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Optical properties of nucleobase thin films as studied by attenuated total reflection and surface-enhanced Raman spectroscopy

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ABSTRACT

Optical properties of nucleobase thin films were studied by attenuated total reflection (ATR) and surface-enhanced Raman spectroscopy (SERS). Adenine and guanine films were deposited on fused silica and silver at room temperature by thermal evaporation, and the normal dispersion of refractive indices of transparent adenine and guanine films in the visible and near-infrared regions were analyzed. The measured ATR spectra of adenine (guanine) films and numerical simulations by optical transfer matrix formalism demonstrate that the shift of surface plasmon resonance (SPR) wavelength is approximately linearly proportional to the adenine (guanine) film thickness, indicating that SPR can be used for quantitative measurements of biomaterials. The Raman spectra indicated that the adenine (guanine) films can be deposited by thermal evaporation. The adenine (guanine) films on silver exhibited Raman intensity enhancement as compared to those on glass, which was attributed to the SPR effect of silver platform and might play a role as a hot plate for SERS detection of biomaterials.

1. Introduction

Recently there has been much interest in the biological, structural, and optical properties of biological materials [1]. Among various biomaterials, deoxyribonucleic acid (DNA) has received considerable attention in multidisciplinary research groups [2]. Steckl investigated the applications of DNA in organic light emitting devices and optical waveguides [3]. Gomez et al. studied the applications of nucleobases in light emitting diodes [4]. Irimia-Vladu et al. used DNA as exotic materials for bio–organic electronics [5]. Singh et al. described field-effect transistors based on DNA [6]. Samoc et al. studied the linear and nonlinear optical properties of DNA [7,8]. Cosnier and Mailley studied DNA biosensors based on hybridization of single-stranded oligonucleotides [9]. Ionizing irradiation, plasma treatment, ultraviolet (UV) light, and heat treatment can induce structural and biochemical alterations in DNA [10], which can affect the use of DNA in various devices. To study influence of environmental stresses on DNA, it is necessary to measure the optical, structural, and biological properties of DNA and/or nucleic components. DNA consists of the nucleobases and the deoxyribose–phosphate backbones. Four nucleobases are adenine, thymine, guanine, and cytosine. The optical properties of nucleobases, backbones and DNA are required for understanding the response of DNA to environmental stresses. Since the molecular skeletons of nucleobases can be similar to those of natural DNA, it is worthy to investigate the optical properties of nucleobase thin films and to predict the response of specific nucleobase to environmental stresses. In this research, we studied the optical properties of adenine and guanine thin films by the surface plasmon resonance (SPR) and surface-enhanced Raman spectroscopy (SERS).

Surface plasmon is a collective oscillation of surface electrons around metal ions when the electric permittivity of a metal is negative below the plasma frequency. If the electromagnetic wave is coupled to collective oscillation of electrons at a metal–dielectric interface, surface plasmon wave (SPW) is generated and propagates along the metal surface, and the electric field in the normal direction of interface is nonradiative and localized strongly at the metal–dielectric interface. SPWs have attracted great interest in the scientific community for decades due to the applications in various optical sensors, optical waveguides, nanophotonic devices,

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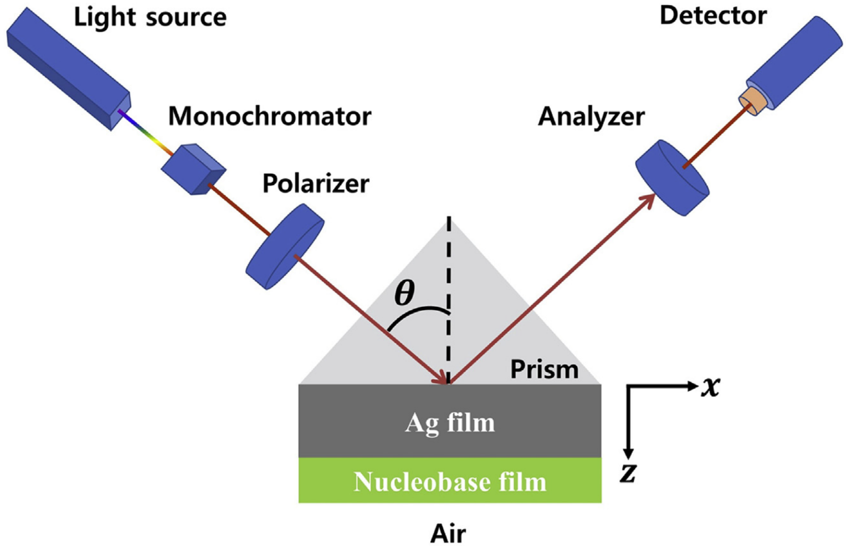

Fig. 1. Schematic diagram of the ATR experiment for [Prism–Ag film–Nucleobase film–Air] structure.

subwavelength plasmonic optics, and optical instruments [11–14]. An attenuated total reflection (ATR) method using a prism as an incident medium is a practical way to excite the SPWs at a metal–dielectric interface. The SPR angle or wavelength at zero reflectance in the ATR measurement has been widely used as a sensor for many applications, such as measurements of index, thickness, and concentration of materials, gas, and liquid. SPR can be used to achieve rapid and sensitive detection of biomaterials. Otto et al. studied the SERS spectra of DNA bases [15], and Barhoumi et al. investigated the SERS spectra of DNA [16]. Lee et al. performed the ATR and SERS experiments to study the optical and structural properties of chiral polyfluorene–phenylene polymer [14]. The Moskovits group used silver nanowire bundles as hot spots for SERS [17], and the Kneipp group studied the SERS in single living cells using gold nanoparticles [18]. Yoon et al. used a single nanowire on a film as an efficient SERS-active platform [19]. Botti et al. studied the SERS of DNA self-assembly on graphene using gold-coated silicon nano-pillars [20].

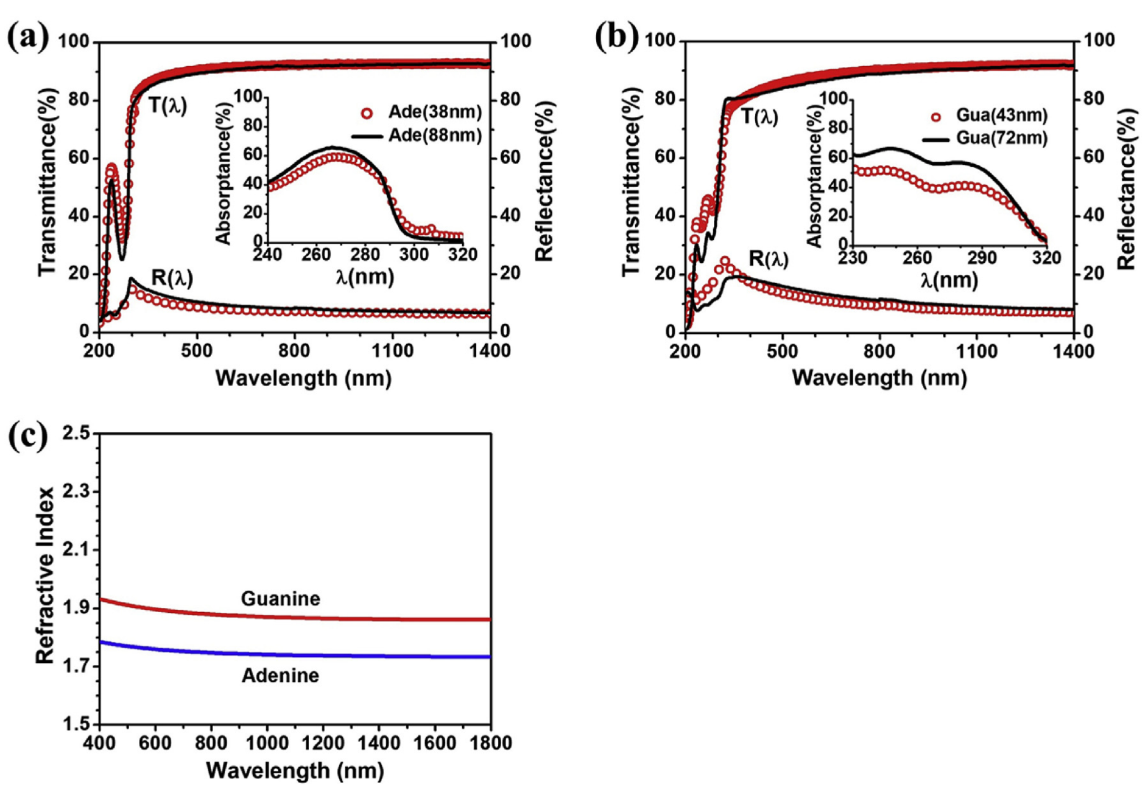

Fig. 2. Transmission and reflection spectra of (a) 38- and 88-nm-thick adenine and (b) 43- and 72-nm-thick guanine films in UV, VIS, and NIR wavelengths. Inset figures show absorption spectra for (a) 38- and 88-nm-thick adenine films, and (b) 43- and 72-nm-thick guanine films. (c) Normal dispersion of refractive indices of adenine and guanine films in VIS and NIR wavelengths.