Surface Enhanced Raman Scattering of Water Solution Specimens Coated on Porous MgF$_2$ Thin Films Dispersed with Ag Nanoparticles

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1. Introduction
Raman scattering spectroscopy has been widely used to analyze molecular structures of materials. Surface enhanced Raman scattering (SERS) is a surface-sensitive technique that enhances Raman scattering by molecules adsorbed on rough or nanostructured metal surfaces [1]. Nanoparticles have surface plasmon resonance (SPR) which is caused by the interaction of incident light with the plasmon in the particles [2]. Enhancement of Raman scattering is expected by the local electric field which is generated around the particles due to SPR. In this study, magnesium fluoride films dispersed with silver nanoparticles were prepared by the sol-gel technique. Enhancements of Raman scattering signals of several specimens adsorbed on these composite materials were observed and discussed about the detection limits of the specimens.

2. Experimental
MgF$_2$ thin films dispersed with Ag nanoparticles were prepared by the sol-gel method with various annealing temperatures (100 - 500 °C) and densities of nanoparticles (molar ratio of Ag to Mg: 10:90, 20:80 and 30:70). The sol solutions were coated on optical glass slides or Si substrates using the dip coating technique. The surface morphologies and lattice structures of the composite films were observed by a SEM and an XRD. The size and shape of nanoparticles were determined by a TEM. The optical properties of composite films were characterized by an UV-Vis-NIR spectrophotometer. Raman scattering spectra of pyridine, benzoic acid and rhodamine 6G water solution specimens adsorbed on the MgF$_2$ or MgF$_2$/Ag films were characterized using a microscopic Raman spectrometer.

3. Result and Discussions
It was confirmed that MgF$_2$ matrix films have porous structures and Ag nanoparticles were dispersed randomly within the composite films as the results of SEM, XRD and TEM measurements. Ag nanoparticles took an almost spherical shape with the diameter of about 10 nm. The optical absorption due to the surface plasmon resonance of Ag nanoparticles was observed at around 450 nm. Raman spectra of MgF$_2$ thin films with and without Ag nanoparticles deposited on Si substrates are shown in Fig. 1. A strong Raman peak of Si substrate is observed at 519 cm$^{-1}$ for all samples. Large enhancements of the Raman intensities of pyridine water solution on MgF$_2$/Ag films were observed compared with the MgF$_2$ film without Ag nanoparticles for the Raman lines at 1006 cm$^{-1}$ and 1031 cm$^{-1}$ corresponding to pyridine stretching modes. The porous structure might work as a good reservoir of the water solution and high efficiency interaction with Ag nanoparticles introduced within the pores induced a SERS effect. The calibration curve for the pyridine concentration in water solution was derived using the enhanced Raman intensities at 1006 cm$^{-1}$. Almost linear calibration curve was obtained in the mol concentration between $3 \times 10^{-6}$ and $6 \times 10^{-5}$ mol. SERS effect of other water solution specimens like benzoic acid and rhodamine 6G were also discussed.

![Fig. 1 Raman spectra of MgF$_2$ thin films with and without Ag nanoparticles coated with pyridine water solution.](image)

4. Conclusion
Composite films with porous MgF$_2$ matrix dispersed with Ag nanoparticles were deposited by using a sol-gel method. Ag nanoparticles in the film were observed almost spherical shape with diameter of around 10 nm. Enhancements of Raman scattering spectra were observed using pyridine water solution coated on the composite film. Almost linear calibration curve was obtained in the mol concentration between $3 \times 10^{-6}$ and $6 \times 10^{-5}$ mol.

References