

論文の内容の要旨

On-chip group IV photonic devices for vibrational spectroscopy

(振動分光のための第 IV 族オンチップ光学デバイス)

氏名: 肖 廷輝

Introduction

Vibrational spectroscopy, including infrared spectroscopy and Raman spectroscopy, is a powerful optical technique to non-invasively probe vibrational signatures of molecules and, thereby, enables analysis of composite systems of physical, chemical, and biological interests due to its inherent selectivity. By virtue of its versatility for studying solid, liquid, and gas samples, vibrational spectroscopy has been used for a variety of intriguing applications, such as chemical detection, disease diagnosis, environmental monitoring, and industrial process control. Unfortunately, most of these applications still remain confined to the laboratory environment. This is partially due to the bulky and costly instrumentation of vibrational spectroscopy with moderate sensitivity.

Realization of on-chip photonic devices provides a promising solution to the above problem owing to its advantages of low cost, high compactness, and high reliability. Various integration platforms of on-chip photonic devices have been developed, involving a wide range of optical materials that include noble metals, two-dimensional materials, chalcogenide glasses, and group IV semiconductors (carbon, silicon, and germanium). Among them, group IV semiconductors provide mature and low-loss material platforms for integration owing to their CMOS-compatible fabrication conditions and all-dielectric environment. However, due to the limited quality and structural designs of traditional photonic devices, realization of on-chip group IV photonic devices for vibrational spectroscopy still remains challenging.

In this doctoral work, I proposed and experimentally demonstrated several on-chip group IV photonic devices with controllable strong light-matter interaction for low-cost, highly sensitive vibrational spectroscopy. Specifically, I developed on-chip germanium photonic devices with high quality (Q) factors for infrared spectroscopy, on-chip silicon photonic devices with tailored resonant nanostructures for Raman spectroscopy, and an on-chip carbon photonic device with strong chemical enhancement for Raman spectroscopy. The developed photonic devices enable

low-cost and highly-sensitive vibrational spectroscopy, which is expected to find diverse applications in analytical chemistry, pharmaceutical science, environmental safety, and pathology.

Demonstration of on-chip germanium photonic devices for infrared spectroscopy

Germanium is selected as the integration material for developing on-chip photonic devices for infrared spectroscopy as it not only carries forward the CMOS compatibility as silicon, but also boasts several advantages over silicon, such as a wider spectral transparency window (2 - 15 μm) and a higher refractive index (~ 4). Especially, the wider spectral transparency window enables the developed photonic devices to work in the mid-infrared spectral range that encompasses the fingerprint region for infrared spectroscopic applications.

To make full use of the wide spectral transparency window of germanium, I developed a germanium suspended-membrane integration platform in my doctoral work. The suspended integration platform was achieved by using hydrogen fluoride (HF) to permeate and etch out the buried oxide (BOX) and Al_2O_3 layers in a homemade germanium-on-insulator wafer. Based on this platform, I experimentally demonstrated three types of mid-infrared high-Q germanium devices. The scanning electron microscope (SEM) images and transmission spectra of the three types of mid-infrared high-Q germanium devices are shown in Figure 1. For each type, a high-Q resonator was integrated with optical waveguides and two focusing grating couplers as shown in Figure 1(a), 1(c), and 1(e). The performance of each device was characterized by measuring its transmission spectrum. The measured transmission spectra of the three types of high-Q germanium devices are shown in Figure 1(b), 1(d), and 1(f). With the optimization of device designs and fabrication recipes, the Q factors of the fabricated devices were increased from ~ 200 to $\sim 18,000$, and finally to $\sim 57,000$. As the Q factor indicates the strength of on-chip light-matter interaction, highly-sensitive infrared spectroscopy that includes the fingerprint region can be expected by using the demonstrated high-Q germanium photonic devices.

Demonstration of on-chip silicon photonic devices for Raman spectroscopy

Silicon is selected for developing on-chip photonic devices for Raman spectroscopy as it is not only cost-effective for high-volume production, but also possesses a high refractive index for realizing strong light-matter interaction on a chip by structural resonance. Compared with conventional metallic integration platforms for surface enhanced Raman spectroscopy, silicon platforms take advantages of high energy efficiency and small photothermal heat

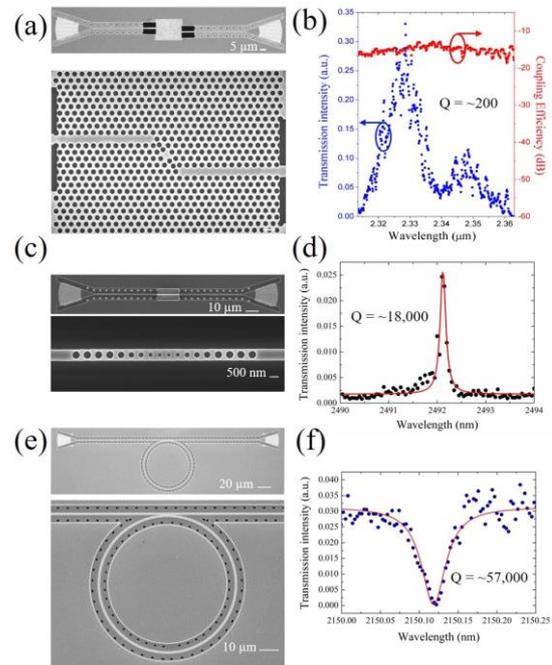


Figure 1. On-chip germanium photonic devices for infrared spectroscopy. (a) SEM images and (b) transmission/fiber-to-waveguide coupling spectrum of a monolithically integrated germanium device that includes a hexagonal-lattice zero-cell photonic crystal cavity. (c) SEM images and (d) transmission spectrum of a monolithically integrated germanium device, that includes a photonic crystal nanobeam cavity. (e) SEM images and (f) transmission spectrum of a monolithically integrated germanium device that includes a microring resonator.

generation, which prevents detected samples from being destroyed by the thermal effect.

To demonstrate the promising capability of on-chip silicon photonic devices for Raman spectroscopy, I theoretically designed and experimentally fabricated two types of on-chip silicon nanostructures for highly-sensitive Raman optical activity (ROA). One type is a chiral nanostructure while the other type is an achiral nanostructure. The chiral nanostructure is a spiral nanoflower with giant optical activity as shown in Figure 2. A largest-to-date circular intensity difference of 35% was experimentally realized by using the nanoflower. The achiral nanostructure is a silicon nanodisk array as shown in Figure 3(a). By using the silicon nanodisk array shown in Figure 3(b), I experimentally demonstrated all-dielectric superchiral-field-enhanced ROA, which is able to significantly increase the ROA signal level with neglectable artifacts. This is enabled by tuning an excited anapole mode in the nanodisks. To show the practical utility of the method, I conducted enhanced ROA measurements of a pair of chemical enantiomers (\pm)-alpha-pinene in a home-made two-phase virtual-enantiomer ROA setup as shown in Figure 3(c). Compared with the Raman and ROA spectra measured at the silica substrate as shown in Figure 3(d) and 3(e), evident Raman and ROA enhancement were observed at the silicon nanodisk array as shown in Figure 3(f) and 3(g), which indicates an enhancement factor of $\sim 10^2$ in the near-field region. The developed superchiral-field-enhanced ROA based on the on-chip silicon photonic devices for Raman spectroscopy is expected to create a highly-sensitive and cost-effective way for structural analysis of chiral molecules which are inaccessible to X-ray crystallography and NMR spectroscopy.

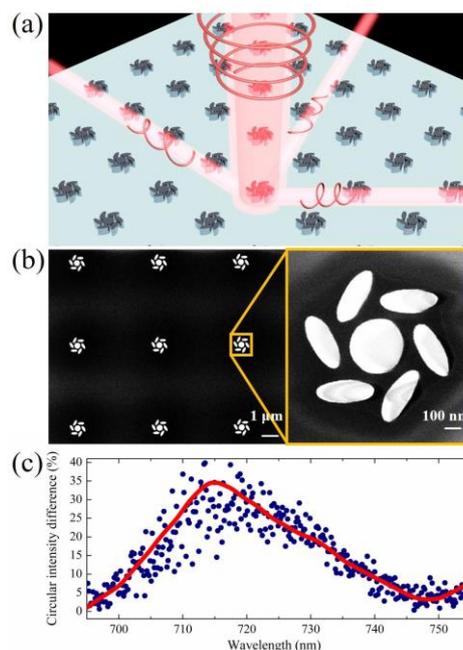


Figure 2. Schematic and experimental demonstration of silicon spiral nanoflowers with giant optical activity. (a) Schematic of an array of silicon spiral nanoflowers. A beam of circularly polarized light normally impinges on a silicon spiral nanoflower. Scattered light is collected to characterize the optical activity of the nanoflower. (b) SEM image of the fabricated silicon spiral nanoflower array with a zoomed image of one of the nanoflowers. (c) Measured circular intensity difference reaching about 35% at 715 nm.

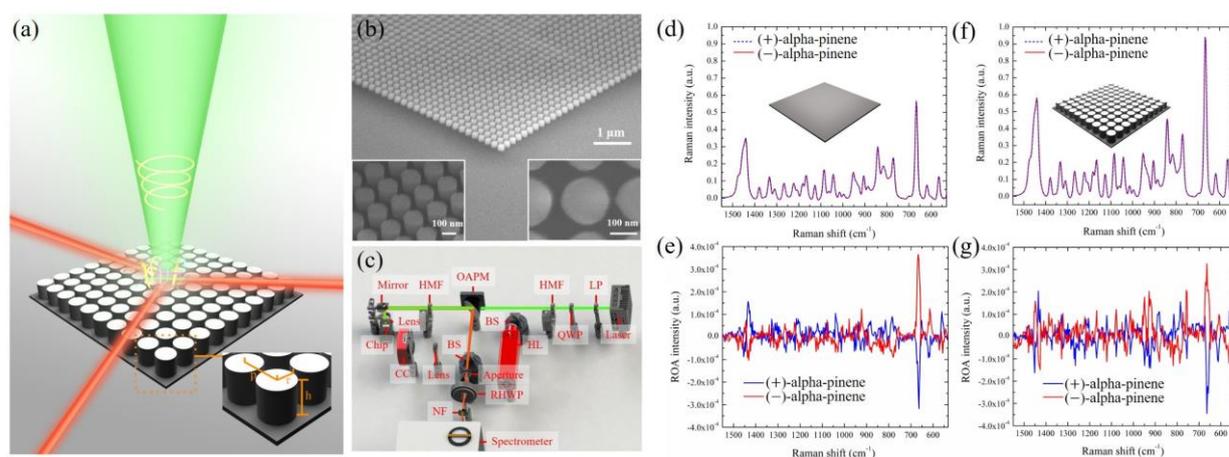


Figure 3. Schematic and experimental demonstration of all-dielectric superchiral-field enhanced Raman optical activity. (a) Schematic of a silicon nanodisk array. (b) SEM images of the fabricated silicon nanodisk array. (c) Two-phase virtual-enantiomer ROA setup. (d) Raman and (e) ROA spectra of (\pm)-alpha-pinene on the silica substrate. (f) Raman and (g) ROA spectra of (\pm)-alpha-pinene on the silicon nanodisk array.

Demonstration of on-chip carbon photonic devices for Raman spectroscopy

Surface-enhanced Raman spectroscopy (SERS) is a powerful technique for vibrational spectroscopy that provides several orders of magnitude higher sensitivity than inherently weak spontaneous Raman scattering by exciting localized surface plasmon resonance on roughened or periodically structured metal substrates. Unfortunately, the benefit of traditional SERS is compromised by the lack of reproducibility due to its dependence on hot spots for high enhancement factors from random aggregates as well as large photothermal heat generation on the metal surface as well as the poor compatibility of the metal surface to biomolecules.

Here I present an on-chip carbon photonic device composed of porous carbon nanowires in a two-dimensional array (shown in Figure 4(a)) as a SERS substrate that offers not only an extraordinarily high enhancement factor of $\sim 10^6$, but also surprisingly high reproducibility and high compatibility to biomolecules. To evaluate the sensitivity of the device, SERS spectra of R6G molecules at reduced concentrations were measured on the substrate, which is shown in Figure 4(b). It is evident from the figure that the detection limit of the substrate for R6G molecules is about 10 nM, which is challenging with conventional metal substrates due to the strong fluorescence of R6G molecules that obscure their weak Raman signal. To assess the substrate-to-substrate consistency of the substrate, a reproducibility test was carried out on 20 different substrates. As shown in Figure 4(c), the differences in the relative intensities of the Raman peaks at 1185, 1309, 1361, 1507, and 1650 cm^{-1} between all of the substrates

are with a standard deviation of 5.7%, indicating the high reliability of the substrate. Moreover, to assess the spot-to-spot consistency of the substrate in Raman signal intensity, SERS mapping of β -lactoglobulin was conducted on the substrate at two characteristic Raman peaks of the molecule (999 cm^{-1} and 1447 cm^{-1}) on both large and small scales, which is shown in Figure 4(d). The substrate has a coefficient of variation (CV) of less than 7.8% on average. This is made possible by the highly doped carbon material and porous structure of the substrate, leading to strong broadband charge-transfer resonance for large chemical enhancement (as opposed to electromagnetic enhancement in traditional SERS), strong adsorptivity (i.e., high surface-to-volume ratio), negligible photothermal heat generation (due to no LSPR), and high homogeneity, as evidenced by our SERS measurements of various molecules. By virtue of these excellent properties, the carbon photonic device holds promise for reliable SERS, providing a novel class of opportunities in diverse fields such as analytical chemistry, pharmaceutical science, food science, forensic science, and pathology.

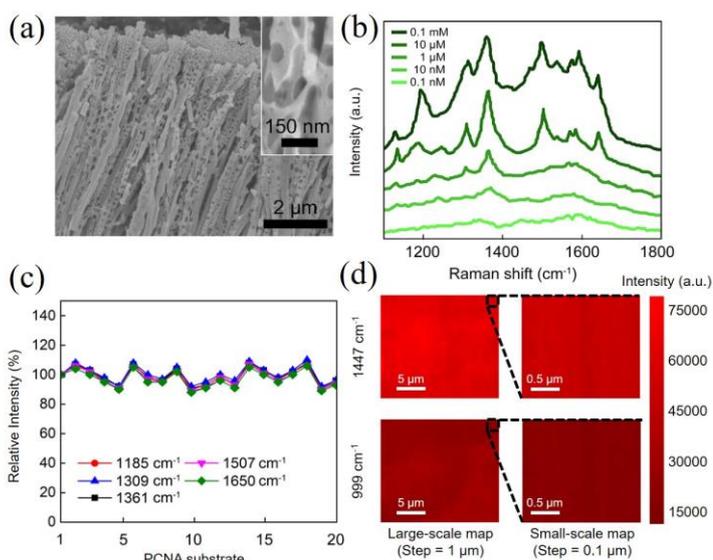


Figure 4. On-chip carbon photonic device composed of porous carbon nanowires in a two-dimensional array for Raman spectroscopy (a) SEM image of the porous carbon nanowires and an enlarged SEM image of a single nanowire (b) Measured Raman spectra of R6G molecules at different concentrations. (c) SERS reproducibility measurements of R6G molecules on different PCNA substrates. (d) SERS maps of β -lactoglobulin on the PCNA substrate, showing high surface homogeneity in Raman