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Bubble-assisted microstreaming during electrode deposition of Mn_2O_3 energy harvesters†

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The deposition of energy-harvesting Mn_2O_3 onto the “Cu” electrode is reported using pulsed laser ablation at the manganese–water interface. Conventionally, laser-induced plasma deposition is carried out by orthogonally placing the substrate (electrodes) in the plasma expansion. Here, underwater material deposition is observed on electrodes placed parallel to the plasma expansion. The possible role played by the fluid dynamically assisted microbubbles in transporting the materials onto electrodes is investigated here. To verify the influence of microbubbles, external electric fields are employed, and implications for the electrodes are characterized. The studies reveal that the external field intensifies the flow of the microbubbles towards the walls, which assists in the deposition of Mn_2O_3 on the electrodes.

1. Introduction

Pulsed laser ablation in liquid (PLAL) with a submerged solid target uses a powerful laser beam that, upon irradiation, ablates the target surface and forms a hot plasma that adiabatically expands against the liquid medium. Due to the suppression of plasma expansion by the surrounding liquid, it forcefully ejects its constituent species into the liquid medium that acts as a nucleation site for the formation of nanoparticles. Later, in these active sites, nanoparticles are surrounded by micrometer-sized bubbles, reportedly known as persistent microbubbles, child bubbles, or microscopic bubbles.^{1–4} In addition, a concurrent vapor layer of a macro bubble (diameter a few mm) encasing the transient plasma is observed at the target–liquid interface.² Following plasma cooling, the remnant nanoparticles are formed inside macro bubbles, oscillating to maintain the surrounding liquid hydrostatic pressure. These nanoparticles are dispersed in the liquid predominantly during the collapse phase.⁵

Numerous reports are available on transient cavitation (macro) bubbles, with more recent work focusing on persistent (micro)bubbles.^{6–9} The microbubbles exhibit a large specific surface area, a higher mass transfer coefficient, slow rising velocity, and larger free radicals, finding implications in precision drug delivery, flotation technology, mineral processing,

industrial wastewater treatment, and biomedical imaging.^{10,11} The role of persistent bubbles in nanoparticle synthesis produced by ablating solid targets such as Ti, Fe, Al, Cu, Au, and Ag in liquid has already been reported.^{4,12} Due to the unique physiochemical properties of the microbubbles, the dynamics of the Mn_2O_3 -filled microbubbles are studied here. Laser irradiation of the Mn target immersed in water leads to the formation of Mn_2O_3 nanoparticles and transient bubbles.¹³ Amongst other available manganese-based oxides, Mn_2O_3 is the most efficient catalyst for water oxidation.¹⁴ Mn_2O_3 shows multiferroicity and magnetoelectric coupling.¹⁵ Trivalent manganese oxide with Jahn–Teller (J.T.) distortion induces high activity for the oxygen evolution reaction (OER).¹⁶ Known to be an earth-abundant, low-cost material with less toxicity, it acts as an energy harvesting material and finds use in fuel cells, water splitting, supercapacitors, metal–air batteries, rechargeable batteries, and cathode materials in aqueous and non-aqueous batteries.^{2,6,17}

Recent trends in sustainable cooling use microfluidics in the thermal management of electronic devices. Thus, the velocity gradients imparted by macro bubbles leading to microstreaming and perturbing the trajectories of microbubbles for electrode deposition of Mn_2O_3 materials are investigated.¹⁸ In this work, external electrodes with D.C. are placed across the laser-irradiated manganese target in water. Electric field-assisted laser ablation in liquids (EFLAL) is used to study its effect on electrode deposition.^{19,20}

2. Experimental set-up

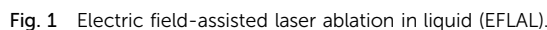
In Fig. 1, a target holder is used to hold a manganese target of size 4 mm at the bottom of the liquid cell filled with a distilled-

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3.2. Electrode deposition

Post laser ablation, deposition on “Cu” electrodes is analyzed. The micro-Raman spectra of the electrode at 0 V m^{-1} and 3750 V m^{-1} are shown in Fig. 4(a). Four Raman modes are observed in the absence of the electric field; however, an extra peak at 330 cm^{-1} emerges in the presence of an electric field of 3750 V m^{-1} . The Raman modes at 220 cm^{-1} and 416 cm^{-1} are assigned to the $2E_g$ and A_g vibrational modes of Cu_2O , respectively.²⁴ The one at 330 cm^{-1} is due to the $B^{(1)}_g$ vibrational modes of CuO .^{24,25} The Raman peaks of the Mn_2O_3 nanoparticles deposited on the electrodes have redshifted to 530 cm^{-1} and 626 cm^{-1} peaks. The peaks are assigned to the asymmetric stretching of oxygen bridge species (Mn–O–Mn) and the symmetric stretching mode of Mn^{3+} ions in the Mn–O bond in $\alpha\text{-Mn}_2\text{O}_3$ nanoparticles.²² The substrate (electrode) that collects the Mn_2O_3 nanoparticles is copper which oxidizes in the presence of water.

Fig. 4(b) depicts the XRD pattern of the electrode at 0 V m^{-1} and 3750 V m^{-1} applied electric field. The sharp peaks positioned at 26° , 28° and 34° are assigned to cubic bixbyite $\alpha\text{-Mn}_2\text{O}_3$ nanoparticles, which correspond to reflection from the (220), (310), and (222) planes.²⁶ The other peaks at 269° and 36° correspond to the (110) and (111) planes of Cu_2O , respectively,

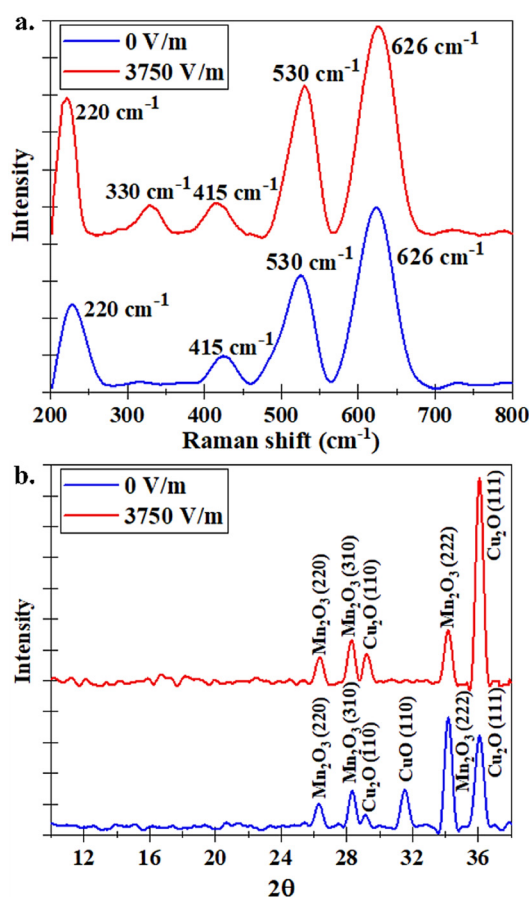


Fig. 4 (a) Micro-Raman spectra of the electrodes without (0 V m^{-1}) and with (3750 V m^{-1}) applied electric field. (b) XRD pattern of the electrodes at an applied electric field of 0 V m^{-1} and 3750 V m^{-1} .

whereas that at 31° is due to reflection from the (110) plane of CuO .²⁴ Thus, the deposition of $\alpha\text{-Mn}_2\text{O}_3$ on the electrodes is also affirmed.

Conventionally, the pulsed laser deposition in liquids is carried out by keeping the substrate parallel to the target for optimum deposition of target materials.²⁷ Laser plasma in liquid depicts ~ 70 times smaller expansion velocities as compared to ambient air with the ion and electron densities mostly confined along the direction of the laser plasma.²⁸ The ejection of materials from the collapse of transient bubbles (macro) attached to the target is also predominantly directed toward the source laser. In contrast, the electrode deposition here is observed by placing the electrodes orthogonal to the target geometry. Thus, it is intriguing to explore the dynamics of the underwater electrode deposition. To divulge more, the Cu electrode where Mn_2O_3 gets deposited ($0^\circ - 45^\circ$) is characterized using SEM.

The nanoparticles formed by nanosecond PLAL are said to be negatively charged due to the absorbed electrons onto the nanoparticles synthesized using this technique.²⁹ Hence, SEM analysis has been carried out on the positively charged electrode. The SEM images of the electrodes, as shown in Fig. 5, at (a) 0 V m^{-1} and (b) 3750 V m^{-1} show the deposition of $\alpha\text{-Mn}_2\text{O}_3$ nanoparticles on the “Cu” electrodes. The EDX data (not shown here) reveal an increment in Mn content by 10% with the application of an electric field. Also, in the presence of an

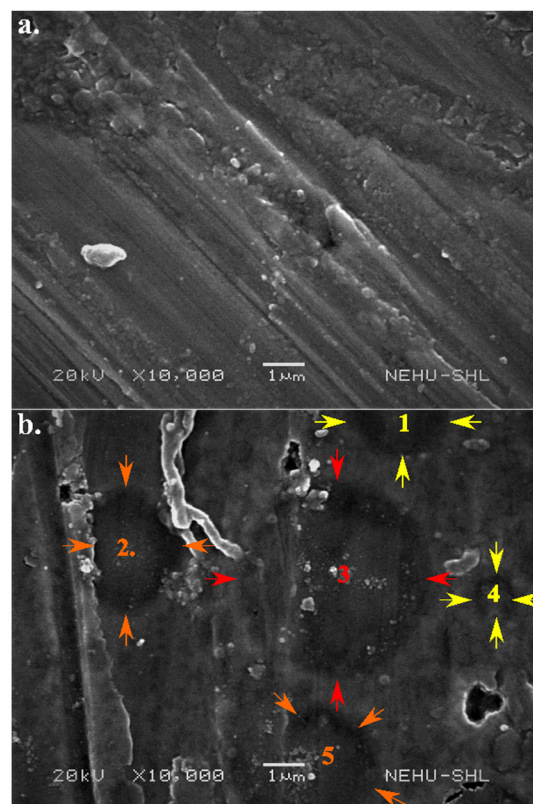


Fig. 5 SEM images showing the surface of electrodes post-ablation at (a) 0 V m^{-1} and (b) 3750 V m^{-1} deposition. To divulge more, the Cu electrode where Mn_2O_3 gets deposited ($0^\circ - 45^\circ$) is characterized using SEM.

external electric field (Fig. 5(b)), micro-sized circular layers of dimension 2–5 μm (arrows marked as 1–5) on the electrodes are visible. These circles are attributed to forceful bombardment by the periphery of micro-sized bubbles onto the electrodes. The dimension of these circular impacts depends on the contact radius.³⁰ Most microbubbles collapse, disperse nanoparticles in the liquid, or act as nucleation sites, while few get deposited onto the electrodes.

3.3. Streamline motion of microbubbles

The microbubbles in PLAL are also observed using imaging at the target–liquid interface. Fig. 6 shows the shadowgraph image of macro (MB) and micro (Mi-B) bubbles at the target–liquid interface at 0 V m^{-1} . The image is taken after 7 μs of pulsed laser irradiation on a fresh target and water surface. The experimental details of shadowgraphy are reported elsewhere.³¹ Here MB represents the macro bubble (dimension: 1000 μm) is attached to the target, while Mi-B represents microbubbles (dimension: 40–190 μm) dispersed in the surrounding liquid. These persistent bubbles are observed if the applied laser fluence is above the threshold.² Fig. 7(a) represents the coordinates of these microbubbles taken from shadowgraphy data repeated over 20 laser shots. The angular coordinates “ θ ” and radial coordinate “ r ” of microbubbles are defined about the center of the macro bubble with radius “ a .”

The macro bubble oscillations (growth, collapse, rebound) impart a gradient in the surrounding liquid flow.³² The oscillations of the macro bubble will create a streaming motion around it due to its non-linear effects which are localized near its wall with a flow pattern based on the mode of its oscillations. Here, one side of the macro-bubble is fixed to the wall (target), and the bubble undergoes volumetric and translational motion.³³ The bubble streaming Reynolds number (Re_s) is³⁴

$$\text{Re}_s = \varepsilon^2 \sqrt{\left(\frac{\omega a^2}{\eta}\right)} \quad (1)$$

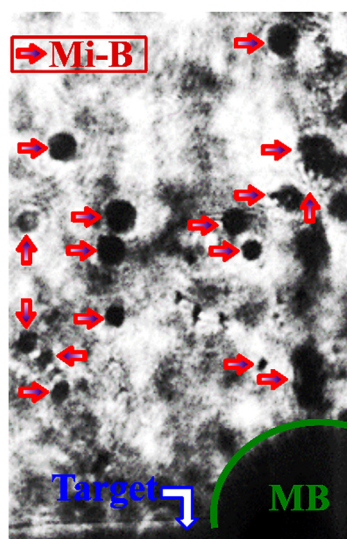


Fig. 6 Shadowgraph image of the target–liquid interface (MB: macro bubble, Mi-B: micro bubble).

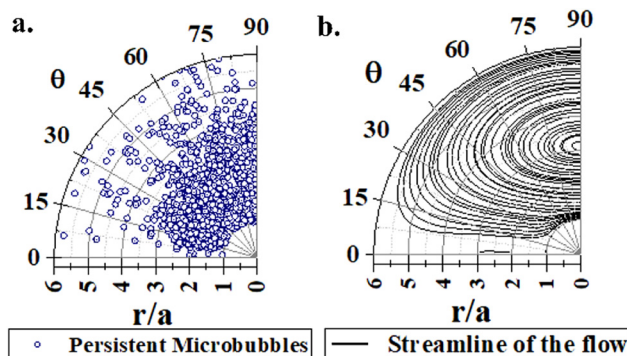


Fig. 7 (a) Coordinates of the microbubble at 0 V m^{-1} . (b) Simulated streamline flow of the microbubbles induced by the oscillations of the macro bubble at 0 V m^{-1} .

where ε , ω and η are the radial oscillation amplitude, frequency of oscillation (2.32 kHz), and kinematic viscosity ($1 \times 10^{-5} \text{ ms}^{-2}$), respectively. The value of Re_s is found to be 0.27. Since $\text{Re}_s < 1$, Rayleigh–Nyborg–Westervelt (RNW) streaming is considered which is a secondary flow pattern.^{34,35} Longuet-Higgins solved the RNW microstreaming (Ψ_2^s) due to the oscillation of a fixed bubble described below:³³

$$\psi_2^s = \frac{\varepsilon^2}{4} a^3 \omega \sin(\Delta\phi) \left[-2\frac{r}{a} + \frac{a}{r} + \left(\frac{a}{r}\right)^4 \right] (\sin \theta)^2 \quad (2)$$

The parameter $\Delta\phi$ is the phase difference between the volumetric and translational motions of the macro bubble and θ is the flow angle with respect to the horizontal axis along the target surface.

The RNW flow pattern (Ψ_2^s) obtained from eqn (2) is shown in Fig. 7(b). This simulated flow pattern complies with the dispersion pattern of the microbubbles, as shown in Fig. 7(a). For the flow pattern, the higher order contribution in the Navier-Stokes equations is not considered as the shadowgraph image resolution is $\sim 3 \mu\text{s}$, and thus the faster transients are not recorded.

3.4. Effect of external electric field on the streamline motion of microbubbles

The influence of the external electric field on the dimension of the macro bubble is reported in the literature.³⁶ Fig. 8(a) shows the electric field distribution outside the macro bubble. The electric field is given by^{37,38}

$$E = \sqrt{E_N^2 + E_T^2} \quad (3)$$

where

$$E_N = E_a \cos \theta \left[1 - \frac{2(k_l - k_v)}{(2k_l + k_v)} \left(\frac{a^3}{r^3}\right) \right] \quad (4)$$

and

$$E_T = -E_a \sin \theta \left[1 + \frac{(k_l - k_v)}{(2k_l + k_v)} \left(\frac{a^3}{r^3}\right) \right] \quad (5)$$

are the normal and tangential electric field components, respectively. E_a , k_l and k_v are the applied electric field and dielectric constants of the liquid and vapor inside the macro

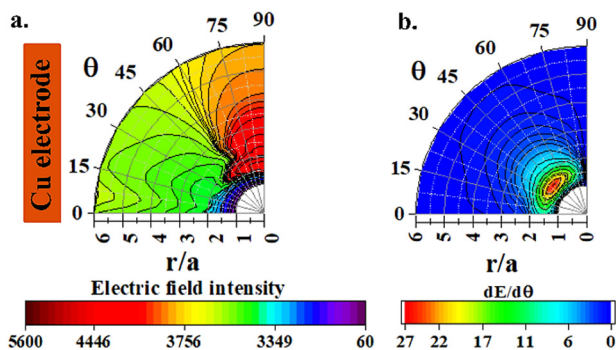


Fig. 8 (a) Electric field intensity outside the macro bubble at 3750 V m^{-1} . (b) An angular gradient of electric field intensity at 3750 V m^{-1} .

bubble, respectively. The angular gradient of the electric field directed away from the wall of the macro bubble is depicted in Fig. 8(b). This indicates that the microbubbles, in addition to microstreaming, experience the electric field gradient directed towards the “Cu” electrode as the nanoparticle-filled bubbles in water exhibit plasma charging.²⁹ These gradients explain the reason for the higher “Mn” yield and observation of microbubble bombardment onto the “Cu” electrode in the SEM images of Fig. 5(b), explicitly at 3750 V m^{-1} . The effect of the electrostatic double layer (EDL) is not considered here as the laser-assisted phenomena are highly transient and occur at much faster time scales.^{13,39} This is experimentally validated by the recent works on electric field-assisted laser ablation in liquids.^{37,40}

4. Conclusions

In summary, microbubbles are observed in underwater laser-induced material processing of energy-harvesting Mn_2O_3 nanoparticles. An external electric field is applied to confirm the possible role played by these Mn_2O_3 nanoparticle-filled bubbles for electrode deposition. The external electric field with angular gradients directs the microbubbles onto the electrode. The microbubbles bombard the electrode, exhibiting an enhancement in electrode deposition.

Conflicts of interest

There are no conflicts to declare.

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