Colloids and Surfaces A: Physicochem. Eng. Aspects 487 (2015) 42–48

Contents lists available at ScienceDirect

Colloids and Surfaces A: Physicochemical and Engineering Aspects

journal homepage: www.elsevier.com/locate/colsurfa

Effects of physicochemical properties of particles and medium on acoustic pressure pulses from laser-irradiated suspensions

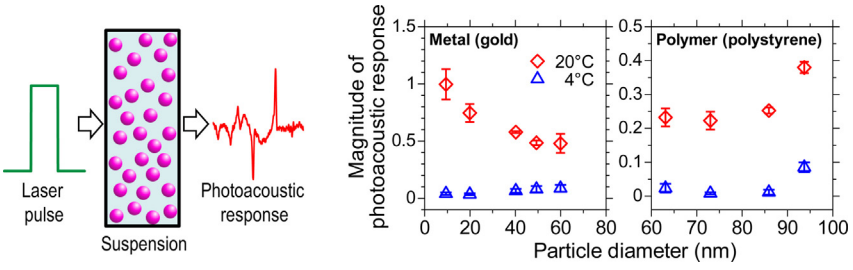
Tomonori Fukasawa[a,b], Shota Noguchi[a], Hiroyuki Shinto[c,*], Hiroyuki Aoki[d,e], Shinzaburo Ito[d], Masahiro Ohshima[a]

[a] Department of Chemical Engineering, Kyoto University, Katsura, Nishikyo-ku, Kyoto 615-8510, Japan
[b] Department of Chemical Engineering, Hiroshima University, 1-4-1 Kagamiyama, Higashi-Hiroshima, Hiroshima 739-8527, Japan
[c] Department of Chemical Engineering, Fukuoka University, 8-19-1 Nanakuma, Jonan-ku, Fukuoka 814-0180, Japan
[d] Department of Polymer Chemistry, Kyoto University, Katsura, Nishikyo-ku, Kyoto 615-8510, Japan
[e] Advanced Biomedical Engineering Research Unit, Kyoto University, Katsura, Nishikyo-ku, Kyoto 615-8510, Japan

HIGHLIGHTS

- Photoacoustic (PA) phenomena of nanoparticle (NP) suspensions are studied.
- PA pressures from aqueous suspensions of metal and polymer NPs are measured.
- The effects of NP material, NP size, and temperature on PA pressure are investigated.
- The experimental results are compared with the estimations from a physical model.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 15 July 2015
Received in revised form 9 September 2015
Accepted 17 September 2015
Available online 21 September 2015

Keywords:
Photoacoustic imaging
Photoacoustic pressure
Physicochemical properties
Metal nanoparticles
Polymer nanoparticles
Contrast agents

ABSTRACT

We experimentally measured the photoacoustic responses from monodispersed suspensions of spherical nanoparticles (NPs) of metal (gold, diameter = 9.4, 19.9, 40.2, 49.3, and 59.9 nm) and dye-containing polymer (polystyrene, diameter = 63.1, 73.0, 85.9, and 93.7 nm) in water at different NP concentrations and temperatures (4, 20, and 37 °C), where the samples were irradiated with 5-ns laser pulses at low laser fluence. The obtained experimental results were explained by a physical model, where the acoustic pressure pulse was represented by a sum of two contributions from the NPs and the surrounding liquid medium. These results revealed that the photoacoustic responses from a laser-irradiated NP suspension are influenced by the physicochemical properties of the NPs and medium. We also proposed a strategy on how to design NPs for photoacoustic contrast imaging on the basis of obtained results.

1. Introduction

Photoacoustic (PA) imaging is one of rapidly growing techniques for biomedical imaging, because it is a noninvasive imaging modality with the advantages of both optical and acoustic imaging techniques. The PA imaging technique utilizes a PA effect, which results from the conversion of absorbed light into acoustic waves that can be detected outside of the subject of interest. The contrast in PA imaging depends on the optical-to-acoustic conversion efficiency and can be improved greatly by using nanoparticles (NPs) as contrast agents [1–6]. Photoacoustic flow cytometry (PAFC) also relies on this NP-induced PA contrast enhancement to detect

* Corresponding author. Fax: +81 92 865 6031.
E-mail address: hshinto@fukuoka-u.ac.jp (H. Shinto).

http://dx.doi.org/10.1016/j.colsurfa.2015.09.051
0927-7757/

various circulating targets (e.g., circulating tumor cells, circulating blood clots, and pathogens) in living systems [6–9]. Various NPs have been synthesized for the PA contrast agents, such as nanostructured metal particles [10–15], carbon nanotubes [16,17], and dye-containing NPs [18–20]. The focus of these studies has been placed on how to improve the optical absorption efficiency of the NPs, because the amplitude of PA signal increases with increasing absorption efficiency [21].

Recently, Chen et al. have shown that the PA signals generated from laser-irradiated suspensions of silica-coated gold nanorods [22,23] and nanospheres [24] are influenced by the thickness of silica shells. They also have demonstrated that the PA signals from the suspensions of spherical 26-nm gold NPs are influenced by the temperature-dependent properties of the host liquid media and are dominated by the contribution from the surrounding media rather than that from the gold NPs themselves [24]. These results have revealed that the PA signal generated from a particle suspension is affected not only by the optical absorption efficiency of the particles, but also by the physicochemical properties of the surrounding medium and the particle–medium interface.

Our previous study has demonstrated that the amplitude of PA signal generated from the aqueous suspension of spherical gold NPs at an ambient temperature decreases with increasing particle size [25]. This dependence of the PA signal amplitude on the particle size is explained by our phenomenological model [25,26], where the PA pulse is represented by a sum of two contributions from the NPs and the medium. In contrast, Aoki et al. have reported that the PA signal amplitudes from the aqueous suspensions of polymer NPs containing dyes increase with particle size [27]. This difference in particle-size dependence of the PA signal amplitude between the aqueous suspensions of gold NPs and those of polymer NPs would be attributable to the difference in physicochemical properties between gold and polymers. Nevertheless, the effects of physicochemical properties of NPs on the PA phenomena are not well understood and remain to be explored experimentally and theoretically from a fundamental point of view.

The present study reports the experimental and theoretical results on how the physicochemical properties of NPs and medium influence the PA responses from a laser-irradiated suspension. We have carried out the measurements of PA signals, where the suspensions of spherical gold and polystyrene (PS) NPs with different diameters in water at different temperatures are irradiated with nanosecond laser pulses at low laser fluence. The results from the experiments are compared with those obtained from a phenomenological model developed in our previous studies [25,26]. We also propose a strategy on how to design NPs for PA contrast imaging on the basis of our findings.

2. Experimental methods

2.1. Gold nanoparticles

The aqueous suspensions of spherical gold NPs with different diameters (d_p = 9.4, 19.9, 40.2, 49.3, and 59.9 nm at number concentrations of 5.7×10^{12}, 7.0×10^{11}, 9.0×10^{10}, 4.5×10^{10}, and 2.6×10^{10} particles/mL, respectively) were purchased from British BioCell International (Cardiff, UK). The concentrated suspensions were prepared in clean test tubes by solvent evaporation at 60 °C [26]. Before and after this concentration procedure, no significant change was observed in the optical density (OD) spectra of the gold NP suspensions, indicating that the concentration procedure did not significantly affect the morphology and the monodispersity of the gold NPs. Thus, the suspensions of three different concentrations for each particle size were prepared, as listed in Table 1.

Table 1
Suspensions of the gold NPs and the DiI-containing PS NPs for measurements of PA responses.

Dispersoid	Diameter d_p (nm)	Optical density at λ_{ex} = 560 nm OD_{560} (−)	Temperature T_{init} (°C)
Au-10	9.4	0.033, 0.093, 0.208	4, 20, 37
Au-20	19.9	0.065, 0.122, 0.206	4, 20, 37
Au-40	40.2	0.057, 0.124, 0.260	4, 20, 37
Au-50	49.3	0.081, 0.178, 0.324	4, 20, 37
Au-60	59.9	0.107, 0.238, 0.323	4, 20, 37
PS-63	63.1	0.086, 0.193, 0.279	4, 20, 37
PS-73	73.0	0.142, 0.185, 0.275	4, 20, 37
PS-86	85.9	0.096, 0.151, 0.186	4, 20, 37
PS-94	93.7	0.094, 0.176, 0.297	4, 20, 37

2.2. Dye-containing polymer nanoparticles

NPs of a polymer containing dyes were prepared via a nanoemulsion method. The polymer, dye, and surfactant used in the present study were polystyrene (PS, approximate M.W. = 22000; Scientific Polymer Products, NY, USA), 1,1′-dioctadecyl-3,3,3′3′-tetramethylindocarbocyanine perchlorate (DiI; PromoKine, Heidelberg, Germany), and sodium dodecyl sulfate (SDS; Tokyo Chemical Industry, Tokyo, Japan), respectively. Chloroform was purchased from Nacalai Tesque (Kyoto, Japan). These reagents were of analytical grades and used without further treatment. All water used in the experiments was purified using a Direct-Q 3 UV system (Merck Millipore, Darmstadt, Germany) to give a resistance of 18.2 MΩ cm and a total organic carbon of less than 5 ppb.

A typical preparation procedure for the dye-containing polymer NPs is described elsewhere [27]. Briefly, 800 μL of a chloroform solution containing PS (5 or 10 mg/mL) and DiI (0.25 or 0.50 mg/mL), where the DiI/PS ratio was fixed at 0.05, was added to 10 mL of an aqueous solution containing SDS (1, 2, or 4 mg/mL). The oil phase was emulsified via ultrasonication at a frequency of 22.5 kHz and a power of 20 W (Microson XL2000; Misonix, NY, USA) for 30 s at 0 °C. The emulsified solution was stirred at 40 °C for 90 min, whereby the chloroform was allowed to evaporate and removed from the solution. The DiI-containing PS NPs obtained were washed three times by a series of centrifuge filtration (Nanosep 100K Omega; PALL, NY, USA) at 5000 × g for 7 min (Model 3500; KUBOTA, Tokyo, Japan) and redispersion in water. As summarized in Table S1 of Supplementary data, a variation of the PS and SDS concentrations enabled us to obtain the PS NPs with different diameters (d_p = 63.1, 73.0, 85.9, and 93.7 nm), which were estimated by dynamic light scattering with ELSZ-2 (Otsuka Electronics, Osaka, Japan). The suspensions of three different concentrations for each particle size were prepared by diluting with water, as listed in Table 1.

2.3. Setup for detection of photoacoustic responses

Fig. 1a shows our experimental setup for the PA signal detection, which is almost the same as employed in our previous studies [25–28], except for the laser device. A sample cuvette with a light-pass length of L = 0.92 mm was immersed in a temperature-controlled water bath with precision of ±0.1 °C and illuminated by a pulsed beam from a tunable laser system with optical parametric oscillator (Opolette 355 II; OPOTEK, Carlsbad, CA, USA), which exhibited the pulse width of t_L = 5 ns and the repetition rate of 20 Hz. The wavelength of this laser was set at λ_{ex} = 560 nm, and the energy was $I_0 \approx 100$ μJ/pulse. The beam diameter was reduced to 1.0 mm by a plano-convex lens with a focal length of 150 mm. Accordingly, the cross section of the specific region irradiated with the laser pulse was $s_L \approx 0.785$ mm^2