

COMBUSTION OF HYDROGEN–OXYGEN MIXTURE
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Observation of a spontaneous reaction between hydrogen and oxygen in bubbles in water whose diameter is smaller than a threshold value around 150 nm is presented. The effect is attributed to high Laplace pressure and to fast dynamics in nanobubbles and is the first indication on combustion in the nanoscale. The bubbles were produced by water electrolysis in specially designed microchips using successive generation of H₂ and O₂ above the same electrode with short voltage pulses in the microsecond range. Different signatures indicating the combustion process are described.

Introduction

It is known that gas-phase reactions in bubbles can be driven by acoustic [1] or hydrodynamic [2] cavitation, but there were no reports on spontaneous chemical reactions. Burning of hydrocarbons in millimeter sized bubbles in water was demonstrated [3], where the reaction was ignited by an electrical discharge. Combustion in three-dimensional microscopic volumes has never been observed. Ignition of exothermic reactions in small volumes is considered as difficult or not possible at all due to significant heat losses on the volume boundary [4, 5]. This puts strong restriction on the design of microengines.

Below a certain size, the material properties can change drastically [6]. For example, the surface tension can support metastable phases of nanocrystals [7] that exist only at high pressure for bulk materials. In liquids, the surface tension results in significant pressure

inside the nanobubbles that together with fast dynamical processes can promote unexpected behavior of the chemical reactions. Moreover, it is clear that the classical combustion theory [8] cannot be applied to nanobubbles because the bubble size is much smaller than the reaction zone size.

In the present work, the reaction started spontaneously in nanobubbles containing H_2 and O_2 gases in amounts close to the stoichiometric ratio if the size of bubbles was smaller than a threshold value of 100–200 nm. A simple way to produce such nanobubbles is electrolysis of water in microsystems with short voltage pulses of alternating polarity. It was observed that for pulses shorter than 25 μs , the bubble production disappears unexpectedly accompanied by a considerable damage of the electrode surface. At the same time, the short pulses of single polarity still produce gases (H_2 or O_2) in agreement with the Faraday law and do not damage the surface. The gas disappearance was observed in the system interferometrically. The pressure waves produced by exploding bubbles were directly observed via the movement of the membrane in the closed system. Thermal effect of the reaction was measured with a probe positioned in the vicinity of the electrodes.

Experimental

For the experiments, the microchips containing the pairs of microelectrodes of different shapes and sizes on glass or silicon substrates (Fig. 1a) have been used. The electrodes materials were Pt, Pd, W, and Au deposited up to 100 nm on separate substrates and patterned. The solution for electrolysis was 1 M of Na_2SO_4 in deionized water. The process was observed with a homemade stroboscopic system [9] that controlled the electric and light pulses on the scale of microseconds.

The electrochemical process at short times of 10–100 μs was tested by applying negative or positive voltage pulses to the working electrode (the other one was grounded) and producing hydrogen or oxygen above this electrode. To create the bubbles containing both gases, there were applied square voltage pulses of alternating polarity repeated with a frequency f so that hydrogen and oxygen were produced alternately above the working electrode. The experiment demonstrated that for

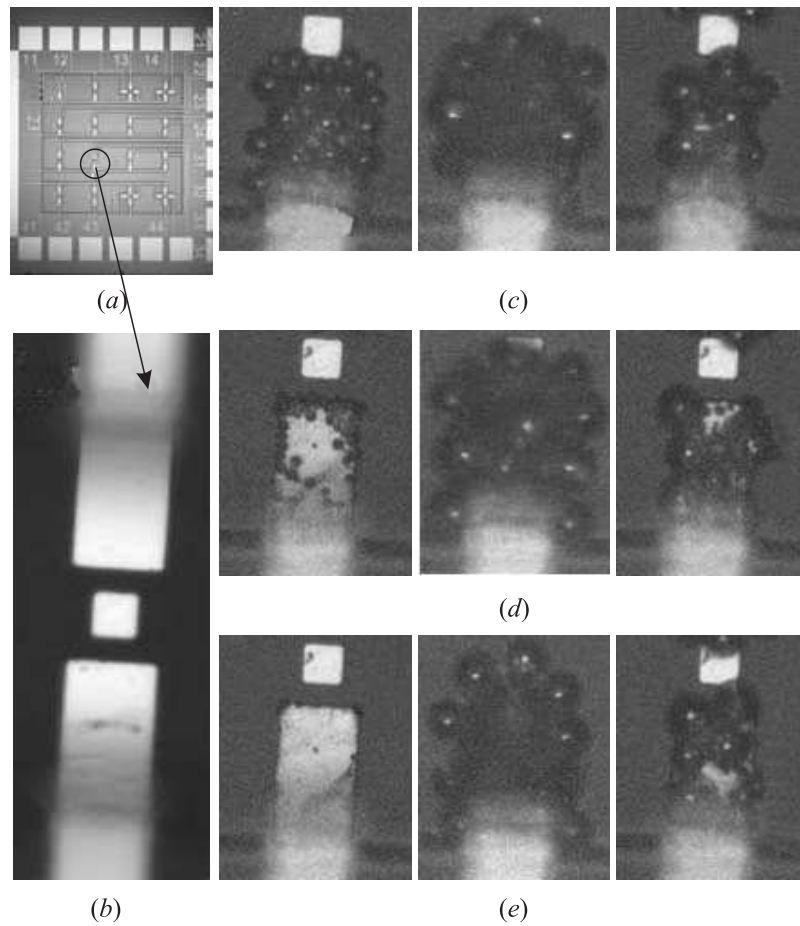


Figure 1 Disappearance of gas production for alternating polarity pulses: (a) chip; (b) Pt electrodes before the process; (c) gas production after 1-millisecond process. The left image is for alternating sign ($f = 20$ kHz), both H_2 and O_2 gases are produced. The middle image is for negative voltage pulses, only H_2 is produced. The right image is for positive voltage pulses, only O_2 is produced; (d) the same as (c), but for $f = 50$ kHz, small amount of gas is visible in the left image; and (e) the same as (c), but for $f = 100$ kHz, no gas is visible in the left image

$f > 20$ kHz, the gas volume produced by pulses of alternating polarity was drastically decreased (Fig. 1). The effect of gas disappearance is related to its stoichiometric production. Deviation of the duty cycle of the pulses from 50% in any direction leads to an increase in the visible gas volume revealing excessive H_2 or O_2 .

Electrolysis with alternating polarity pulses results in a significant modification of the electrode surface that is clearly visible in an optical microscope (Fig. 2a). This effect has never been observed when the fixed polarity pulses have been used. The modification becomes stronger with the process time. It was observed for all electrode materials but was strongest for gold and weakest for tungsten, correlating with the material's yield strength. The atomic force microscopy (AFM) scans show significant displacement of the electrode material (Fig. 2b). The process changes also the structure of the rough surface (Figs. 2c and 2d). The authors conclude that the surface modification has a mechanical origin.

To gain a deeper insight into the disappearance of gas production, the process with a vibrometer (Polytec MSA-400) has been observed. A laser beam ($\lambda = 633$ nm), with a diameter of $1.5 \mu\text{m}$, was focused on the electrode at some distance (around $5 \mu\text{m}$) from the edge. The signal $v(t)$ (velocity) is nonzero because the current results in gas formation, which changes the refraction index of the liquid. This is true so long as the gas does not form bubbles comparable in size with λ/π ; otherwise, scattering on the bubbles becomes overwhelming, and the signal cannot be related to the amount of gas in liquid (Fig. 3a). When the bubbles are small enough, the signal unambiguously demonstrates a response to the current pulses (Figs. 3b and 3c). The peaks in the signal are related to the gas disappearance in the reaction.

Discussion

All observed phenomena can be understood as a chemical reaction that occurs in nanobubbles. Hydrogen produced by a negative voltage pulse creates high supersaturation in the liquid. This results in homogeneous nucleation of H_2 bubbles that immediately start to grow. The positive half of the pulse produces oxygen, which diffuses into the existing H_2 bubbles. For high frequencies, the gas composition in a bubble becomes

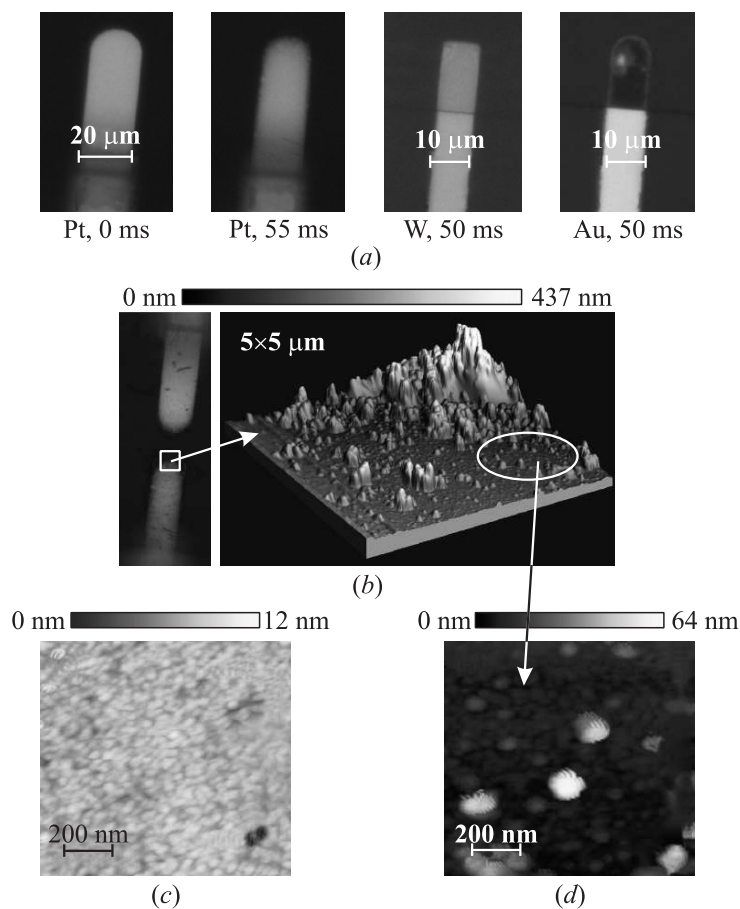


Figure 2 Modification (wear) of the electrode surface with the process ($f = 100$ kHz): (a) electrodes of different materials in liquid after a fixed process time. The left image is a Pt electrode before the process (reference); (b) the optical image in air (left) of the well-worn Pt electrodes (55 ms). The right image is an AFM scan made in the highlighted region. A significant displacement of the electrode material is visible; (c) Pt electrode before the process (reference); and (d) zoomed area image demonstrates significant change in the surface roughness

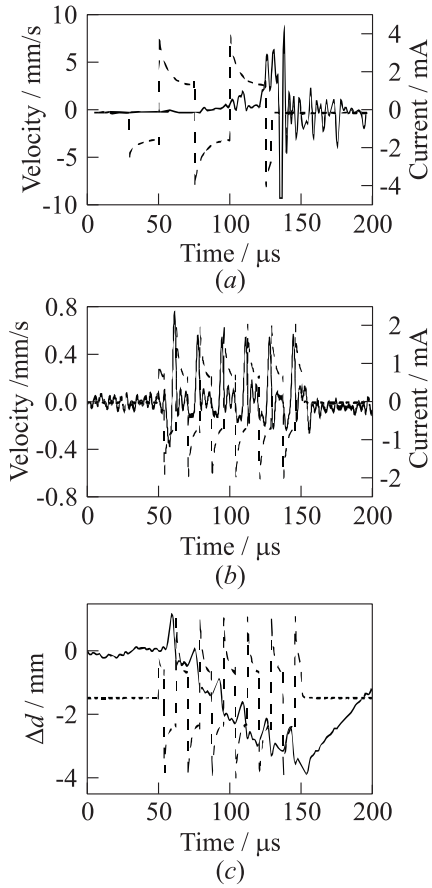


Figure 3 Observation with a vibrometer: (a) processing at low frequency, $f = 20$ kHz, results in the formation of bubbles comparable in size with λ/π , which scatter light significantly. No information can be extracted; (b) the vibrometer signal and current as functions of time at $f = 60$ kHz. The thick curve is the signal and the thin curve is the current. The signal peaks are clearly related to the current pulses; and (c) the signal in (b) integrated in time (thick curve). The dashed curve (current) is given for eye guidance. The peaks in $\Delta d(t)$ indicate the presence of a reaction between gases

stoichiometric while its size is far below 1 μm . The capillary pressure in bubbles (28 bar for a bubble 100 nm in diameter) promotes ignition of the reaction. The precise mechanism of this promotion is not yet clear, but the chemical equilibrium in bubbles is shifted [10] and it is known that fast dynamical processes play the role of ignition on the macroscale [11, 12]. If the frequency is low, the bubble reaches the stoichiometric composition for the larger size, and the capillary pressure is not sufficient to ignite the reaction. The critical diameter of a bubble is estimated as $d_c = 100\text{--}200$ nm. The reaction in a bubble is accompanied by the release of a considerable amount of chemical energy, fast condensation of the reaction product, and fast change in the pressure. As a result, the bubble is destroyed in a violent act, but the details are not yet clear. The violent evolution of bubbles is the reason for the visible damage of the electrode surfaces.

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