Revealing the Dynamics of Catalytic Splitting of Water to Produce Hydrogen by Gold Nanorods

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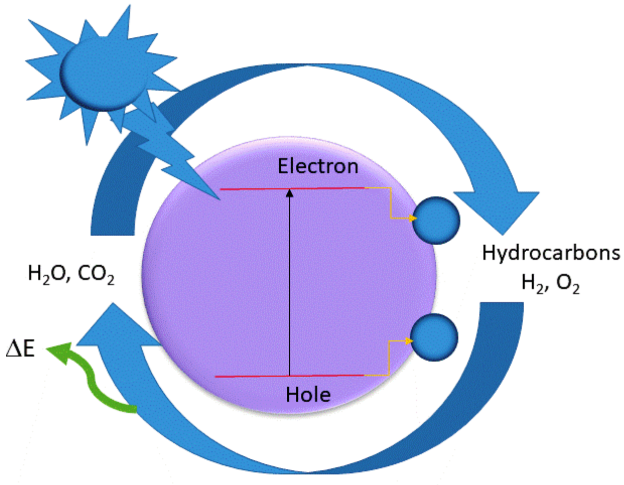
Abstract

Photocatalytic splitting of water by nanostructure on suitable semiconductor surface receives wide attention due to their potential application for both clean energy production and environmental difficulties. Clean energy production and overcoming environmental issues at a worldwide level got the significant attraction. So it is crucial to construct a system that can produce clean energy in order to resolve such issues. Since hydrogen is an ultimate source of green energy. At present, hydrogen is mostly produced by petroleum and natural gas at high temperature, which needs massive energy. Therefore, the expansion of an unconventional hydrogen production technique is undoubtedly imperative to mitigate environmental and energy issues.

Introduction

Fossil energies are important sources for humankinds. Particularly in modern society, the planet has realized the significance of energy capitals to the improvement of individually nation. The over utilization of fossil energy enhanced the exhaustion of these non-renewable energy resources. In the meantime, the conventional energy resources are also suffering from the releasing of contaminated air which is responsible for the greenhouse effect and pollutions. These pollutants released from the burning of fossils fuel is unacceptable for the environment and effect the whole ecosystem. Consequently, there is an essential requirement for the improvement of renewable energy which is clean and green and sustain the requirement of the world. Among the renewable energy alternatives, hydrogen is one of the most encouraging energy sources since of its green, clean easy to store, and high calorific characteristics.[1, 2] Technologies that widely used to produce hydrogen are water splitting, photocatalytic and photo electrochemical methodologies.[3] Between all the technologies water splitting is most promising approach for hydrogen production. Honda and Fujishima revealed photoassisted electrochemical water splitting to hydrogen and oxygen in 1972.[4] Later on various approaches to split water have been developed. Photocatalytic splitting of water on suitable semiconductor surface is the best methodology to produce green energy (Scheme 1).

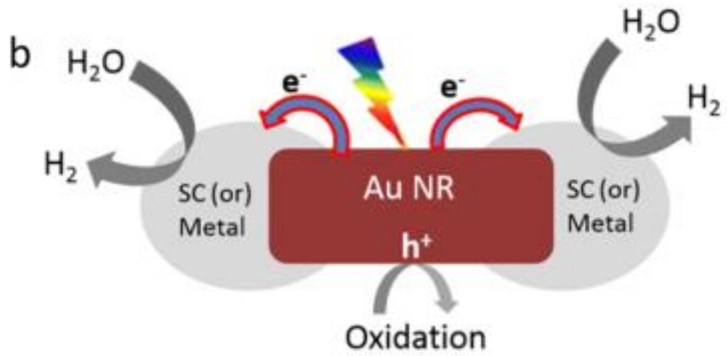


Scheme 1. Photocatalytic hydrogen production upon suitable semiconductor

Discussion

The overall water splitting reaction: $H_2O \rightarrow H_2 + ½ O_2$, ΔG^0 = 273 kj/mol, So the calculated potential deference is $\Delta E^0 = \Delta G^0/nF$, for water splitting required electrons are 2. Calculated ΔE^0 for this reaction is 1.23 V. This means the required energy for water splitting should be larger than the 1.23 ev, which resembles to wavelength smaller than ~1000 nm. So we need a material that can enhance the reaction without providing the extra energy.[4] When a photocatalyst is excited with light, electron-hole pair will be generated and the photoexcited electrons and holes are yields that promoted the water splitting. Valance band hot electron can to the conduction band. High mobility and low recombination rate of carriers can enhance the rate of hydrogen production progress which is very essential to increase the effectiveness of photocatalyst. The researchers are focused on the efficiency of hydrogen production and basically used nanostructure to promote the facile transfer of electron to reduce the water in to hydrogen.[5] Nanomaterials can rise the surface area and sites that is used for reduction of water to hydrogen, which consequence in improving the catalysis. Among all the nanomaterials gold nanorods are found to be the best candidates for the hydrogen production and getting attention due to their large surface area and easily tuneable of aspect ratio (length/width).

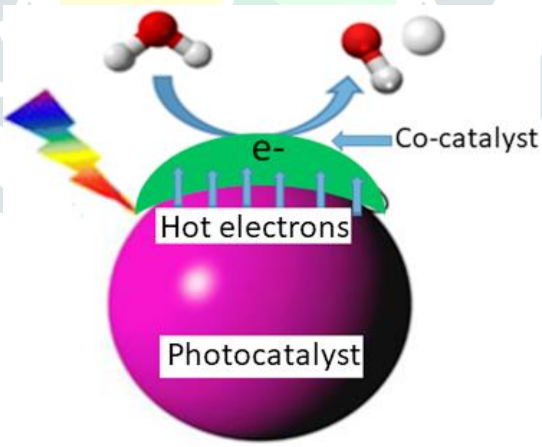
The absorption area of plasmonic gold nanorods increases (depend on the size and other properties), which effects the generation of additional hot carriers available for more photocatalytic process. The greater extinction coefficient leads to absorption of light which result in the generation of hotness near the vicinity of used system, and can be responsible for the enhancement of kinetics of photochemicals conversions. Thus all these exceptional properties of nanorods make them auspicious applicants for light prompted photocatalysis rather than with conventional semiconductor catalyst and other nanoparticles (Scheme 2).



Scheme 2. Graphic presentation of hot-electron transfers from gold nanostructure to the adjacent appropriate semiconductor/used system or metallic surface for effective charge separation prominent to water reducting process.

Role of co-catalyst on the surface of gold nanorods

By using co-catalyst on the surface of nanorods can enhance the overall quantum yield of the process. The main role of the co-catalyst is to reduce the recombination rate and accelerate the transfer of electron. Mainly transition metals and their oxides have been extensively used as cocatalysts to recover the rate of the photoreduction process of the proton.[6] The main role of co-catalyst to reduce the activation energy of overall process which redirect the facile transfer of electron which can reduce the H^+ . After on electron will not be available for recombination with the hole. So basically the role of co-catalyst to take apart of electron from hole (Scheme 3).



Scheme 3. Charge transfer process route between photocatalyst and co-catalyst.

When a co-catalyst is attached to the surface of suitable photocatalyst, the produced hot charge carriers roam to the surface of the photocatalyst and are captured by co-catalyst which is used for the process. The Fermi energy level of appropriate co-catalyst is constantly inferior than that of the semiconductor photocatalyst.[7] In the meantime, photogenerated hole migrate to the surface resulting the effective separation of charge carries and responsible for their roles as water splitting process. Metallic surface such as Pt, Au, Pd, and Rh, have been described to be very effective co-catalyst.[8-10]

Role of Sacrificial agent

As we discussed above that the electrons can be trapped by co-catalyst and the whole dynamics of hydrogen progress can enhance. But the recombination rate of hot electrons and holes are quite enough and very fast. To overcome this issue, it is very essential to eliminate hole as well. Adding sacrificial reagents or hole scavengers that can improve the electrons concentration in the system, to react with the photo-generated holes can also reduce the electron/hole recombination rate and boost the photocatalytic separation. This results developed quantum productivity. Since electron donors are spent in the catalytic process, constant accumulation of electron donors is essential to sustain hydrogen production. Nada et al. supported a qualitative exploration to reveal the effect of electron donors on the production of hydrogen.[11]

Conclusion

Nanostructured are well established for solar hydrogen evolution from water due to their distinguished properties and potential performance in photocatalytic splitting. Moreover, surface characteristics of photocatalytic nanostructure materials are very important due to the increment of light absorption, carrier transfer. Consequently, suitable selection of co-catalyst is very important to exclude recombination of electron and hole and other back processes. On other hand, proper adjustment in semiconductor could proficiently recover the water reducing abilities because of the high effectiveness of photogenerated electron-hole separation and carrier transfer on gold nanorod surface.

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