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Research paper

Hydrogen emission under laser exposure of colloidal solutions of nanoparticles

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ABSTRACT

We report the generation of molecular hydrogen from water by laser irradiation, without any electrodes and photocatalysts. A near infrared pulsed nanosecond laser is used for exposure of colloidal solution of Au nanoparticles suspended in water. Laser exposure of the colloidal solution results in formation of breakdown plasma in liquid and emission of H_2. The rate of H_2 emission depends critically on the energy of laser pulses. There is a certain threshold in laser fluence in liquid (around 50 J/cm^2) below which plasma disappears and H_2 emission stops. H_2 emission from colloidal solution of Au nanoparticles in ethanol is higher than that from similar water colloid. It is found that formation of plasma and emission of H_2 or D_2 can be induced by laser exposure of pure liquids, either H_2O or D_2O, respectively. The results are interpreted as water molecules splitting by direct electron impact from breakdown plasma.

1. Introduction

Laser ablation of solids in liquids is a physical method of generation of large variety of nanoparticles. Typically, a solid target is placed into liquid, which is transparent for laser radiation. If the laser fluence on the target is enough for its melting, then this melt is dispersed into surrounding liquid as nanoparticles (NPs). Virtually any liquid is suitable for generation of NPs in this way, water being the most common of them. Organic solvents, such as alcohols, are also frequently used for preparation of colloidal solutions of different NPs in them. Laser ablation of solids in liquids is accompanied by formation of plasma plume above the target. Plasma is also observed under laser exposure of colloidal solutions of NPs. If laser intensity is high enough for NPs to reach temperatures of about 10^4–10^5 K, some part of their atoms may be ionized [1]. When the fraction of these atoms reaches the critical value, plasma formation occurs [2]. Such type of plasma is often referred to as 'nanoplasma' [3] due to its confinement in the small region in the NP vicinity. At high laser pulse repetition rates these small sources of plasma may unite between each other resulting in the liquid breakdown plasma formation. This means that the medium inside the laser beam undergoes strong overheating and ionization. In these conditions both the liquid and the material of NPs are affected resulting in chemical changes of their composition. In case of organic solvents, e.g., ethanol, this leads to deep pyrolysis of the liquid down to formation of elementary glassy carbon [4]. In [5] the formation of hydrogen gas from a mixture of pure carbon powder and water via laser irradiation was reported with intense nanosecond laser pulses without any electrodes or photocatalysts. The authors suggest that carbon acts like a catalyst, since gaseous products contain CH_4, CO, CO_2, and H_2. The peak power density of laser radiation is of order of 100 mJ/cm^2, which is apparently insufficient for direct water breakdown. However, presence of carbon in reaction products indicates that carbon is not just a catalyst but rather initial component of the reaction.

The aim of the present work is search of one of most probable product of solvents degradation, namely, hydrogen. For this purpose we exposed colloidal solutions of Au NPs in water and ethanol to pulsed radiation of a Nd:YAG laser [6]. Presence of NPs provokes laser breakdown of the liquid and formation of microscopic plasma channel in it.

2. Experimental technique

Colloidal solutions of Au NPs were prepared using the technique of laser ablation in liquid. For this purpose, an Ytterbium fiber laser with pulse duration of 70 ns, repetition rate of 20 kHz and pulse energy of 1 mJ at 1060–1070 nm was used as irradiation source for NPs generation. Laser radiation was focused on metallic plate made of corresponding metal immersed into deionized water by

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an F-Theta objective. Laser beam was scanned across the sample surface at the speed of 1000 mm/s by means of galvo mirror system. Size distribution of obtained NPs was analyzed with Measuring Disc Centrifuge (CPS Instruments). Initial colloidal solution of Au NPs typically contained about 10^{12} NPs/ml with maximum of their size near 15 nm. Further irradiation of NPs colloidal solutions in absence of the target and diluted in necessary proportion was carried out using the radiation of the Nd:YAG laser at wavelength of 1064 nm and pulse duration of about 10 ns (FWHM). Laser radiation was focused inside the liquid by an F-Theta objective with focal distance of 90 mm (Fig. 1). Laser beam was scanned across the window along circular trajectory about 8 mm in diameter at the velocity of 1000–3000 mm/s by means of galvo mirror system. Laser exposure of 4 ml portions of colloids was carried out at 2 mJ energy per pulse and repetition rate of laser pulses of 10 kHz. Estimated diameter of the laser beam waist was 50 μm, which corresponds to laser fluence in the liquid of 80 J/cm^2. Bright cylinder made of plasma appeared 2–3 mm above the window inner surface and looks continuous for eye.

Amperometric hydrogen sensor was used to monitor the concentration of H_2 in the space above the liquid surface. Excessive pressure in the system was released to ambient air through a glass capillary dipped in 2 mm thick water layer. In this case the total pressure in the cell was equal to atmospheric one. Inner electrolyte of the sensor is separated from the cell atmosphere by a membrane pervious only to H_2. The sensor indicates either the concentration of H_2 in μg/l or its partial pressure in Torrs. Calibration of the sensor was performed in air (no H_2) and in 1 atmosphere of H_2. The precision of H_2 concentration measurements is 5%. Total volume of the atmosphere above the water level can be estimated as 10 ml. The characteristic time of sensor response in current geometry is about 5 min.

3. Results

Laser exposure of the colloidal solution is accompanied by formation of plasma. The liquid breakdown produces sound though its frequency is less than the repetition rate of laser pulses. This means that the breakdown occurs not at each laser pulse.

Typical evolution curve of H_2 concentration under exposure of the colloidal solution of Au NPs is presented in Fig. 2, which shows three consecutive laser exposures of the same colloidal solution. As one can see, the emission of H_2 is well-reproducible. Hydrogen detector was purged by air between exposures. Typically, partial pressure of H_2 amounts to 200–300 Torr. For the given setup the highest rate of H_2 emission is achieved at 10 min of laser exposure. Au NPs in the laser-exposed solution are fragmented to smaller NPs [7] with measured final size of few nm.

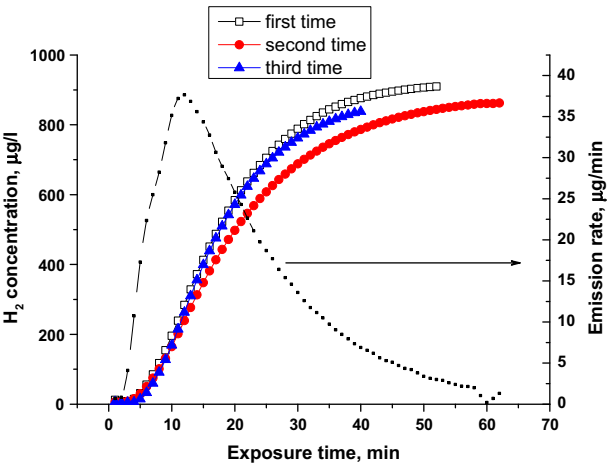

Fig. 2. Time dependence of H_2 concentration under 3 consecutive laser exposures of the same colloidal solution. Scanning velocity of 1000 mm/s, energy per pulse is 2 mJ, concentration of Au NPs of 10^{10} cm^{-3}. Dashed line is the rate of hydrogen emission for the second laser exposure.

It was found that the stationary concentration of emitted H_2 depends on the concentration of Au NPs at otherwise equal experimental conditions. Namely, the concentration of H_2 decreases with the increase of concentration of Au NPs.

Laser exposure of the liquid is accompanied by formation multiple gas bubbles that ascends to the liquid surface. From time to time during exposure these bubbles can enter to the laser beam. This leads to micro-explosion of bubbles with well-discernable sound.

The decrease of H_2 content with the increase of concentration of NPs is due to both scattering and absorption of laser radiation in water by NPs. As a result, the peak intensity of laser radiation inside the beam waist decreases, and plasma formation is dumped. Similar tendency is shown in Fig. 3 for various levels of laser pulse energy with the same position of the laser beam waist with respect to window. Interestingly, H_2 emission can also be observed under

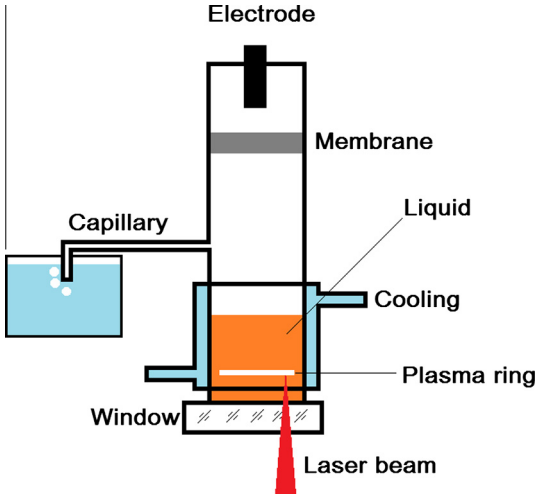

Fig. 1. Experimental setup for hydrogen emission.

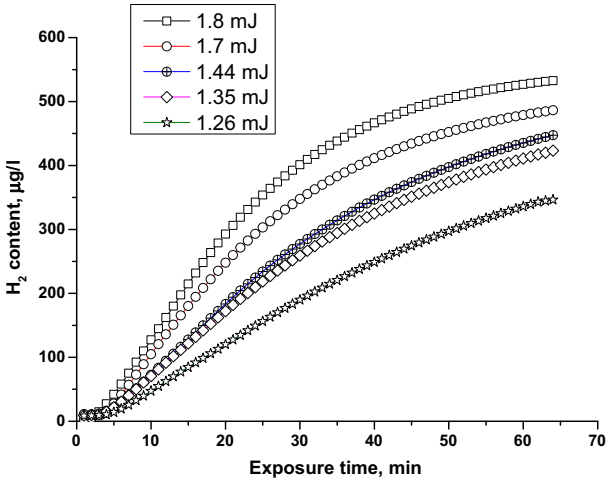

Fig. 3. Dependence of H_2 content above the liquid on exposure time of laser irradiation at various values of energy per pulse. Scanning velocity of the beam of 3000 mm/s, technical water.