Advanced Laser Science Research Section

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1. Introduction

Laser is a very powerful tool to probe physical or chemical processes and fabricate/modify the target materials. This year we have developed a few different techniques to probe the electrochemical processes, fabricate the functional metal surfaces, and modify the size and shape of nanoparticles.

2. Probing the electrochemical process through optical detection of laser-assisted bubbles during electrolysis

In recent years hydrogen evolution reaction (HER) through electrolysis of water is considered to be one of the promising methods to store renewable energy. While water electrolysis is a well-known process, realization of highly efficient HER still remains very challenging, since, first of all, nucleation of hydrogen gas bubble formation itself is not yet very well-understood, and this is particularly true for the case of macroscopic commercial electrodes which do not provide ideally flat and smooth surfaces. Recall that nucleation dynamics crucially depends on the surface roughness. Not only the nucleation dynamics but also the detachment of the bubbles also critically depends on the surface structures with a roughness of sub-μm.

Last year we have developed a new technique to probe the concentration profile of dissolved gas by optically monitoring the ascending bubbles in vicinity to the electrode, and extrapolated the concentration profile toward the electrode surface, because the direct probe of bubbles on the electrode was technically difficult. This year we have developed a new technique to directly probe bubbles on the electrode. The electrolysis condition where our optical technique is applicable is also extended to the lower current density where no bubbles are formed. The key technique is to introduce a laser pulse to form laser-assisted bubbles on the electrode even under very low current densities. The experimental setup is shown in Fig. 1. Representative photos of the bubbles formed on the electrode upon irradiation of a laser pulse from the bottom is shown in Fig. 1(a) and (b). Obviously the higher the current density the more the laser-assisted bubbles are formed underneath the electrode.

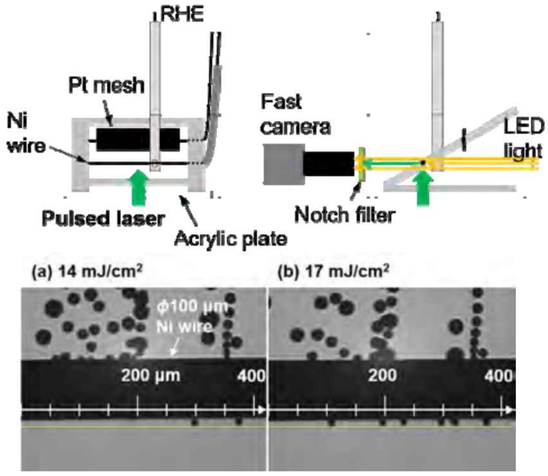

Fig. 1 (top) Experimental setup to detect laser induced bubbles during electrolysis and the measured bubbles underneath the Ni wire electrode at 20 ms after the laser pulse at the laser fluences of (a) 14 and (b) 17 mJ/cm^2.

Using a diffusion model we can estimate the dissolved H_2 gas concentration from the growth rates of the bubbles which varies in time after the laser pulse. Employing the two methods we have developed last year and this year, we estimate the dissolved H_2 gas concentration as a function of current density, and the results are compared in Fig. 2. We notice that the H_2 gas concentrations at the electrode obtained by the two methods, i.e., optical monitoring of ascending bubbles in vicinity to the electrode and laser-assisted bubbles on the electrode, are in reasonable agreement, and the latter shows the nicer linearity in current density, indicating the superiority of the method uti-

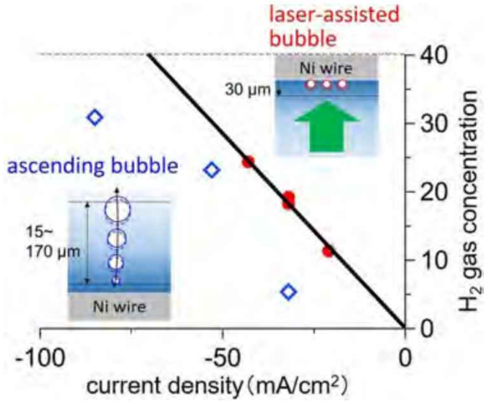

Fig. 2 Comparison of dissolved H_2 gas concentration at the Ni wire electrode by the two different methods we have developed, i.e., detection of ascending and laser-assisted bubbles.

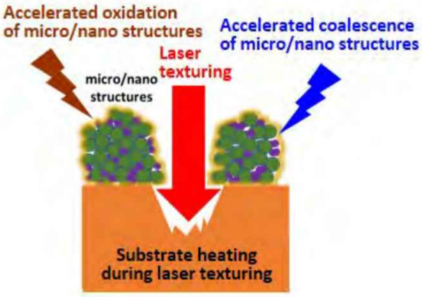

Fig. 3 Enhanced light absorption of metal surfaces by heat-assisted laser texturing.

lizing laser-assisted bubbles on the electrode.

3. Broadband light absorption of metal surfaces by heat-assisted laser texturing

Metal surfaces with high absorbance draw a lot of attention in recent years. In this work we have developed a new technique, heat-assisted laser texturing, to fabricate metal surfaces with broadband light absorption. In Fig. 3 we illustrate the underlying mechanism of enhanced light absorption by laser textured metal surfaces. Briefly, it comes from the geometric light trapping by micro/nano structures produced by laser texturing. The essence of heat-assisted laser texturing is to elevate the substrate temperature (by a few hundred °C) during laser texturing so that the texturing efficiency and oxidation speed are significantly promoted.

In Fig. 4 we summarize the reflectance of the Cu surfaces textured by the three different methods, i.e., laser texturing at room temperature, laser texturing at room temperature followed by thermal annealing at 300 °C for 1 hour, and heat-assisted laser texturing at 300 °C. It is clear that heat-assisted laser texturing is most effective.

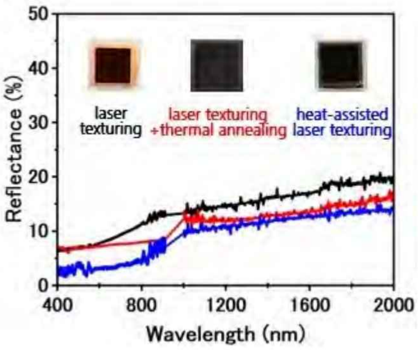

Fig. 4 Reflectance of Cu surfaces fabricated by the three different laser texturing methods.

4. Enhancing laser-nanoparticle interactions using a diffused laser beam

A laser beam with a good (flat-top or Gaussian) spatial profile is usually believed to be a prerequisite to maximize laser-matter interactions. What we have found in this work is that this is not necessarily true. As an example we demonstrate the efficient size-reduction of colloidal nanoparticles by a diffused laser beam. Representative results are summarized in Fig. 5, where colloidal silver nanoparticles with an initial diameter of 100 nm are irradiated by the pulsed laser beam at 532 nm with two different spatial profiles, normal and diffused beams. The normal beam directly coming from the laser output is converted to the diffused beam simply by placing a commercial holographic diffuser with transmission of 85 % and divergence angle of ~0.5°. From Fig. 5 we notice that the diffused beam significantly outperforms the normal beam in terms of the size reduction efficiency of nanoparticles, and the eminent peak appeared at ~400 nm by the diffused beam implies the very rapid size reduction of 100 nm Ag nanoparticles. To find the physical origin of this counterintuitive results we measure the beam profile to find that there are many bright speckles in the diffused beam as shown in the middle of Fig. 5. The XY-cuts of the normal and diffused beam profiles shown in the bottom of Fig. 5 clearly shows that the height of the speckles are by a few time higher than that of the normal beam with a nearly flat-top shape. Therefore, we can conclude that the physical origin of the counter-intuitively efficient laser-nanoparticle interactions by the diffused beam arises from the redistribution of laser energy by the formation of speckles where the local laser fluence exceeds the threshold of laser-induced size reduction.

Clearly, the demonstrated technique should be applicable to any kinds of nanoparticles and nanorods for size-reduction, reshaping, welding, etc., where a certain laser fluence threshold for the process exists.

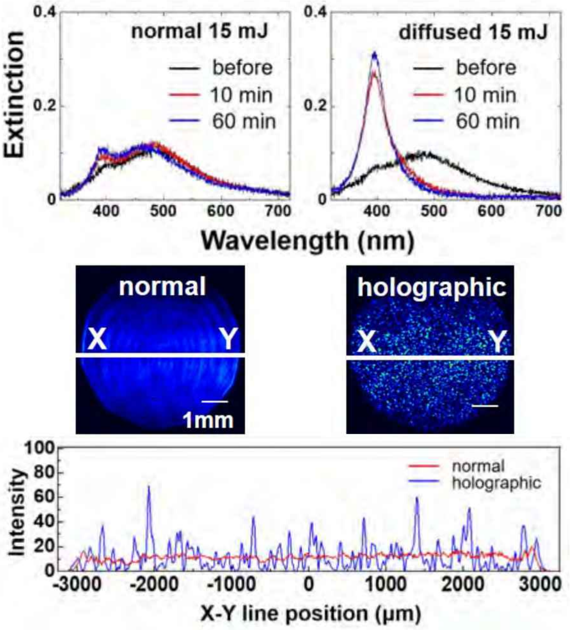

Fig. 5 Laser-induced size-reduction of Ag nanoparticles by the normal and diffused beams through a holographic diffuser.

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中嶋隆，新エネルギー・産業技術総合開発機構，水素利用等先導研究開発事業/水電解水素製造技術高度化のための基盤技術研究開発/アルカリ水電解及び固体高分子形水電解の高度化

Publications

K. Ando, Y. Uchimoto, T. Nakajima, Probing the Dissolved Gas Concentration on the Electrode through Laser-Assisted Bubbles, Journal of Physical Chemistry C, 125, 38, 20952-20957, 2021

Presentations

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