Ultrasonics Sonochemistry 32 (2016) 1–7

Contents lists available at ScienceDirect

Ultrasonics Sonochemistry

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

Inertial cavitation initiated by polytetrafluoroethylene nanoparticles under pulsed ultrasound stimulation

Qiaofeng Jin [a], Shih-Tsung Kang [a], Yuan-Chih Chang [b], Hairong Zheng [c,*], Chih-Kuang Yeh [a,*]

[a] Department of Biomedical Engineering and Environmental Sciences, National Tsing Hua University, Hsinchu, Taiwan
[b] Institute of Cellular and Organismic Biology, Academia Sinica, Taipei, Taiwan
[c] Paul C. Lauterbur Research Center for Biomedical Imaging, Institute of Biomedical and Health Engineering, Shenzhen Institutes of Advanced Technology, Chinese Academy of Sciences, Shenzhen, China

ARTICLE INFO

Article history:
Received 8 December 2015
Received in revised form 5 February 2016
Accepted 6 February 2016
Available online 6 February 2016

Keywords:
Inertial cavitation
PTFE nanoparticles
Interfacial nanobubbles
Passive cavitation detector
Free radical

ABSTRACT

Nanoscale gas bubbles residing on a macroscale hydrophobic surface have a surprising long lifetime (on the order of days) and can serve as cavitation nuclei for initiating inertial cavitation (IC). Whether interfacial nanobubbles (NBs) reside on the infinite surface of a hydrophobic nanoparticle (NP) and could serve as cavitation nuclei is unknown, but this would be very meaningful for the development of sonosensitive NPs. To address this problem, we investigated the IC activity of polytetrafluoroethylene (PTFE) NPs, which are regarded as benchmark superhydrophobic NPs due to their low surface energy caused by the presence of fluorocarbon. Both a passive cavitation detection system and terephthalic dosimetry was applied to quantify the intensity of IC. The IC intensities of the suspension with PTFE NPs were 10.30 and 48.41 times stronger than those of deionized water for peak negative pressures of 2 and 5 MPa, respectively. However, the IC activities were nearly completely inhibited when the suspension was degassed or ethanol was used to suspend PTFE NPs, and they were recovered when suspended in saturated water, which may indicates the presence of interfacial NBs on PTFE NPs surfaces. Importantly, these PTFE NPs could sustainably initiate IC for excitation by a sequence of at least 6000 pulses, whereas lipid microbubbles were completely depleted after the application of no more than 50 pulses under the same conditions. The terephthalic dosimetry has shown that much higher hydroxyl yields were achieved when PTFE NPs were present as cavitation nuclei when using ultrasound parameters that otherwise did not produce significant amounts of free radicals. These results show that superhydrophobic NPs may be an outstanding candidate for use in IC-related applications.

1. Introduction

Mechanical, chemical, and thermal effects are produced during inertial cavitation (IC), which involves the rapid expansion and subsequent violent collapse of a cavity under the action of an acoustic pressure wave [1]. Many common applications such as ultrasound cleaning, sonochemistry, and therapeutic ultrasound rely on IC. In general, initiating IC requires cavitation nuclei that are either artificially added or excited by ultrasound. While gas bubbles are ideal candidates for cavitation nuclei, they are unstable in water and will either dissolve due to the Laplace pressure from surface tension or rise and disappear from the surface due to buoyancy. This means that it is crucial to introduce stable nuclei in cavitation-related applications.

Recent studies have used various methods to confirm the presence of interfacial nanobubbles (NBs) with an extremely long lifetime (on the order of days) at the interface of hydrophobic solid surfaces [2–7]. As shown in Fig. 1, under an atomic-force microscopy (AFM) these NBs resemble spherical soft domains with heights of the order of 10 nm and diameters of the order of 100 nm, which are expected to dissolve within microseconds due to the large Laplace pressure inside such a small size [3]. Their anomalously long lifetime has attracted increasing attention due to their promising applications in many fields [8]. Whether these stable interfacial nanobubbles could serve as cavitation nuclei is an important issue in many applications. Both Borkent et al. and

* Corresponding authors at: Paul C. Lauterbur Research Center for Biomedical Imaging, Institute of Biomedical and Health Engineering, Shenzhen Institutes of Advanced Technology, Chinese Academy of Sciences, 1068 Xueyuan Avenue, Shenzhen 518055, China (H. Zheng). Department of Biomedical Engineering and Environmental Sciences, National Tsing Hua University, No. 101, Section 2, Kuang-Fu Road, Hsinchu 30013, Taiwan (C.-K. Yeh).

E-mail addresses: hr.zheng@siat.ac.cn (H. Zheng), ckyeh@mx.nthu.edu.tw (C.-K. Yeh).

http://dx.doi.org/10.1016/j.ultsonch.2016.02.009
1350-4177/

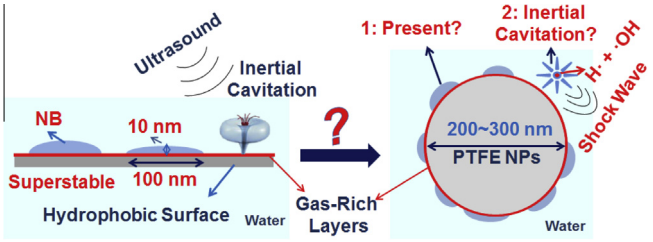

Fig. 1. Diagram of interfacial NBs and their IC on a hydrophobic surface, H·, and ·OH represent the hydrogen atom and hydroxyl, respectively.

Brotchie et al. reported that interfacial NBs could not induce cavitation, based on observations of NBs variations using AFM [9,10]. However, the temporal resolution of AFM imaging (which operates on the order of minutes) is too long to detect variations caused by IC activity (which is on the order of microseconds) [11]. In contrast, based on counts of the pits formed during cavitation using SEM images, Belova and his colleagues concluded that interfacial NBs play a crucial role in heterogeneous cavitation processes [11–13]. Furthermore, Borkent et al. and Rivas et al. both used a charge-coupled-device camera to reveal that these NBs could initiate cavitation by observing the cavitation activities of NBs on artificial hydrophobic and superhydrophobic pits under stimulation with a shock-wave generator [14–16].

The above-mentioned studies are helpful for understanding the behavior of interfacial NBs under ultrasound. However, the number of pits is limited by the surface area of the wafer. Additionally, the rapid erosion of their structure caused by IC and their large dimensions would both greatly limit their application [17]. In fact, suspended particles, especially nanoparticles (NPs) would supply much larger areas to absorb NBs as cavitation nuclei and keep NBs staying on the surfaces of NPs. It has been found that hydrophobic and corrugated particles (with dimensions on the order of 10–100 μm) facilitated the cavitation activity but hydrophilic and smooth particles did not, which is consistent with crevice theory [18,19]. This further suggests that hydrophobicity is a crucial factor for NPs to attach to NBs. Furthermore, it has been demonstrated that superhydrophobic pits with contact angles larger than 160° remained active after hundreds of ultrasound pulses, whereas hydrophobic pits were deactivated after a single pulse [14]. Therefore, superhydrophobicity may be important for sustaining IC.

This study used a real-time passive cavitation detection system to investigate whether NBs can attach on the surface of superhydrophobic polytetrafluoroethylene (PTFE) NPs (Fig. 2A). The IC activities in water and ethanol were compared to evaluate the presence of NBs on PTFE NPs. The NPs concentration dependence and their sustainability over time for stimulation by multiple pulses were also investigated. The intensity of IC was further assessed by using terephthalic acid dosimetry, which quantified the amount of hydroxyl radicals based on measurements of their fluorescence intensity. Finally, the effects of acoustic parameters such as the peak negative pressure, number of pulses, and pulse repetition frequency (PRF) are also discussed.

2. Experimental section

2.1. Materials

A PTFE NPs dispersion (60% w/w) and anhydrous ethanol were purchased from Sigma–Aldrich (St. Louis, MO, USA), terephthalic acid was purchased from Showa Chemical (Tokyo, Japan), and all of the other chemicals used in this study were of analytical grade and used as received without further purification. A 2 mM terephthalic acid dosimetry solution was prepared by dissolving terephthalic acid (0.332 g), NaOH (0.200 g), KH_2PO_4 (0.589 g), and Na_2HPO_4 (0.981 g) in 1 L of MilliQ (18.2 MΩ) deionized (DI) water by heating and stirring.

To prepare the PTFE NPs suspension, the surfactant in the PTFE solution was removed by centrifugation (7500 g for 5 min once and 5000 g twice), then resuspended and diluted with DI water. All of the NPs solutions were diluted by the same volume of a 2 mM terephthalic acid dosimetry solution to allow simultaneous IC activity measurements and chemical dosimetry, with the exception of the suspensions in ethanol. DI water or ethanol was used as a control substitute for the PTFE NPs suspension. Degassed samples were degassed for at least 1 h at room temperature, which yielded a dissolved oxygen concentration of 30% (970 DO2 meter, Jenway, Dunmow, Essex, UK). Lipid microbubbles (MBs) were prepared using the same formula and the method described by Fan et al. [20]. MBs with a concentration of 10^8 per milliliter were used in all of the experiments involving MBs. The phantom with a 6-mm-diameter hollow chamber was fabricated by 1.5 g of agarose powder (UltraPureTM Agarose, Invitrogen Corp., Carlsbad, CA, USA) dissolved in 100 mL of DI water.

2.2. IC intensity measurements and signal processing

2.2.1. Experimental setup

A passive cavitation detector (PCD) was used to receive cavitation signals in the focal zone. The experimental setup (Fig. 2A) comprised a PCD with a 1 MHz focused transducer (V303, Olympus, Waltham, MA, USA) having a focal length of 1.5 cm and a diameter of 1.27 cm, which was positioned perpendicularly to a 2 MHz high-intensity focused ultrasound (HIFU) transducer (Su-101, Sonic Concepts, Bothell, WA, USA). The two transducers were adjusted to have an overlapped focus point at a 23 gauge needle, which was inserted in the 6-mm-diameter hollow chamber with a pulse-echo method. The HIFU transducer was driven by an amplifier (150A100B, Amplifier Research, Souderton, PA, USA) and a waveform generator. An acoustic absorber was positioned opposite the HIFU transducer in order to minimize acoustic reflections. The PTFE NPs were slowly injected into the hollow chamber in the agar phantom to avoid bubble generation. Broadband shock-wave signals induced by IC were received by the PCD transducer and amplified by the pulser/receiver (PR5072, Olympus). Finally, the signals were sampled at 25 MHz and displayed on an oscilloscope (LT322, LeCory, Chestnut Ridge, NY, USA) while simultaneously being sampled using a PCI data acquisition card (IEEE488.GPIB, National Instruments, Austin, TX, USA) controlled by LabVIEW software (National Instruments). The time delay was set according to the time of flight between the focal lengths of the two transducers.

2.2.2. IC dose quantification

To determine whether IC occurred and to quantify its intensity during ultrasound exposure, wideband IC signals received by the PCD were analyzed. Conventionally, these signals are acquired by using a transducer with a center frequency that is much higher than excitation frequency. Nevertheless, a recent study suggested that periodic shock wave emissions during intense IC events can give rise to the emissions of high order subharmonic signals (less than half the excitation frequency) [21]. That means the lower frequency parts reflect more information and lead to higher sensitivity in IC detection. Thus, the 1-MHz PCD (−6 dB bandwidth of 70%) was used to receive the subharmonic signals. Various methods have been investigated for quantifying IC activity [22–26]. The method used in the present study was similar to that described by Kang et al. involving evaluations of the wideband shock-wave emissions generated by IC [26]. Briefly, each recorded waveform