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# Evidence of nano-galvanic couple formation on in-situ formed nano-aluminum amalgam surfaces for passivation-bypassed water splitting

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## ABSTRACT

Reaction of Al metal with water is a well-known technique for large scale production of hydrogen. However, this method suffers from kinetic limitations due to formation of a passivation layer on Al, preventing optimal operations. Using high resolution Scanning Kelvin Probe Force Microscopy (SKPFM), we show the origin of formation of 'nano-galvanic couple' on in situ formed nano-aluminum amalgam surfaces in a water splitting system; passivation based limitations are completely bypassed in this approach. Furthermore, they offer an opportunity to beneficiate and recover mercury in contaminated water. The nano-galvanic corrosion due to substantial lateral variation in surface contact potential is responsible for the observed high throughput of hydrogen production (720 mL/min per 0.5 g Al salt). It may be noted that this process fares better than in situ prepared nano-Al based hydrogen production, wherein 600 mL/min of hydrogen is obtained for 0.5 g Al salt. Investigations using Cyclic Voltammetry (CV) and Electrochemical Impedance Spectroscopy (EIS) provide evidence for passivation-bypassed hydrolysis and favourable kinetics for in situ derived nano-ALHg hydrolytic agents (when compared to nano-Al). This study, to the best of our knowledge, reports the first direct proof of nano-galvanic couple formation on in-situ prepared nanoaluminum amalgam surface; paving a direct way to overcome the long standing passivation problem in Al hydrolysis. It is found that the hydrogen production rate and standard deviation (SD) of the contact potential of nanoaluminum amalgam are directly related to the rate of addition of the reducing agent, offering an opportunity for kinetic control for the in situ hydrolytic process.

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## Introduction

Hydrogen has a high calorific value of 141 kJ/g, and hence is considered an efficient source of energy [1–4]. Its oxidation does not produce pollutants unlike fossil fuel combustion,

making hydrogen a clean fuel [5–8]. Thus, hydrogen is a promising fuel for future [9–12]. The most used technology for the industrial-scale production of hydrogen is the steam reformation of natural gases, which produces significant emissions of greenhouse gases [13,14]. Hydrogen production from water by the reaction of aluminum metal is a well-

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known area of research [15–18]. However, Al metal and its derivative are passivated by the  $\text{Al}_2\text{O}_3$  layer on their surface [19–21].

While attempts have been carried out using Al nanoparticles instead of Al metal, additional capping agents are required to protect the nanoparticles from forming the oxide layer [22]. We envisage that an in situ approach might overcome the passivation related problem if the reaction takes place as soon as the Al nanoparticles are formed. Higher rate of reaction is a prerequisite for such an approach, as slow reaction might provide enough time for the passivation layer formation. To achieve this goal, nano-scope approach might serve better due to enhanced surface area to volume ratio.

It may be noted that in most of the reports dealing with water splitting, pure water has been used for hydrogen generation [23–27]. Hence, water splitting technique that allows use of (i) tap water, or/and (ii) contaminated waste water is a relevant area of research for both energy and environmental science. In our recent work [28], we have demonstrated an in situ co-reduction approach for hydrogen generation from mercury contaminated waste water and simultaneous removal of mercury. This process simultaneously deals with sequestration and beneficiation of mercury with a record hydrogen production rate of 720 mL/min for 0.5 g of Al salt (i.e. 1440 mL/min per gram) at room temperature.

While the rate of hydrogen production is higher than what is reported in the literature [29–33], mechanistic investigation and a deepened understanding of the precise role of mercury and comparison with in situ prepared aluminum nanoparticles have not been explored. Herein, we use Scanning Kelvin Probe Force Microscopy (SKPFM), Cyclic Voltammetry (CV), and Electrochemical Impedance Spectroscopy (EIS) to arrive at the mechanism of the nanoaluminum amalgam based water splitting. We also report hydrogen production from in-situ prepared aluminum nanoparticles at a rate of ~600 mL/min for 0.5 g Al salt.

Nano-Al particles are synthesized in situ at room temperature in ambient condition, in aqueous media via the reduction of  $\text{Al}_2(\text{SO}_4)_3$  by  $\text{NaBH}_4$ . As soon as it is formed, it produces hydrogen leaving the end product  $\text{Al}(\text{OH})_3$ . The primary advantage of this approach is that there is no need to prepare any samples and store it for the reaction. The precursor Al salt and mercury contaminated water (for AlHg system) can be stored as it is, and need no further treatment. At the time of the hydrogen production on demand, it just need to add the Al salt to the mercury contaminated water followed by the addition of reducing agent 'in situ' to co-reduce Al and Hg salts. The nano-AlHg formed is highly reactive, and this helps with in-situ hydrogen production leaving no time for passivation layer formation.

It is observed that the nano-galvanic couple formation results in rapid nano-galvanic corrosion due to substantial lateral variation in surface contact potential in nano-scale. Nanoscopic variations in the surface contact potential, which in turn results in nano-galvanic corrosion phenomena is responsible for the observed high throughput hydrogen production. This is, according to the best of our knowledge, the first report of direct evidence of galvanic couple formation in nano-scale on the in situ prepared nano-aluminum amalgam surface in the area of water splitting. Furthermore,

we show unambiguously that use of amalgam offers better kinetics when compared to use of nano-aluminium particles based hydrolysis.

## Methods

$\text{Al}_2(\text{SO}_4)_3 \cdot 16\text{H}_2\text{O}$  (purity  $\geq 98\%$ , purchased from Merck) and  $\text{HgCl}_2$  ( $\geq 99.5\%$ , purchased from Merck) are used for making stock aqueous  $\text{Al}^{3+}$  and  $\text{Hg}^{2+}$  solutions respectively. All solutions are prepared with tap water. Mercury contamination is simulated with  $\text{HgCl}_2$ . Al salt (0.2 g) is dissolved in 30 mL mercury contaminated water (0.2 g  $\text{HgCl}_2$ ) in a two necked round bottom (RB) flask. One neck is kept closed with a septum for injecting the reducing agent ( $\text{NaBH}_4$ ); another neck is closed with a stopper which is connected to an inverted measuring cylinder for collecting the hydrogen gas by water displacement. 0.2 g of  $\text{NaBH}_4$  (purity  $\geq 96\%$ , purchased from Spectrochem) is dissolved in 30 mL water in a beaker.  $\text{NaBH}_4$  is injected to the RB through the septum at different rates and amounts. The above mentioned concentrations are used for all experiments except comparative rate calculation of hydrogen production by nano-AlHg and Al NP. For comparative study, 0.5 g of the respective salts is taken in 100 mL water into 250 mL RB (0.5 g of Al salt for Al NP, and 0.5 g of each Hg and Al salts for nano-AlHg). ~30 mL of the reducing agent (of concentration 0.5 g of  $\text{NaBH}_4$  in 50 mL water) is added as described above with similar addition rate (for 1 min study  $\text{NaBH}_4$  is added at an average rate of 0.5 mL/Sec) for both nano-AlHg and Al NP.

The contact potential difference (CPD) on the surface of the hydrolysed product is measured by Scanning Kelvin Probe Force Microscopy (SKPFM) in an Asylum Research Atomic Force Microscope (AFM) instrument. For CPD measurements, a silicon tip coated with Ti/Pt is used. Radius of the tip is  $28 \pm 10$  nm. The lever frequency ( $f$ ) and force constant ( $k$ ) of the SKPFM probe are 70 kHz and 2 N/m respectively. The lever is made with silicon and coated with Al.

Cyclic Voltammetry (CV) and Electrochemical Impedance Spectroscopy (EIS) study is carried out in CHI 660A (CH instrument, USA). Glassy carbon (GC) electrode is used as working electrode. Ag/AgCl and platinum electrodes are used as reference and counter electrodes respectively. 0.1 M aqueous KCl solution is used as electrolyte. Scanning electron microscope (SEM) images and Energy-dispersive X-ray spectroscopy (EDS) are recorded in FEI Quanta 200FEG microscope. Transmission electron microscope (TEM) images are recorded in JEOL JEM 2100 FEG 200 keV instrument.

## Results and discussion

In situ prepared aluminum amalgam is taken out of the reaction vessel as soon as it is formed. However, a certain amount of AlHg does react with water during the time required to transfer the nano-amalgam out of the reaction vessel. The end product  $\text{Al}(\text{OH})_3$  has different shape and size, mostly hexagonal or octahedral; poly-dispersity is seen in SEM and TEM (Fig. 1). In Fig. 1(a) and (c) are the SEM and TEM images respectively; (b) and (d) correspond to the zoomed-in

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