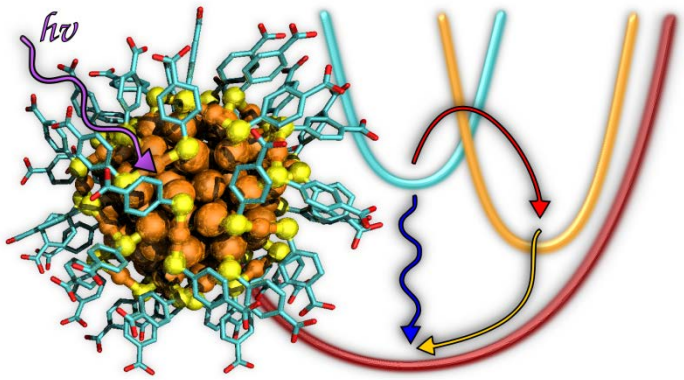

Figure 2. $Au_{102}(p\text{MBA})_{44}$ (*p*MBA = *para*-mercaptobenzoic acid) cluster and a schematic presentation of the lowest potential energy surfaces.

References:

B1. Mustalahti et al. Ultrafast Electronic Relaxation and Vibrational Cooling Dynamics of $Au_{144}(SC_2H_4Ph)_{60}$ Nanocluster Probed by Transient Mid-IR Spectroscopy. *J. Phys. Chem. C*, **118**, 18233 (2014).

B2. Mustalahti et al. Molecule-like photodynamics of $Au_{102}(pMBA)_{44}$ nanocluster. *ACS Nano*, **9**, 2328 (2015).