Catalysis Today 201 (2013) 203–208

Contents lists available at SciVerse ScienceDirect

Catalysis Today

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

Ultrasonic wave induced mechanoluminescence and its application for photocatalysis as ubiquitous light source

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ARTICLE INFO

Article history:
Received 15 January 2012
Received in revised form 30 March 2012
Accepted 1 April 2012
Available online 27 May 2012

Keywords:
Mechanoluminescence
Ubiquitous light source
Ultrasonic wave
TiO_2 photocatalyst

ABSTRACT

For the purpose of mechanoluminescent (ML) ubiquitous light source, we focus on ultrasonic wave as non-destructive and non-invasive stimulation for bio-tissue. Actually we have investigated ultrasonic wave induced mechanoluminescence (USML) and successfully detected the mechanoluminescence response accompanied by the ultrasonic wave irradiation. The USML intensity depends on kinds of ML material, input intensity of ultrasonic wave and so on. The USML properties, such as sustainability, temperature dependence and input mechanical load dependence, were same as the ML properties shown in conventional ML test by using universal testing machine so far. Furthermore, though it was in primitive stage, we successfully detected degradation of methylene blue dye accompanied by US irradiation to mixture solution with visible light responding TiO_2 photocatalyst and europium doped strontium aluminate (SAOE), and demonstrated the USML acted as the light source for a photo-activation of TiO_2 photocatalyst for the first time.

1. Introduction

A practical material that is mechanoluminescent (ML) in the elastic deformation region has been developed in our laboratory for the first time [1–6]. The ML material can continuously emit high-intensity visible light under the application of mechanical stress such as deformation, friction, or impact. In previous studies, we were able to achieve the following:

1. Dramatic improvement of conversion efficiency between mechanical and optical energy has been realized.
2. The intensity of the mechanoluminescence is proportional to the time variation of the strain energy that is applied to the material.
3. The preparation of nanometer size ML particles has been accomplished.

By using the ML material, two-dimensional stress distributions in plants, structures, and living bodies can be observed from the viewpoints of safety and reliability against mechanical stress and strain (Fig. 1(a)). Further, the mechanoluminescence exhibited even under the application of a small mechanical stress such as that generated by scratching the material with a finger, and it can be easily observed with a naked eye. Thus, by increasing the ML conversion efficiency, ML materials can be expected for utilizing as light sources [7–9].

The ML material is powder of ceramics, and the one by one particle itself shows ML properties as the own characters without forming to composite film or pellet. Recently, we succeeded to synthesize the ML nanoparticle with the size of 10 nm, and it is enough small to inject and use in bio-body. In addition, the ML light source must be electric lead free for emission. Actually, we have demonstrated the ML material acted as light source for solar cell [7], stress historical-log recording system [9] and fluorescent molecular probe for bio-imaging [10] so far. One of the remaining main problems for achievement of ML ubiquitous light source must be the non-destructive and non-invasive mechanical stimulation method for the mechanoluminescence and its application in a condition that can be treated even in the dark bio-tissue and cell (Fig. 1(b)). For the purpose, we have focused on ultrasonic wave as the mechanical stimulation for generation of mechanoluminescence, because the ultrasonic wave has already been utilized as non-destructive and non-invasive inspection for construction field and human body. Furthermore, the ultrasonic wave shows mechanical factors, for example, sound pressure, acoustic radiation force, rapid babble expansion and collapse of cavitation, pressure gradient between nodes and loops in standing wave and so on [11]. Meanwhile, there has been much amount of reports on photo-utilizing on-site techniques in bio-tissue and cell, for example phototherapy and

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http://dx.doi.org/10.1016/j.cattod.2012.04.040

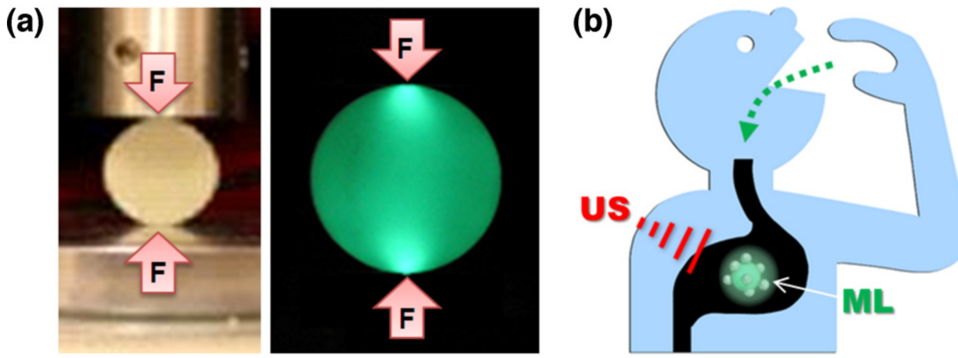

Fig. 1. (a) ML image and photograph during application of compressional load using mechanical testing machine. (b) Schematic illustration of concept of ML ubiquitous light source and ultrasonic wave induced mechanoluminescence (USML).

bio-imaging with high social interest [12–14]. In these cases, the light source for excitation inside a life body has been recognized as serious challenge because of low interpenetration efficiency of light for bio-tissue and damage against undesirable peripheral parts especially on the optical pass. For the crucial needs, if the ML material can provide light under the application of ultrasonic wave, the ML material can be considered as one of the first candidates for providing the ubiquitous light source to the photo-functional materials even in the on-site of bio-tissue and cell.

From these viewpoints, we have investigated USML, and we successfully detected the mechanoluminescence that depends on the input intensity of ultrasonic wave irradiation. Furthermore, though it was in primitive stage, we successfully demonstrated the USML acting as the light source for a photo-activation of TiO_2 photocatalyst for the first time.

2. Experimental

2.1. Materials

In our previous work, we have succeeded in developing ML materials with various emission colors, ultraviolet, blue, green, yellow and red [1–6,15,16]. In this time, however, europium doped strontium aluminate (denoted as $SrAl_2O_4$:Eu, or SAOE) was mainly used as the ML material, because SAOE was one of the most efficient ML material at this time. The emission peak is located at around the wavelength of 520 nm, produced by the transition of Eu^{2+} ions between $4f^7$ and $4f^65d^1$ in SAOE. From the SEM images, the size of the SAOE ceramic particles synthesized by solid phase method was estimated to be ca. 3–5 μm (Fig. 2). In addition, Eu^{2+}-doped $CaYAl_3O_7$ (CYAE, particle size: 1–5 μm, λ_{em} = 440 nm) was used as a blue emissive ML material at the experiment of ML material dependence on USML.

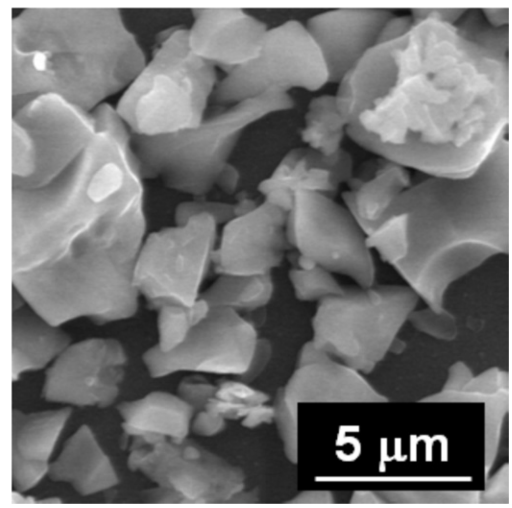

Fig. 2. SEM image of SAOE particle.

2.2. Experimental setup

2.2.1. Ultrasonic wave induced mechanoluminescence (USML)

The experimental setting is shown in Fig. 3. The ML particle was blended into adhesion matrix, and immobilized at the bottom of the sample tube with the depth of 2 mm. The ML particles immobilized sample tube was set at the center of the water bath (300 mm × 240 mm × 85 mm) of a commercial ultrasonic cleaner, with immersing 2 mm from the bottom.

Before the USML measurements, the ML sample tubes were irradiated by UV light (365 nm, 0.7 mW/cm^2) for 1 min and kept in the dark for 5 min to let their afterglow emission settle. The measurement protocol was same as those of conventional ML measurement using universal testing machine (Tensilon RTC-1310A), and the protocol greatly helped us to obtain quantitative results.

As to a mechanical stimulation for USML, 37 kHz of ultrasonic wave was irradiated through the water bath. The intensity of the input ultrasonic wave was controlled by changing the duty ratio of ultrasonic wave, and the intensity was measured by sound pressure meter (HUS-5, HONDA ELECTRONICS Co.), and it was shown as a relative output values as voltage. Emissive light from the ML sample tube was detected by using a photomultiplier and photon-counter (C-8855, Hamamatsu Photonics). The edge of the light fiber of the photomultiplier was set at the distance of 45 nm from the ML adhesion matrix at the bottom of the ML tube. As to the USML measurement, the ultrasonic wave was irradiated during 15 s at first, and then the ultrasonication was off during the next 15 s, and after that, the on and off process was done alternatively.

The measurement temperatures were kept constant from 20 – 60 °C by using circulating water and thermostatic bath during the measurement (Fig. 3).

2.2.2. Mechanoluminescence driven photocatalysis

The measurement was carried out through methylene blue method; it was standard evaluation technique for the TiO_2 photocatalyst. For the evaluation test, 100 mg of visible light responding TiO_2 (MPT-623, ISHIHARA SANYO KAISHA, LTD) was dispersed in 5 ml of 20 μM methylene blue ethanol (EtOH) solution, to obtain