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Time-correlated single photon counting system and light-collection system for studying fluorescence emitters under high-vacuum conditions: Use of immersion objective and ionic liquid

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ABSTRACT

In this paper, we introduce a time-correlated single photon counting system and an efficient light-collection system for studying fluorescence emitters under high-vacuum conditions; the latter system has an immersion objective, and an ionic liquid is used as a refractive index matching medium. The ionic liquid is positioned in high vacuum. The time-correlated single photon counting system has modified photomultiplier tubes that act as photon detectors. The light-collection system is designed to be simple, compact, and easy to use. In order to verify the performance of these systems, the optical properties of colloidal semiconductor nanocrystals (CdSe/ZnS) and fluorescent dye molecules are studied as examples.

1. Introduction

The combination of a time-correlated single photon counting (TCSPC) system and a pulsed laser with a high pulse repetition frequency has been used for performing measurements of luminescent decay curves, time-resolved fluorescence anisotropy, transient fluorescence phenomena, and fluorescent resonant energy transfer [1]. Single-molecule spectroscopy along with TCSPC and laser systems has been widely used for the characterization of individual organic fluorescent molecules [2], individual colloidal semiconductor nanocrystals [3], and individual biomolecules labeled with fluorescent moieties [4]. The studies conducted on such single photon emitters include measurements of fluorescence decay curves, emission spectra, fluorescence correlation spectroscopy, fluorescence intensity time traces for investigating photobleaching and blinking phenomena and the characterization of single-photon sources (photon antibunching) by using the Hanbury-Brown and Twiss setup [5–7]. A confocal optical system and a TCSPC system with avalanche photodiodes (APDs) of high quantum efficiency are commonly used in single-molecule spectroscopy [5–9]. A general objective with a high numerical aperture (NA) (~0.95), preferably, an oil immersion objective with a very high NA (1.3–1.4) is used in single molecule spectroscopy.

Generally, an oil immersion objective with a high NA cannot be used for optical spectroscopy under high-vacuum conditions. This is because the immersion oil used as the refractive index matching medium contains volatile molecules. An objective having a long working distance and placed in ambient air is commonly used for the photoexcitation and collection of photons through the optical window that separates the high-vacuum atmosphere from the ambient air. Generally, the NA of an objective having a long working distance is not so high. An objective with a high NA (~0.95) that can be used under high-vacuum conditions is sometimes used for photoexcitation and the collection of photons [10].

Recently, ionic liquids [11,12], which are ambient temperature molten salts, have been extensively studied because of their unique material properties such as a wide liquid range, a high electrical conductivity, extremely low vapor pressure, low combustibility, and excellent thermal stability. In this paper, we focus on the extremely low vapor pressure of ionic liquids and try to use them as the refractive index matching medium for an immersion objective under high-vacuum conditions; their use in a light-collection system under high-vacuum conditions enhances the efficiency of the system. Background fluorescence and volatility in high vacuum were examined for various ionic liquids. We observed that some of them were suitable for our purpose.

Our time-correlated single photon counting system has modified photomultiplier tubes (PMTs) as photon detectors, which has a high quantum efficiency, relatively large active area and extremely small dark counts. The characteristics of the modified PMTs facilitate the adjustment of the optical parameters and the achievement of high light-collection efficiency.

In this paper, for studying fluorescence emitters under high-vacuum conditions, we introduce a time-correlated single photon counting system and an efficient light-collection system comprising an immersion objective and an ionic liquid that acts as a refractive index matching medium; the ionic liquid is positioned in high vacuum. To verify the performance of these systems, we have measured fluorescence decay curves, fluorescence intensity time

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traces, and photon antibunching of individual colloidal semiconductor nanocrystals (CdSe/ZnS) as well as fluorescence decay curves of fluorescence dye molecules. Such measurement systems are useful for the characterization of fluorescence emitters under high-vacuum conditions. Their applications could be extended to various optical measurements under high-vacuum conditions.

2. Experimental setup

Colloidal CdSe/ZnS core/shell nanocrystals (Qdot ITK Organic Quantum Dots solution; Q21721MP) purchased from Invitrogen were used in our experiments. The peak photoluminescence wavelength of the quantum dots (QDs) was around 655 nm. The QD solution was diluted with toluene to a concentration of 1×10^{-9} mol/L. A separate solution was prepared by dissolving poly(methylmethacrylate) (PMMA) (4 g/L) in toluene. The diluted QD solution and the PMMA solution were mixed in the ratio of 1:10, and a QD/PMMA/toluene solution containing QDs with a concentration of 1×10^{-10} mol/L was obtained. The QD/PMMA/toluene solution was spin cast onto a pre-cleaned, synthesized quartz cover slip substrate at 2000 rpm. This sample substrate was used in our experiments. We also prepared chlorobenzene solution containing Coumarin 6 (C6) with a concentration of 2.5×10^{-9} mol/L and PMMA with a concentration of 2 wt.%. The C6/PMMA/chlorobenzene solution was spin cast onto a pre-cleaned, synthesized quartz cover slip substrate at 2000 rpm. This sample substrate was also used in our experiments.

The optics and electronic components of our laser system that was used in the TCSPC experiments are illustrated in Fig. 1. We used a mode-locked Ti:sapphire laser (Tsunami, Spectra-Physics) adjusted to a wavelength of 892 nm, a frequency doubler, and a pulse selector (Model 3980, Spectra-Physics) for the laser system. Laser pulses with a wavelength of 446 nm, pulse width of 2 ps, and repetition frequency of 8 MHz were used for our measurements. The laser beam was slightly expanded by a couple of lenses, and it was then introduced into an efficient light-collection system under high-vacuum conditions after being passed through an infrared cut filter to block the residual Ti:sapphire laser beam; subsequently, the beam was passed through neutral density filters, a quarter waveplate, and a dichroic mirror. The laser beam spot on the sample substrate located in the light-collection system was observed using a charge-coupled device (CCD) monitor in the reflected direction; the CCD monitor is not shown in Fig. 1.

We shall now briefly describe the light-collection system under high-vacuum conditions, as shown in Fig. 2. For this purpose, we chose a new optical geometry in order to place an immersion objective with high NA and an ionic liquid (that acts as a refractive index matching medium) in high vacuum. A 100× Plan Fluor immersion objective (NA 1.3) manufactured at Nikon was used. N,N-diethyl-N-(2-methoxyethyl) ammonium bis(trifluoromethanesulfonyl)imide (Kanto Chemical Co., Inc.) was used without further purification as the ionic liquid. We tested various ionic liquids and chose this ionic liquid; the reason for this will be described in the Results and discussion section. As shown in Fig. 2, the light-collection system is designed to be simple, compact, and easy to use. The immersion objective can be moved by moving the *Z*-translation stage that is positioned outside the vacuum, and the sample substrate in high vacuum can also be moved with the aid of *XY*-translation stages that are outside the vacuum; all the translation stages are moved by employing the elasticity of the vacuum bellows. The high vacuum was maintained by a turbomolecular pump (Turbo-V70, Varian). The typical background pressure without the ionic liquid was approximately 8×10^{-6} Torr.

In the light-collection system, the laser beam was focused on the sample substrate by using the immersion objective in a modified inverted microscope system. The laser beam diameter on the sample substrate was approximately 1 μm; the fluorescence was collected by the same immersion objective, passed through the dichroic mirror, and was filtered using a color filter, passed through a couple of lenses and a pinhole, split by using a 50–50% non-polarizing beam splitter, and focused on two modified photomultiplier tubes (PMTs). Thus, we positioned the Hanbury-Brown and Twiss-type setup at the end of the apparatus for conducting the photon antibunching experiments.

Below, we briefly explain the modified PMT detector. The modified PMT detector (H7422P-40MOD) was specially fabricated at Hamamatsu, and it has an active area of 0.7 mmϕ (GaAsP photocathode), the typical dark counts (1–2 counts/s), and a high signal-to-noise ratio; furthermore, it has high sensitivity in the wavelength range 300–720 nm and a high quantum efficiency of 40% at 600 nm. The relatively large active area of the detector facilitates the easy adjustment of the optics and the achievement of high light-collection efficiency. In most of the studies on single-molecule spectroscopy, APDs have been used because of their high quantum efficiency; however, in our study, we select H7422P-40MOD by considering the advantages of an extremely low dark count, a relatively large active area, and a quantum efficiency that is high but a little lower than that of the SPAD modules.

A time-correlated single-photon counting (TCSPC) computer board (SPC-630, Becker & Hickl) was used to record the following parameters of individual photons: (i) the time delay between the start pulse and the stop pulse with a picosecond time resolution and (ii) the absolute arrival time after the beginning of the acquisition with a resolution of 50 ns. Typically, in the fluorescence decay curve measurements, the signal from the PMT was used as the start pulse, while the signal from the PIN photodiode that was synchronized with the laser pulse by introducing an appropriate delay was used as the stop pulse. In the typical photon antibunching measurements, the signal from a PMT was used as the start pulse, while the signal from another PMT was used as the stop pulse with an appropriate delay

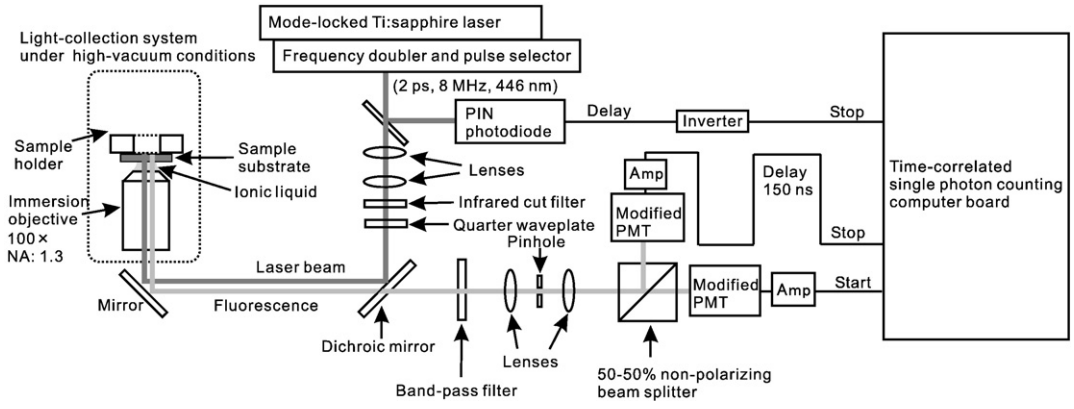

Fig. 1. Experimental setup; our laser system, its optics and electronic components used for the TCSPC experiments.