



(RESEARCH ARTICLE)



Influence of Fe₂O₃ Nanoparticles Synthesized by using Nd: Yag laser (532) nm on the Anaerobic digester performance

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Abstract

In this work, the hydrogen evolution reactions on stainless steel electrodes in ultra-pure water (UPW) and water-based Fe₂O₃ and Zinc oxide colloid solutions have been investigated. Ultra-pure water with electrical conductivity (0.45μs) was used to synthesize Fe₂O₃ and ZnO nano colloidal using pulsed laser ablation of zinc metal in water. All experiments were performed using a Q-switched Nd-YAG laser operating at second harmonic 532nm with 9ns pulse duration, at fixed laser output energy (750mJ). Different number of pulses (250 and 500) was applied with the aim to affect the concentration of synthesized Fe₂O₃ and ZnO colloidal. Hydrogen generator-fuel cell driven by 30 volts as input source is developed with Fe₂O₃ and ZnO Nano colloidal. Variation of Fe₂O₃ Nano concentration according to different number of pulses, which gives the maximum H₂/O₂ output of 1.1 mL/s.

Keywords: Laser Ablation; Fe₂O₃ Nano-Colloidal; Electrolysis & Hydrogen Generation, Nano colloidal Synthesis, Q-switched Nd-YAG Laser

1. Introduction

The chemical and physical properties of materials at Nano levels differ greatly when compared to micro levels. These properties show big differences in physical and chemical properties from the bulk material of which they are made [1]. Ultra-small metal NPs with a high surface-to-volume ratio and “clean” surface, and hence a high density of active sites exposed to reactants, are significant for heterogeneous catalysis [2]. Preparing metal, metal oxide nanoparticles in a simple technique may be made using Pulsed Laser Ablation in liquid environments (PLAL). This technique has a good advantages compared with other physical and chemical methods like purity, the stability of the fabricated Nano particle colloids, simple chemical preparation and do not require a vacuum chamber. Because of its ability to control NPs size by optimizing the laser parameter, making it the most flexible and promising technique [3]. Hydrogen has been well recognized as one of the most promising alternatives energy resources due to it's a large specific energy capacity (120 kJ g⁻¹) and ecofriendly emissions during combustion [4]. However, efficient and secure hydrogen production remains under considerable progress and ever expanding [5]. Water splitting driven by electrical or solar has gained great interest since one half reactions enable the production of hydrogen. As most technologies breakthroughs were achieved through the development new functional materials, the choice of electrode or electrolyte besides variation of other conditions at the electrode and solution interface can reduce the energy level barrier and thus give a good reaction efficiency performance for hydrogen evolution reactions due to the different mechanism dominating in the given system. The electro-catalyst plays a vital role in the hydrogen evolution reaction (HER), since it can reduce the energy level barrier and thus give optimum reaction efficiency. Platinum (Pt) is the most widely used material as electro catalytic and photocatalytic through the hydrogen-evolution reaction (HER). Even though Pt is highly active and stable

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under the often harsh operational conditions but the scarcity and high cost of Pt greatly hinder its large-scale applications [6]. Furthermore, developing lowered cost electro catalysts, which possess comparable or even better catalytic activity than Pt, led to having a way to solve these problems is to make a Pt alloy with a 3rd transition metal such as cobalt, nickel, iron and Iron Phosphide Nanoparticles[7,8].

On the other hand, ZnO nanoparticles synthesized by solution method have been studied for visible light-assisted photocatalytic hydrogen generation besides other applications for photo detection, solar cell application and sensing [9, 10]. In this work, Laser ablation in a liquid medium has been adopted to synthesized ZnO nanoparticles. Their electrochemical performance has been studied and compared with ultra-pure water using electrical hydrogen generator.

2. Materials and methods

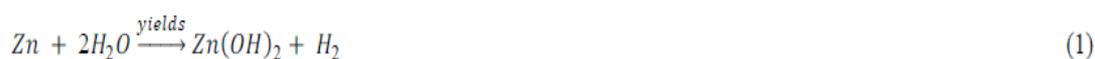
ZnO nanoparticles were produced by laser ablation of a Fe₂O₃ and Zn plate (1×1cm²), 99.9%) placed on the bottom of a glass vessel filled with 30 mL of UPW. The Zn target was irradiated directly by a Q-switched Nd-YAG laser (λ = 532nm, pulse duration 9 ns) operated at 5 Hz. The vessel was continuously rotated to minimize the target etching effect, for production homogenous nanoparticles. The energy of laser pulses is 750mJ. A different number of pulses (250 and 500) were applied, to provide four solutions with different concentrations of Fe₂O₃ and ZnO NPs.

Hydrogen generator consists of a glass container has 12 stainless steel plates (10cm × 7cm × 0.1cm) as electrodes, is filled firstly with UPW driven by a direct current voltage equal to 30 volts, then the hydrogen generator is filled with prepared samples of ZnO NPS at different concentration each time. When the cell starts operating, the water is separated into hydrogen and oxygen and the produced gas is directed into a second graded glass tube, accumulated hydrogen volume was estimated by the water displacement method.

3. Results and discussions

3.1. Liquid-Phase Laser Ablation of Zinc Target

According to previous studies [11, 12], both physical and chemical reactions happened simultaneously during liquid-phase laser ablation (LPLA) will control the formation of ZnO nanostructures. Physical interaction initiates when a laser beam falls on a metal surface; absorbed energy from the laser pulse is converted into heat, a small amount of the sample will melt and evaporate to create a dense plasma above the metal interface[13]. This dense plasma expands at high velocity until the plasma extinguished and zinc clusters are formed. Consequently, the zinc clusters formed from plasma react chemically with the surrounding water medium to form zinc hydroxide, Zn(OH)₂, the latter will further decompose to form ZnO nanoparticles. The chemical equations described the formation of ZnO are given by Equations. 1 and 2 respectively [14]:



The presence of ZnO nanoparticles in ultra-pure water was justified by both the color change of the solution right after the laser ablation. Nanoparticle size and concentration, will lead to variation in the color of zinc oxide nanoparticle solution in water [15]. As shown in Figure 1 the color of solution turns gray right after the laser ablation, depending on the number of pulses color became darker. The color variation is due to the high temperature and pressure released from the plume producing ZnO nanoparticles due to high kinetic energy of the laser beam onto the metal surface [16]. The solution in the beaker is warm when touched right after the laser ablation indicating the occurrence of the liquid-phase laser ablation mechanism. This experimental observation is in agreement with other studies [17].

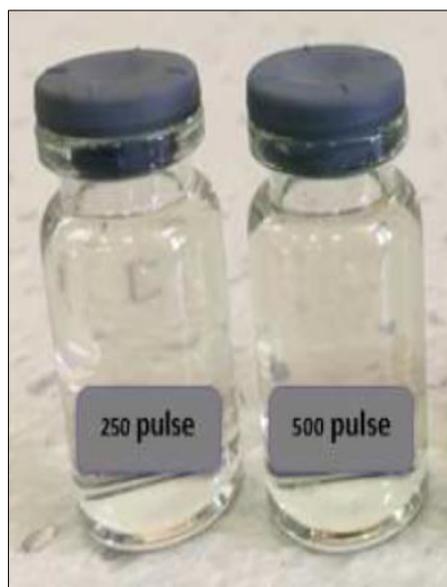


Figure 1 ZnO Nanoparticles Samples in Distilled Water

3.2. Accumulated Gas Volume

Hydrogen generation experiments using ultra-pure water (UPW) and Fe_2O_3 , ZnO nanoparticles synthesized at different laser pulses ablation were carried out via electrochemical water splitting and accumulated gas was quantified using liquid displacement at room temperature. Figure 5 shows the accumulated gas volume by electro-splitting of pure water and with Fe_2O_3 and ZnO nanoparticles synthesized at the different number of pulses. It can be observed that all samples have clearly shown hydrogen evolution that increased linearly with respect to time. Amongst all samples, it was observed that higher rate of accumulated hydrogen generated is (380mL) for Fe_2O_3 and ZnO NPs concentration (1000 laser pulses) with pH 8.1 and electrical conductivity $15.8\mu\text{s}/\text{cm}$, compared with water and other Fe_2O_3 and ZnO samples which may be due to its high concentration. The hydrogen generation rate was further increased by an increase of pH of the solution.

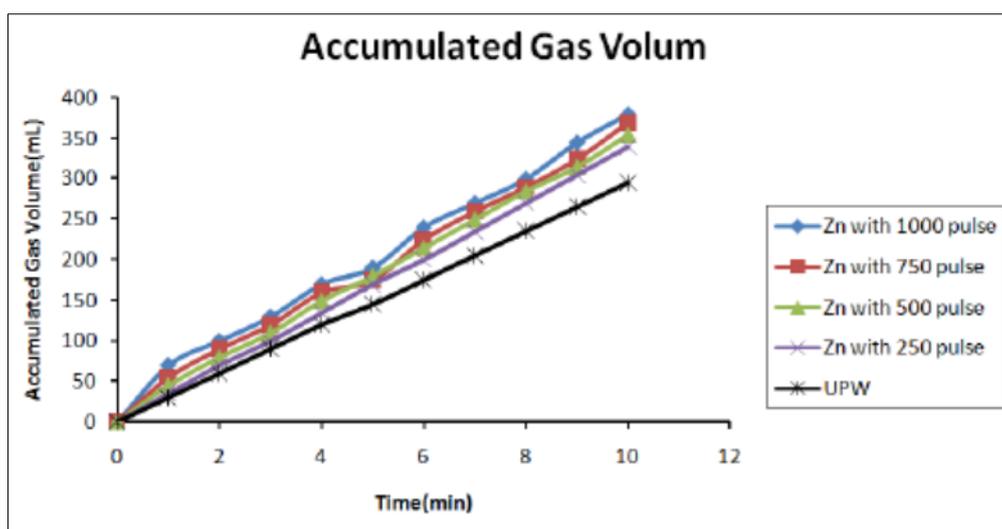


Figure 2 Accumulated Gas Volume as a Function of Time with Ultrapure Water and with Fe_2O_3 and ZnO Nanoparticles Synthesized at different Number of Pulses

To further investigate chemical reactions inside the cell, the electrical current of the cell has been measured as a function of accumulated gas volume and the reaction time. As shown in Figures 3 and 4, the current shows the same trend for all samples. There is an increase in current with increasing of time and the volume of accumulated gas.

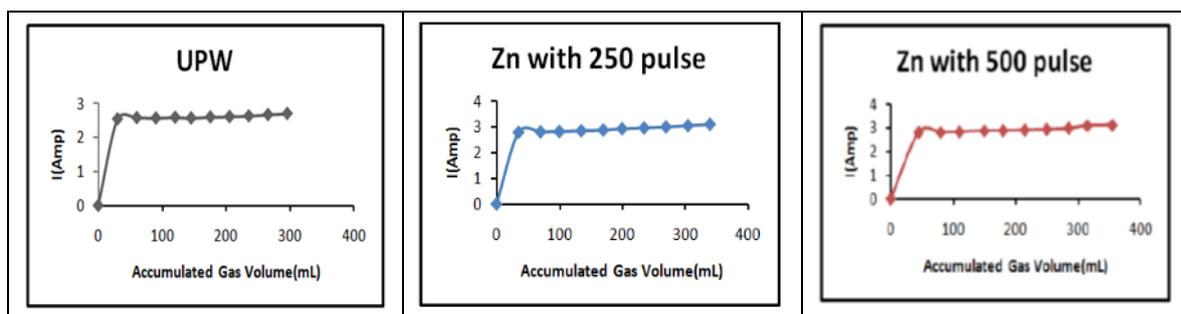


Figure 3 Accumulated Gas Volume as a Function of the Current with Ultrapure Water and with Fe_2O_3 and ZnO Nanoparticles Synthesized at different Number of Pulses

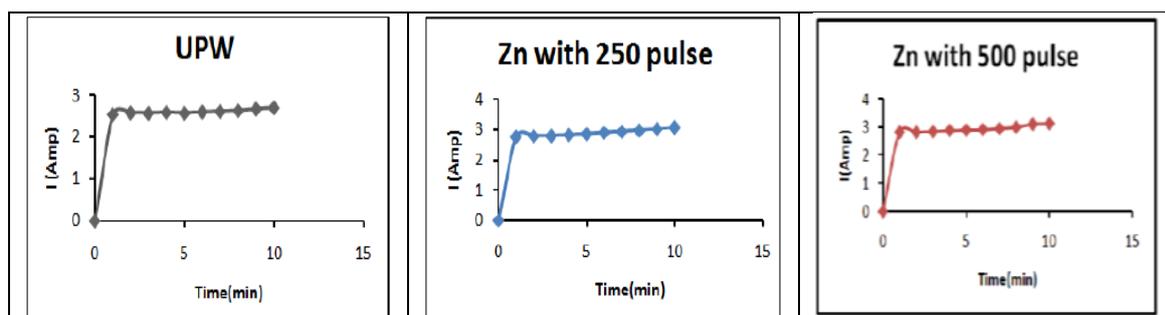


Figure 4 The Current Consumption as a Function of Time with Ultrapure Water and with Fe_2O_3 and ZnO Nanoparticles Synthesized at different Number of Pulses

4. Conclusions

Zinc Oxide nanoparticles were synthesized by pulsed laser ablation of zinc target in ultra-pure water. The effect of laser number of pulses was studied using a 532nm wavelength of an Nd: YAG laser with an exerted energy of 750 mJ/Pulse. Majority of nanoparticles in all samples are about 25 nm as depicted in AFM micrograph. The results indicate that higher number of laser pulses produce a higher concentration of dispersed nanoparticles which play a crucial role that influences the effective of increasing pH and electrical conductivity of Nano colloidal suspension, this suspension is used as an electrolyte in the hydrogen generator, which led to increment in the hydrogen accumulated gas production. Electrochemical results confirm an overall enhancement of hydrogen evolution reaction with Fe_2O_3 and ZnO nanoparticles.

Compliance with ethical standards

Disclosure of conflict of interest

No conflict of interest to be disclosed.

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