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Self-Assembled Monolayer Stabilized Gold-Vanadate Nanoflute for Water Splitting Reactions

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Vanadium oxide (VOx) decorated with gold-nanoparticles *via* self-assembled monolayer approach is herein reported to be an efficient electrocatalyst for both oxygen and hydrogen evolution reactions (OER and HER) in alkali medium. The voids created in the nanoflute of gold-vanadate were believed to be responsible for high mass transfer allowing the material to be highly applicable as a catalyst for water splitting and nitro-arene reduction. The nanoflute exhibited high current density with low onset potential value in both OER and HER. The overpotential value at 10 $mAcm^{-2}$ was observed to be 310 mV with onset potential of 1.43 V in case of OER while the overpotential value for HER was measured to be 282 mV. The nanocatalyst was found to be stable upto 10 h with minimal increment in the overpotential value. The Tafel plot value of 127 $mVdec^{-1}$ in OER and 131 $mVdec^{-1}$ in HER also signified for the high efficacy of the catalyst towards splitting of water molecules under high basic condition. The same material was also used as catalyst for reduction of various nitro-arenes in isopropanol with 0.25 M KOH. The liberation of hydrogen *via* the oxidation of isopropanol was supposed to be responsible for reduction of nitro-arenes. The ability of the catalyst to oxidize isopropanol was substantiated from electrochemical studies.

Introduction

The continuous decrease in the fossil fuels and the increase in the global warming caused by the emission of greenhouse gases compelled the researchers to search for alternate clean and renewable source of energy.[1] Generation of hydrogen fuel from water either by electrochemical or photochemical process is considered to be one of the environmentally benign process.[2,3] Therefore, finding an electrocatalyst for water splitting reactions viz oxygen evolution and hydrogen evolution reaction (OER and HER) requires high attention towards the development of new technology for generation of hydrogen fuel.[4,5] The commercialization of electrocatalyst from precious metal like Pt, Ru, Ir is limited by their high cost, low abundancy and stability.[6,7] Apart from the designing of cost effective electrocatalyst it is also reasonable to find materials that could sustain for a longer period under high acidic or alkaline medium.[4,5,8] At the same time it is also beneficial to look for new heterogeneous catalysts that are able to perform both the OER and HER in the same medium.[4,5,9] Most often performance of a particular catalyst in HER is excellent in acidic medium while it loses its stability in alkaline medium and the reverse is observed in OER.[4,5] Hence synthesis of a catalyst performing both OER and HER with high efficiency within the same medium is more desirable.[4,5,8,10] To the best of our knowledge only few numbers of Au supported metal oxides has been reported for OER and HER.[2,3,11–] Recent studies suggested that the water splitting reactions in alkali medium is more beneficial in comparison to acidic medium.[4,5] So, current emphasis has been put towards the synthesis of new materials for electrocatalytic splitting of water (either OER and HER) under alkali medium.

Like the OER[2] and HER,[5] the success in nitro-arene reduction (NAR) reactions using isopropanol as internal reducing agent is very much limited.[14–15] Till date only few catalytic systems are known to do the NAR at the expense of isopropanol oxidation.[14–16] NAR reactions are commonly performed using reducing agents like sodium borohydride,[17] hydrazine[18] etc. However, the presence of such reducing agents hampers the chemo-selectivity of the product and also destroys the heterogeneity of the nanocatalyst.[19] Nowadays, isopropanol is considered to be one of the alternate sources of hydrogen with no toxicity in NAR.[14,15] Therefore, the catalyst that would do the NAR in isopropanol is highly demanding making the process to be much greener.

In this regards, gold nanoparticles (Au NPs) supported on various metal oxide or alloyed with other metals appeared to be promising catalyst for water splitting reaction[2] and NAR.[20] Among the different forms of Au NPs, the one stabilized by self-assembling monolayer (SAM) formation of thiol-based carboxylic acids has drawn specific attention due to their high applicability in sensing, surface patterning and molecular electronics.[21—22, 23] But such type of Au NPs despite of having good redox potentials have not been explored in water oxidation reaction and in NAR. Apart from SAM stabilized Au NPs,[21] VOx are also known as promising semiconducting materials for its suitable band gap.[24] VOx also serves as good

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