



## Emerging clay-aryl-gold nanohybrids for efficient electrocatalytic proton reduction



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### ABSTRACT

There is an ever growing demand for renewable sources of energy to replace conventional fossil fuels. One of the alternatives is usage of hydrogen production by electrochemical hydrogen evolution reaction (HER). Toward this end, we have successfully prepared a novel, robust electrocatalyst for HER containing Au nanoparticles dispersed on a natural bentonite using a simple one-pot reduction process. It is one of the most effective ways to minimize Au nanoparticle production cost, stability and usage.

Bentonite clay was first modified using two coupling agents (mercaptosilane (MPS) or the diazonium salt of diphenyl aminoaniline (DPA)) to increase interlamellar spacing distance and to provide anchoring sites for the perfluorinated diazonium tetrachloroaurate (III) salt used as a unique source of zero-valent gold nanoparticles dispersed on bentonite surface. Successful intercalation was confirmed by the detection of F1s peak in X-ray photoelectron spectroscopy (XPS) at  $\sim 689$  eV, in line with fluorine in C–F bonds, and the reduction of gold (III) into metallic gold. Both nanohybrids showed efficient electrochemical activity for HER in acidic condition (0.1 M H<sub>2</sub>SO<sub>4</sub>) with high current density up to  $-25$  mA.cm<sup>-2</sup> at  $-1$  V and 0.148 mV onset. Negligible decreasing in current density and slight shift in onset was observed after 1000 cycles. The results obtained so far open new avenues for the preparation of low cost, efficient and stable HER catalyst on the one hand, and will contribute to the knowledge of the surface chemistry of the diazonium salts, on the other hand.

### 1. Introduction

Nowadays progress in renewable energies have generated new revolution [1], and becomes a fundamental constituent of sustainable development [2]. Particularly, energy harvested from renewable sources such as wind power [3], solar energy [4], thermal [5,6], electromagnetic radiation [7] and water [8], has always been considered as a desirable approach to fulfill the need for sustainable energy from hydropower generation [9], thermoelectric materials [10–12], lithium ion batteries [13], super capacitors [14], energy storage systems [15] to photovoltaic systems [16] and fuel cells [17]. Renewable energy-producing systems are ecofriendly since they have the potential to decrease the amount of greenhouse gases being released into the atmosphere by the burning of coal [18].

In this regard, electrocatalytic water splitting is a process in the frontline of research, producing usable O<sub>2</sub> and H<sub>2</sub> as fuel in power

generation devices, heat engines [19] and in fine chemical production, through two half reactions namely, oxygen evolution reaction (OER) and hydrogen evolution reaction (HER). The reduction half reaction in particular has gained widespread attention in recent years as it is considered the future fuel with high mass energy density.

Particularly, hydrogen production is a smart and important strategy to provide clean energy [20]. It is heavily used in power generation devices, heat engines [19], in fine chemical production in the pharmaceuticals and the perfumery industry [21] without any environmentally harmful side products [22]. High over-potential [23], however the cost difference between inexpensive metals (e.g. Cu, Fe) and some relatively more expensive ones (e.g. Au, Ag) becomes more and more significant. Therefore, choice of catalyst materials will depend more on the performance and especially on processing cost. Platinum catalysts are known to be the most efficient and typical electrocatalyst for this reaction with a relatively low overpotential [24].

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However, Because of the very high cost and low abundance, such clean energy could be unaffordable in industrial applications. For these reasons, and in order to replace Pt it is essential to find alternative materials that can (i) efficiently decrease the overpotential and (ii) enhance the hydrogen evolution reaction at reduced cost [22]. In addition, it is required that the alternative catalytic materials have improved physical properties such as large specific surface area and good transport properties [25,26].

Incorporating few percentages of certain noble metal nanoparticles (NPs) on a suitable support was found to reduce the price and enhance the catalytic activity of the overall material immensely [27]. In this respect, gold nanoparticles (AuNPs) hybrid materials are quite remarkable in numerous applications due to their high electrical conductivity, specific physical and chemical properties related to their metallic nature and nanoscale size, high surface/volume aspect ratio, their high chemical reactivity and the chemisorption of different kind of molecules [28].

Different methods have been described in order to fabricate gold nanoparticles, as photo and chemical reduction [29,30], thermal decomposition [31], with or without organic polymers [32]. These usual methods have huge limitations such as the formation of aggregated bulk nanoparticles due to aggregation. In addition, it is known that bulk gold is chemically inert and generally considered as a poor catalyst [33]. However, when gold is in the nanometric size and dispersed on selected support, it exhibits outstanding activities [34].

A very recent research showed that the photocatalytic activity of hydrogen production from aqueous solutions was dramatically improved with the incorporation of metallic nanoparticles into halloysite, a natural clay used as catalytic support. This may be explained by the change in the well dispersion of the used metallic nanoparticles and the shifting of the valence bands and conduction bands due to the formation of chemical bonds between the natural aluminosilicate and the metallic nanoparticles [19].

Toward this end, it is interesting to develop a cost-effective method via chemical reduction route, which prevents the coagulation or aggregation related issues. In this context, several inorganic supports were employed in recent years such as zeolites, silica, and clays [35], as well as polymer supports [36]. As far as we are concerned, we have selected bentonite clay as a support due to its abundance in nature and low cost, but mostly because of its unique crystal structure that induces high surface area, surface electric charges, and cation exchange capacity (CEC) [37]. Clays can be modified using a range of compounds [38] including onium salts [39–42] and silanes [37,43]. Interestingly, Garea and co-workers [44] pre-modified layered silicates with two co-surfactants prior to their polymerization using tetraethoxysilane between the nanosheets that resulted in highly porous clay.

In this work, we investigated the propensity of bentonite as a low cost and natural active platform for surface immobilization and reactivity of a perfluorinated diazonium tetrachloroaurate (III) salt in order to prepare a hybrid clay-based catalyst for HER reaction. One key aspect of this work is to counterbalance the high cost of catalytic noble metals by employing nanohybrid catalysts. In addition, recovery of the catalytic system is important; this issue is addressed after determination of the catalytic performances of gold nanoparticle-decorated diazonium modified bentonite for electrochemical hydrogen evolution (HER), a reaction that is industrially applied.

To the very best of our knowledge, such an investigation has never been conducted previously. This is what has motivated this work.

## 2. Experimental

### 2.1. Reagents

The natural bentonite clay was purified according to standard procedure previously described [45–47] in order to eliminate the impurities present in the interlayer spaces and to make it homoionic by

replacing the existing compensating cations with a single type of cation, here sodium cation  $\text{Na}^+$ . Briefly, after collecting the raw bentonite clay from the deposit, crushing and quartering, it was purified by 6 cycles of string-centrifuging of the raw clay suspension using 1 M of NaCl solution. Then 2 wt% bentonite clay dispersion was placed in graduated cylinder to allow particles  $> 2 \mu\text{m}$  to settle. The dispersion at a depth of 10 cm was collected, followed by several washings with distilled water and dialysis, in order to eliminate the excess chloride ions. Finally the purified bentonite was collected and dried at  $60^\circ\text{C}$ . The final, purified sodium clay (Bp) particles have  $\sim 80 \mu\text{m}$  diameter. The cationic exchange capacity (CEC) of the bentonite was determined and found to be equal to 101.86 meq/100 g [37].

N-phenyl-p-phenylenediamine (Acros, 98%), isopentyl nitrite (Alfa Aesar, 97%), ammonium persulfate (APS, Acros, 98%), and nitric acid (Carlo Erba, 60%) were used as received. 3-mercaptopropyltrimethoxysilane coupling agent was used without further purification (99%) and  $\text{NaBH}_4$  (95%) were purchased from Sigma-Aldrich.

$[\text{C}_8\text{F}_{17}-4-\text{C}_6\text{H}_4\text{N}\equiv\text{N}]\text{AuCl}_4$  was prepared as reported by Mohamed and co-workers [48]. The organic solvents were of analytical grade and deionized (DI) water was used for washing and solution preparations.

In the following, materials will be abbreviated as Bp: purified bentonite, DPA: 4-diphenylamine diazonium tetrafluoroborate salt, MPS: 3-aminopropyltriethoxymercaptosilane,  $\text{ArC}_8\text{F}_{17}\text{Au}$ : perfluorinated diazonium tetrachloroaurate (III) salt, Bp-MPS- $\text{ArC}_8\text{F}_{17}\text{Au}$ : nanohybrid of bentonite pretreated with MPS and modified with gold-aryl nanoparticles, and Bp-DPA- $\text{ArC}_8\text{F}_{17}\text{Au}$ : nanohybrid of bentonite pretreated with DPA and modified with gold-aryl nanoparticles.

### 2.2. Preparation of 4-Diphenylamine diazonium tetrafluoroborate salt (DPA)

The synthesis of 4-diphenylamine diazonium tetrafluoroborate salt was performed using the following standard procedure. N-phenyl-p-phenylenediamine (0.46 g, 2.5 mmol) was dissolved in 3 mL of acetone, cooled in an ice bath, and subsequently 2 mL of  $\text{HBF}_4$  from 48 v/v% aqueous solution was added. Isopentyl nitrite (0.63 g, 5.5 mmol) was added drop-wise to the mixture over 10 min under stirring. The diazonium salt was left to decant overnight in the fridge and the precipitate was washed with copious amount of cold ether.

### 2.3. Silanization of the bentonite clay

2 g of purified clay (Bp) were dispersed ultrasonically in 200 mL of water for 5 min, and to this clay suspension a solution of 3-aminopropyltriethoxymercaptosilane (114.7 mg) in 25 mL of ethanol/acetone (95/5) mixture was added at room temperature. After 72 h, the silanized clay was washed several times by 4 cycles of centrifugation (8000 rpm for 15 min) and redispersed in ethanol. The final product was dried in the oven at  $60^\circ\text{C}$  for 24 h. The silanized clay will be noted Bp-MPS.

### 2.4. Preparation of the hybrid gold nanoparticles

1 g of Bp-MPS was dispersed mechanically in 100 mL of anhydrous acetonitrile, then a suspension of  $[\text{C}_8\text{F}_{17}-4-\text{C}_6\text{H}_4\text{N}\equiv\text{N}]\text{AuCl}_4$  (2.1 mmol/100 mL) in anhydrous acetonitrile [48] was added drop-wise. Finally, sodium borohydride (2.4 mmol/10 mL) was added under vigorous stirring over 1 h. The solution color changed from yellow to ruby red, which confirmed the reduction of the diazonium gold salt to gold nanoparticles on the clay surface.

The resulting nanohybrid abbreviated as Bp-MPS- $\text{ArC}_8\text{F}_{17}\text{Au}$  was treated with 70 mL of toluene and washed with 0.5 M  $\text{H}_2\text{SO}_4$  ( $2 \times 30 \text{ mL}$ ), 0.5 M  $\text{Na}_2\text{CO}_3$  ( $2 \times 30 \text{ mL}$ ), and MilliQ water by centrifugation and filtration and finally dried in the oven at  $60^\circ\text{C}$  for 24 h.

The same procedure was used for the synthesis of BP-DPA in order to construct Bp-DPA- $\text{ArC}_8\text{F}_{17}\text{Au}$ .

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