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Synthesis of two-dimensional lead sheets by spark discharge in liquid nitrogen

Ahmad Hamdan[a,1], Hiba Kabbara[a], Cédric Noël[a,b], Jaafar Ghanbaja[a], Abdelkrim Redjaimia[a], Thierry Belmonte[a,b,*]

[a] Université de Lorraine, Institut Jean Lamour, UMR CNRS 7198, Nancy F-54042, France
[b] CNRS, Institut Jean Lamour, UMR CNRS 7198, Nancy F-54042, France

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ABSTRACT

A simple method to synthesise hexagonal lead sheets, which belong to the class of two-dimensional materials, is proposed. These objects are collected on a substrate located under two lead electrodes, between which nanosecond-pulsed spark discharges are ignited in liquid nitrogen. The hexagonal sheets are single crystals produced by gas phase condensation. Once nitrogen completely evaporates, the sheets change to PbO_2 by oxidation in air. The oxidation process induces stress that pleats the uppermost sheets or open cracks at the centre. The thickness of the individual objects typically varies from 4 to 20 nm. When the number of discharges is more than about 2000, in addition to sheets, two types of PbO_2 sticks start to form: bundles composed of nanosticks (length 5 μm and diameter 50 nm) and isolated sticks (length 20 μm and diameter 500 nm). These new nanostructures mainly form because of the way the discharge erodes the lead electrodes. Initially, anisotropic erosion driven by the orientation of the crystallographic planes of the lead crystals produces octahedra and nanosticks, and the nanosticks grow on the electrode surfaces as discharge proceeds. After about 2000 discharges, the nanosticks are sufficiently long that they can be easily broken, probably by mechanical stress, and they fall onto the underlying substrate.

Introduction

Plasmas in liquids or in contact with liquids have been investigated to understand and control the interaction between plasmas and materials (Graham & Stalder, 2011; Mariotti & Sankaran, 2010). Plasmas generated in liquids have attractive characteristics, such as high temperature, high pressure, high density of chemically active species, shock waves, and intense radiation (Akiyama, 2000). This environment has potential applications in the fields of materials (Mariotti & Sankaran, 2010) and medicine (Fridman et al., 2007; Lee et al., 2009). Furthermore, discharge in liquids is known to achieve the highest production yields of nanomaterials by physical methods, which makes it important for mass production at low cost.

Because electrodes can be considered as a reservoir of matter to synthesise nanoparticles (Schur et al., 2007), a large variety of materials can be processed by discharge in liquids. Using different materials as the anode and cathode can lead to synthesis of metallic alloys or core–shell structures (Abdullaeva et al., 2012). The chemical and physical properties of the liquid play a crucial role in this process. The liquid can be inert (e.g., nitrogen or helium), reactive (e.g., water or alcohol), or used as a source of matter (e.g., hydrocarbons or organosilicon). For instance, discharge in hydrocarbons spontaneously produces carbon nanoparticles (Ahmed, Aitani, Rahman, Al-Dawood, & Al-Muhaish, 2009), while discharge in liquid nitrogen with carbon electrodes produces different carbon nanostructures, such as nano-onions, nanohorns, and nanowires (Sano & Ukita, 2006). The electrical parameters also greatly affect the way the electrodes are eroded, and they change the chemical processes in the plasma. There are two main categories of electrical discharges: high current–low voltage (~100 A, 30 V) (Sano, 2004) and high current-high voltage (~100 A, 10 kV) (Kuskova, Boguslavskii, Smal'ko, & Zubenko, 2007). Plasma ignition is only possible in the former category if the electrodes are placed in contact.

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[*] Corresponding author at: Université de Lorraine, Institut Jean Lamour, UMR CNRS 7198, Nancy F-54042, France.
E-mail address: thierry.belmonte@univ-lorraine.fr (T. Belmonte).
[1] Current address: Groupe de physique des plasmas, Université de Montréal, C.P. 6128, Succ. Centre-ville, Montréal, Québec H3C 3J7, Canada.

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Lead nanostructures have applications in several fields. They can be used for the development of sensors in nanotechnology. Metallopolymer films containing lead nanoparticles exhibit sensor activity in the presence of ammonia (Bochenkov, Stephan, Brehmer, Zagorskii, & Sergeev, 2002). Lead oxide nanosheets could be used as the active materials of lead–acid batteries (Karami et al., 2008). Shi, Xu, and Li (2008) showed that the morphology and size of the electrode components affect the operating electrochemical activity of the electrodes in batteries.

Deposition of lead thin films is of great scientific and technological importance in superconductivity. For example, there is a superconductor–insulator transition in lead thin films with disorder, where the onset of superconductivity is defined by the critical sheet resistance (Haviland, Liu, & Goldman, 1989; Strongin, Thompson, Kammerer, & Crow, 1970). Because the critical sheet resistance is inversely proportional to the film thickness, the transition temperature rapidly decreases in ultrathin films (Eom, Qin, Chou, & Shih, 2006).

The magnetic properties of lead are attractive for biomolecular studies by nuclear magnetic resonance. Lead nanostructures can also be used as probes to study the metal–ion binding sites in proteins because there is a large dispersion in the chemical shifts of the ^{207}Pb signals in proteins. This illustrates the remarkable sensitivity of this element to subtle differences in the chemical environment within proteins (Aramini et al., 1996).

In this study, we investigated the lead nanostructures formed by electrical discharge in liquid nitrogen between two lead electrodes submitted to high voltage and high current. Experiments were also performed in water rather than liquid nitrogen to clarify some aspects of the growth mechanisms.

Experimental

The experimental setup used to study discharge in the pin-to-pin configuration is shown in Fig. 1(a). Two lead wires were used as the electrodes (diameter 0.5 mm, purity 99.999%, Good Fellow, UK). The distance between the two electrodes was set to 100 ± 10 μm using a micrometric screw. A high DC voltage power supply (SR15-R-1200–15 kV–80 mA, Technix, France) fed a high-voltage solid-state switch (HTS-301-03-GSM, Behlke, Germany), which typically delivered a current of about 30 A under a voltage of 10 kV for 300 ns in a 50 ns rise time (Fig. 1(b)). The operating frequency was 3 Hz (see Hamdan, Noel, Kosior, Henrion, & Belmonte, 2013) for more details). A Dewar vessel (volume 400 cm^3) was filled with liquid nitrogen. A substrate was placed on the bottom of the vessel to collect the particles synthesized by successive discharges. Four types of substrates were used: silicon wafers, holey carbon grids, aluminium plates, and 316 L stainless steel plates. The aluminium and 316 L stainless steel plates were mechanically polished (final stage 1 μm diamond paste) and ultrasonically cleaned in ethanol. After discharge processing, the liquid nitrogen evaporated and the synthesised nanomaterials were exposed to air. They were then characterized.

Scanning electron microscopy (SEM, Quanta 600 FEG, FEI XL 30, FEI, USA) was performed for structural and chemical characterization. The Quanta 600 scanning electron microscope was equipped with a micro energy-dispersive X-ray (EDX) spectrometer, which was used in mapping mode. The XL 30 scanning electron microscope was equipped with a TLD (through the lens detector) detector and it was used for high-resolution imaging. Atomic force microscopy (AFM) was performed with a SOLVER Nano atomic force microscope (NT-MDT Spectrum Instruments, Solver, Russia) in semi-contact mode (free resonance at 100 kHz and force constant set to 2.0 N/m). A Philips CM200 (Netherlands) transmission electron microscope and a JEOL ARM200F (Japan) cold FEG device were used for transmission electron microscopy (TEM) to investigate the morphology (with atomic resolution), crystallinity, and chemical composition of the nano-objects.

During processing, the volume of liquid nitrogen was kept constant by regularly compensating for loss by evaporation. The growth mechanisms and the influence of the number of discharges on the synthesized nanostructures were thoroughly investigated. Four cases were investigated: 100, 300, 1000, and 2000 discharges. The number of discharges is an important parameter that is directly related to etching of the lead electrodes by the plasma and the nature of the synthesized objects.

Results and discussion

Synthesized nano-objects

After evaporation of liquid nitrogen, the surface of the substrate can be covered by different types of nano-objects. By weighing the substrate after a set of discharges, we estimated that the average deposition rate per discharge is ~1.0 μg. Fig. 2 shows low-magnification SEM images of the most commonly encountered objects after 1000 and 2000 discharges:

1. Hexagonal or half hexagonal sheets (~5 μm in diameter and several nanometres in thickness, Fig. 2(a) and (c)).
2. Isolated sticks (~500 nm in diameter and ~20 μm in length) together with bundles of nanosticks (~50 nm in diameter and ~5 μm in length) (Fig. 2(b), (d), and (e)).

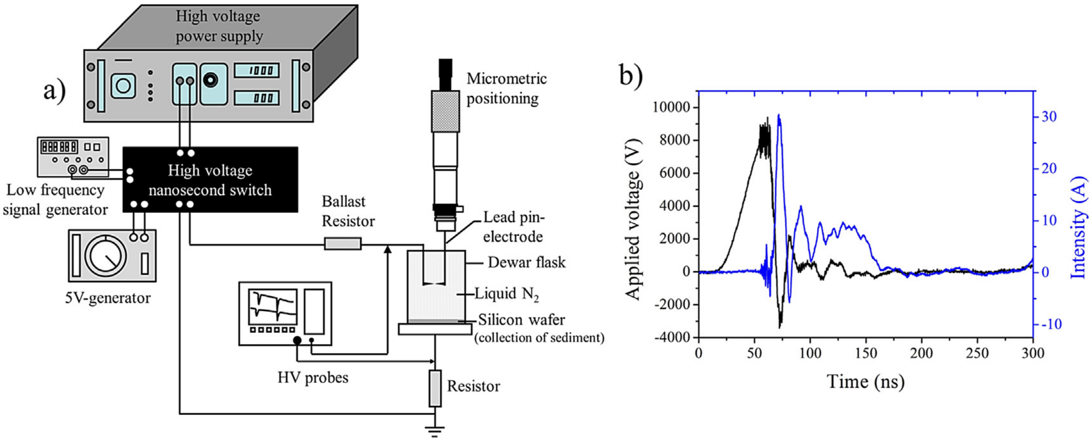

Fig. 1. (a) Experimental setup and (b) electrical characteristics of one discharge in liquid nitrogen.

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