

Photoacoustic Signal Enhancement by Localized Surface Plasmon of Gold Nanoparticles

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Photoacoustic imaging has been widely studied as a deep biological tissue imaging modality combining optical absorption and ultrasonic detection. It enables multi-scale high resolution imaging of optical absorbing intrinsic molecules as well as exogenous molecules. Gold nanoparticles have the primary advantages of large absorption cross section and bioconjugation capability for the imaging contrast agents. In order to design the photoacoustic imaging agents for enhancing the contrast with high specificity to targeted molecules and / or cell, we measured and analyzed time-of-flight photoacoustic signals of aqueous solutions of various shapes and sizes of gold nanoparticles. The signal intensities were sensitive to the shapes and sizes of the gold nanoparticles. We found a strong photoacoustic signal of the polyhedral gold nanoparticle due to the localized surface plasmon resonance. The experimental results derive the strategy of designing the optimum photoacoustic contrast agents.

Keywords: Photoacoustic, Gold nanoparticle, Polyhedron, Localized surface Plasmon resonance, Ultrasound, Pulsed laser, Tomography.

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1. INTRODUCTION

Optical imaging promises to expand existing medical imaging modalities beyond the typical visualization of anatomical features to incorporate functional and pathological information. Molecular imaging using optical technique has received great attention in biomedicine because of non-ionizing radiation and real-time imaging. With selected optical wavelength, a wide variety of intrinsic or exogenous molecules can be visualized to reveal the anatomy, function, metabolism in biological system [1]. However, due to strong light scattering in tissue, optical imaging technique suffers from either shallow penetration depth or poor spatial resolution.

Photoacoustic (PA) imaging, which is based on optical absorption and ultrasonic detection, has overcome the drawback of the optical imaging technique by taking advantages of rich optical contrast and ultrasonic spatial resolution for deep imaging because ultrasonic waves are less scattered. Absorption of photons by optical absorbing molecules (chromophores) thermoelastically induces pressure waves through PA effect. PA images forms images by detecting the induced pressure waves. The physical processes responsible for PA effects are characterized by absorption of nanosecond pulsed light, optical excitation, non-radiative relaxation, heating, and pressure wave generation. The PA imaging apparatus for small animal imaging has been offered commercially. Its technique now is ready to provide clinicians with three-dimensional microvascular network using hemoglobin of different oxygenation states as intrinsic chromophores. Not only intrinsic chromophores but also exogenous molecules have been actively studied as the PA imaging target.

Metal nanoparticles as well as organic dyes and carbon nanotubes have been actively demonstrated as the exogenous contrast agents of PA imaging due to

their unique optical properties arising from the surface plasmon resonance effect. The primary advantages of gold nanoparticles lie in their large absorption cross section with unique spectra due to the surface plasmon resonance effect and bioconjugation capability, which means that the gold nanoparticles can be specifically targeted to molecules and / or cells. For example, gold nanospheres [2], nanorods [3], nanoshells [4], nanocages [5], and nanobeacon [6] have been studied in PA imaging [7].

In this study, we performed a comprehensive PA measurement of gold nanoparticles with various shapes and sizes in order to design exogenous PA imaging agent, which enabled to enhance the contrast for molecular PA imaging.

2. MATERIALS AND METHOD

2.1 Photoacoustic Measurement

PA measurement apparatus consisted of nanosecond pulsed laser, ultrasound transducer, preamplifier, and digital oscilloscope. In this study, the excitation light was sourced from a second harmonic Q-switched neodymium-doped yttrium aluminum garnet (Nd : YAG) laser and a tunable optical parametric oscillator (OPO). The excitation pulsed light was coupled into a multi-mode optical fiber for the illumination. The pressure waves induced by the excitation light source were detected by our originally-fabricated ring-shaped ultrasound transducer consisting of a P(VdF / TrFE) film, which was characterized by broader frequency band than that of a piezoelectric ceramic PZT. The transducer was arranged coaxially with the optical fiber. Using this transducer, the PA signal was measured with constant positional relation between the light excitation and the ultrasonic detection. In order to acquire a PA tomographic image, the ring-shaped ultra-

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sound transducer with the optical fiber was mechanically scanned.

2.2 Gold Nanoparticles

Octahedral, cubic and spherical gold nanoparticles were used in this study. The cetyltrimethylammonium bromide-capped octahedral and cubic gold nanoparticles were synthesized using a slightly modified seed-mediated method reported previously by T. Teranishi [8]. The sizes of the particles were 55.5 ± 1.3 nm (octa-

hedron) and 56.1 ± 2.6 nm (cube). The 50 nm spherical gold nanoparticles were purchased for the comparison. Aqueous solutions of the gold nanoparticles were prepared for the samples.

Size and morphology of the particles were characterized by means of transmission electron microscopy (TEM). Vis-NIR extinction spectra of the aqueous solutions of the gold nanoparticles were measured with a spectrophotometer in the wavelength range of 400-700 nm.

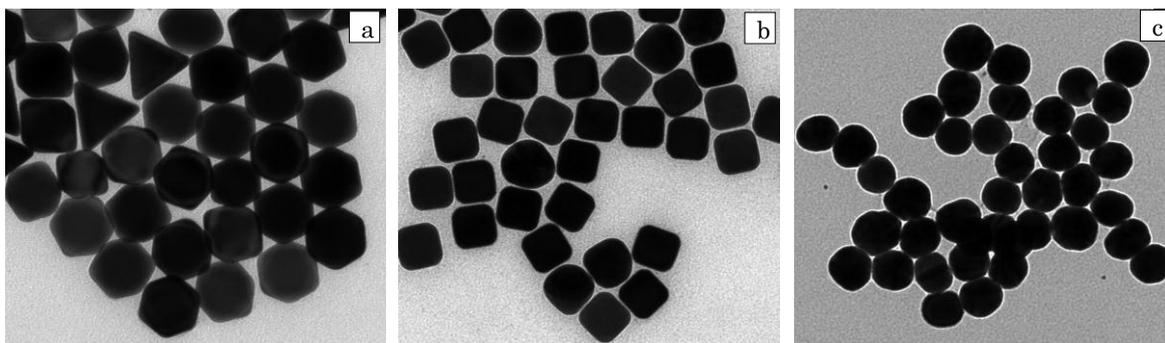


Fig. 1 – TEM images of (a) octahedral, (b) cubic and (c) spherical gold nanoparticles employed in this study

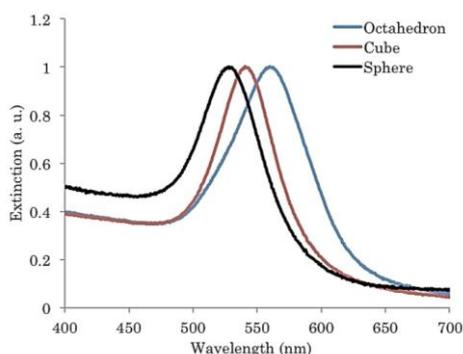


Fig. 2 – Extinction spectra of aqueous solutions of gold nanoparticles employed in this study

3. RESULTS AND DISCUSSION

Fig. 1 shows TEM images of the octahedral, cubic and spherical gold nanoparticles. These images indicate the characteristic shapes and uniform size. It is confirmed that the structure of each nanoparticle is controlled precisely. Fig. 2 shows extinction spectra of the aqueous solutions of gold nanoparticles. All of the nanoparticles exhibited localized surface plasmon resonance peaks, which appear in the region of 500-600 nm region.

The observed waveforms were the time-of-flight PA signals. The waveforms indicated the process of absorption of photons by the aqueous solutions of gold nanoparticles thermoelastically. The amplitudes of the PA signals, which corresponded to the brightness of PA image, showed strong dependence to the shapes of the nanoparticles. The PA amplitudes of the polyhedral nanoparticles were significant higher than that of the spherical nanoparticles. The octahedral samples indi-

cated the highest signal intensity. It is common knowledge that the plasmonic property of gold nanoparticle is dominated by particle shape. The plasmonic enhancement of the polyhedral nanoparticles was stronger than that of the spherical nanoparticles as the strong plasmonic enhancement occurred at the sharp corners of the polyhedral nanoparticles. The PA amplitudes were also depended on the concentrations of the aqueous solutions and illuminating optical energy densities. The stability of the PA signals, signal intensity change with the increase of the number of the laser pulse, also showed the shape dependence. This dependence might be related to thermodynamical stability of the structure.

4. CONCLUSIONS

We performed a comprehensive PA measurement of various shapes of gold nanoparticles. The strong PA signal amplitudes were observed in the case of polyhedral nanoparticles. Especially, octahedral nanoparticles showed remarkable enhancement due to the localized surface plasmon resonance. The structure of a gold nanoparticle was found to be an important parameter to design the PA contrast agents. These insights suggested that it enabled to derive optimum design of exogenous contrast agents using gold nanoparticles.

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