Photothermal studies of single molecules and gold nanoparticles : vapor nanobubbles and conjugated polymers

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Summary

Photothermal microscopy is a highly sensitive method based on the absorption of a sample. It can be exploited to detect the energy and heat dissipation of small absorbers after optical excitation. In this thesis, we use photothermal microscopy and time-resolved pump-probe spectroscopy to study the dynamics of vapor nanobubbles around a continuously laser-heated single gold nanoparticle and the optical properties of single conjugated polymers poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV). The main observations and conclusions in this thesis are summarized as follows.

In order to gain some knowledge of vapor nanobubbles around an optically heated gold nanoparticle, we start our discussions in chapter 2 on the thermal properties of a vapor nanobubble under steady state. Based on the data from the National Institute of Standards and Technology (NIST), we calculate the minimal boiling temperature and pressure as a function of bubble size, and the temperature profile along the radial direction. Results obtained from such calculations show that boiling temperature and pressure of a vapor nanobubble shift to a much higher value compared with ambient conditions due to the large Laplace pressure at the nano scale. The temperature of the gold nanoparticle also shoots up once a vapor nanobubble forms around the particle. This is because of the small thermal conductivity of the vapor shell, which thermally isolates the particle from the contacting liquid. Because of the optical method used in our experiments, we also calculate the optical powers that are required to form a vapor nanobubble around a gold nanoparticle, and the changes in the photothermal signal due to the formation of a vapor nanobubble.

In chapter 3, we use photothermal microscopy to investigate the dynamics of vapor nanobubbles around a continuously laser-heated gold nanosphere, with time resolution from millisecond to nanosecond. We observed a number of interesting phenomena such as explosive formation of vapor nanobubbles, instability of vapor bubbles under constant heating and echo-triggered explosions. We speculate on the mechanism of bubble instability under constant heating, and conclude that the hot liquid layer around the particle at high heating power plays an important role. Thermal energy is stored in the hot liquid layer and superheating of the liquid above the saturation temperature is involved. We also observed that vapor nanobubbles are very sensitive to weak perturbations such as acoustic waves. Vapor nanobubbles can release acoustic

waves when they form. The released acoustic wave can be reflected by nearby interfaces and trigger new explosions. Under current experimental conditions, we showed that by engineering the intensity profile of the heating beam, it is possible to keep a persistent vapor bubble for about 1 μs.

The study of vapor bubbles shown in chapter 3 indicates that the dynamics of the vapor nanobubble is fast, typically on the timescale of nanoseconds. The rise time of vapor nanobubbles during expansion is close to the response time of our photodetector. In order to better resolve the dynamics of vapor bubbles during the initial stage, we use time-resolved pump-probe spectroscopy, in combination with continuous laser heating, to investigate the behavior of vapor bubbles with picosecond time resolution in chapter 4. Continuous-wave laser heating establishes a temperature of the particle close to the boiling threshold of liquid water, while the short pulses trigger bubble explosions. In our experiments, we observed that the optical contrast of acoustic vibrations of a single gold nanosphere is enhanced when the vapor bubble forms around the particle, and the damping of the acoustic vibration decreases, leading to longer decay times. These observations can be seen as an experimental proof that vapor bubbles can enhance the acousto-optical transduction. Our preliminary results show for the first time the detection of vapor bubbles with picosecond time resolution and on the single particle level.

The photothermal signal is related to the thermal properties of the transducing medium around the absorbers. In chapter 5, we use near-critical xenon to enhance the photothermal contrast of 20 nm gold particles. Close to the critical point, supercritical xenon exhibits large compressibility and large refractive index changes in response to small changes in temperature and pressure, and thus is expected to enhance the photothermal signal. Based on the standard data from NIST, we estimate the refractive index change of xenon over temperature and the enhancement factor in xenon under different temperatures and pressures near the critical point. We introduce a home-built pressure cell for the photothermal measurements in near-critical xenon. We experimentally characterize the enhancement factor of the photothermal signal of 20 nm gold particles in xenon at different temperatures and pressures, and compare the results with glycerol that was commonly used in our experiments. We found an enhancement of the photothermal signal up to thousand times in near-critical xenon when the temperature and pressure are optimized. We also examine the dependence of the photothermal signal on the modulation frequency in supercritical xenon, and we find a continuous increase of the photothermal signal at lower frequencies. We attribute this observation to the critical slowing down effect in the near-critical fluid.

The enhanced photothermal signal in near-critical fluid means that much

less heating (excitation) powers are required for the detection of weak absorbers. In chapter 6, we demonstrate the photothermal detection of single conjugated polymer molecules in near-critical xenon. We measure the absorption and emission of single conjugated polymer molecules simultaneously in near-critical xenon, and we get useful information such as the number of monomers in a single conjugated molecule and its apparent quantum yield. The thousand monomers in single conjugated molecules found in our measurements agree with what is expected from sample preparation. Low quantum yield and wide distribution of the absorption cross section are observed as well, which could originate from conformational heterogeneity. Further experiments will be carried out in the near future to investigate how photo-physical properties of single conjugated polymers change with matrix, molecular weight and preparation conditions.