# Nan Particles for Efficient Photo Catalysis: A Review

[1] Saransh Jain, [2] Vatshal Bhanushali
[1][2] Thadomal Shahani Engineering College, Bandra
[1] jainssaransh@gmail.com, [2] vmbhanushali97@gmail.com

*Abstract*— **Hydrogen production from water and sunlight through photo catalysis is one of the most promising means of fulfilment of the ever increasing energy demands. Solar water splitting through semiconductor particulate photocatalysis is the primary focus of this review paper. The quantum efficiency of the photo catalytic process depends on several important factors like visible light harvesting, charge carrier separation, conduction and their utilization that determine the quantum efficiency. The advancement in the semiconductor structural synthesis using nanoscience has further aided in meeting these critical factors of photocatalysis. Plasmonic metal nanostructures play a very essential role in the process of water splitting by acting as visible light harvesters and charge carrier utilizers. Quantum dots are also used in solar water splitting to revolutionize the quantum efficiency.**

*Index Terms*— **$H_2$ production, water splitting, semiconductor, nonmaterial, photo catalysis**

## I. INTRODUCTION

With increasing energy demand and depleting resources, the global research community is focussed towards alternative sustainable resources. Also important is the mitigation of pollution, which is not possible by the use of conventional fossil fuels, depletion of which is a huge concern in itself.

By the year 2050, due to the explosive rise in human population, total energy consumption is expected to double. The most promising answer to the crisis is solar light, because the amount of energy received on earth every hour from the sun is greater than the amount that is required by the entire humanity in one year [1].

Hydrogen has highest specific heat, i.e. about 14304 J/kg and heat density of 41kJ/mol [2]. H2 production mimics the process of natural photosynthesis. This makes it an attractive and clean fuel for fuel cells. Also, water being an abundant and non-carcinogenic resource renders this process environmentally benign and eco-friendly. Hence, the photo-catalytic generation of hydrogen by sunlight is considered to be of the most favorable solutions to solve the global energy crisis and to overcome the environmental issues related with the conventional methods of generating energy.

The mechanistic aspects of water splitting is interpreted as an uphill reaction with high positive free energy (237 kJ/mol) [3]. Hence, the rate of determining O2 production step process underscores severe thermodynamic constraints along with kinetic restraints in the breaking of the $1^{st}$ O-H bond, since it requires 495 kJ/mol [4]. So, in order to overcome the kinetic barriers, various new catalysts including composite oxides, sulphides or nitrides, have been synthesized and studied and it was found that the conversion efficiency depends on a large number of factors, including amount of sunlight absorbed, the energy of the absorbed photons, the transforming efficiency of these absorbed photons in electrons and holes, carrier mobility from the material to the catalyst surface, and finally, how these separated electrons and holes are transferred to produce the desired products (hydrogen and oxygen). This review paper focuses on the usage of nano-materials in hydrogen production from water and its storage.

## II. PRINCIPLE OF PHOTO CATALYSIS

*Step 1*. *Photon absorption*: Semiconductor photocatalyst absorbs photon with energy greater than its band-gap. This energy is used to excite an electron from valence band to conduction band. Thus an exciton pair (electron + hole) is formed.

*Step 2*. *Charge carrier separation*: The electrons and holes are separated in this step. Their migration to surface, where redox reaction should occur, must take place. These two factors are critical in deciding the efficiency of the process because the recombination of the exciton pair occurs in the order of femtoseconds. Electron migration to the surface is possible because of the semiconductor and the co-catalyst's electronic structure, particle size, crystallinity and other morphological factors. [5]

*Step 3*. *Surface chemical redox reaction:* The charge carriers are used for conversion of water molecules into hydrogen and oxygen. The potential of conduction band minimum should be more negative than hydrogen reduction potential.

$$(2H^+ + 2e^- ==> H_2)$$
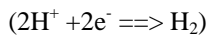
The potential of valence band maximum should be more positive than 1.23 eV at normal hydrogen electrode (NHE). The normal hydrogen electrode (NHE), is a redox electrode which forms the basis of the thermodynamic scale of oxidation-reduction potentials.

*Critical factors to decide the semiconductor can be used effectively for photocatalysis*

❖ Visible light absorption
❖ Charge carrier separation and migration to the surface
❖ Charge carrier utilisation
❖ Photo stability and hydro stability of the photocatalysis.

### III. PLASMONIC METAL NANOSTRUCTURES FOR ENHANCEMENT OF PHOTOCATALYSIS

Extensive researches have been made in photocatalysis by plasmonic nanostructures of noble metals loaded on semiconductors. Metal nanostructures show the phenomenon of optical resonance in visible and near infrared region of the electromagnetic spectrum because of the resonance displayed by the free electrons with respect to the electric field of light, in form of a response as per the Drude model[6][7]. Nano-sized noble metals, transitional metals and their oxygen clusters are known as sensitizers and/or cocatalysts to take advantage of their visible light absorption by surface plasmon resonance (SPR) and hydrogen evolving features [8]. Plasmonic metal nanostructures loaded semiconductors have been explored to a great extent in context of cocatalysis. The phenomenon of SPR causes plasmonic metal nanostructures to interact with UV or visible light photons. The absorption is caused by the bulk, mostly dipolar oscillation of conduction band electrons in the nano-clusters. Gold, silver and copper nanostructures exhibit resonance in the visible region, whereas lead, indium, mercury and cadmium exhibit it in UV region [9]. When metal nanoparticles are exposed to light radiations, the electric field of the incident light induces a collective oscillation in the electrons on the surface, called the localised surface plasmon resonance [10][11]. Plasmonic nanostructures are crucial in improving the process of photocatalysis because they exhibit the following properties –

*Enhanced light absorption* :

Plasmonic metal nanostructures possess up to three magnitudes of higher visible light absorption cross section, scattering power than an organic dye. The SPR induces strong electric fields confined to the surface of the nanoparticles. Due to a strong resonance, the near field is greatly enhanced as compared to the incident field [12]. Thus the localised SPR is forms an enhanced local electromagnetic field around the photocatalytic optical trapping capability and photoelectric conversion rate [13]. At wavelengths below surface plasmon resonance, scattered incident light by nanoparticles yields highly enhanced absorption in the layer of semiconductors. The interacting surface plasmons between nanoparticles can enhance the plasmonic scattering effect [14]. The Plasmonic particles act like an antenna in attracting the light and squeezing it to the nanoparticle size range, thus increasing density of photons, enhancing the electromagnetic fields on the surface [15]. The dynamic aspects of Plasmonic excitations is important in light harvesting, which may not make a difference as such in the cases of biomedicine and sensing application. After photon absorption the electrons oscillate with the mentioned resonance frequency. Before dephasing, this excitation makes up a time viable field oscillating at frequencies the order of 1 femtoseconds. Such a field cannot be used as source of energy for electrochemical processes. The decay of the Plasmonic excitation is caused via the radiative emission of photon i.e. Mie Scattering [16] or via the non-radiatively electron-electron, electron-surface, electron-adsorbate or electron-phonon scattering [17] [18] the radiative decay does not generate electrons or heat. The radiative decay increases with increasing size of nanoparticles. This increased scattering enhances the light trapping capabilities.
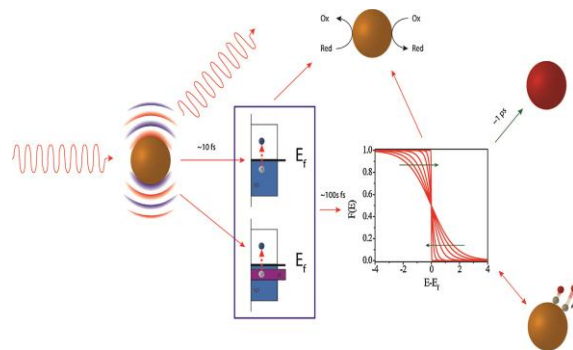
*Fig. 1: Enhanced photon trapping and charge carrier utilization with help of metal nanoparticles [A]*

- *Charge carrier utilisation :*

The presence of a strong Plasmonic near field enhances the electronic transitions of optically interfering particles, absorbers and emitters [19] [20]. The Plasmonic nanostructures are known to build up the LSPR fields which can enhance the existing electric field intensity by about $10^3$ to $10^6$ times the incident photon flux. Under such highly irradiated conditions, photo generated electrons accumulate and thus the Fermi level rises [21]. While doping of the semiconductor based solar cells with metals enhances the efficiency in the form of photothermal heat from the phonon phonon decay of Plasmonic excitation also displays a hint of enhancement [22]. This enhancement is due to the ability to concentrate the heat energy in the immediate neighbourhood at the interfacial contact surface between the semiconductor and the nanoparticle, thereby increasing the charge concentration [23].

- *Cocatalyst :*

Plasmonic metal nanostructures loaded on semiconductor surface acts as sink for photo generated charge carriers. Availability of carriers on surface facilitates the chemical reaction by suppressing recombination of the photo generated exciton pair. Since EF of the metal is lower than that of semiconductor the electron is transferred to the metal. Additionally, the activation energy barrier for H2 evolution is reduced. [24]

- *Variable exploitation :*

As in the silicon based photovoltaic cells, there are three commonly used methods to exploit plasmonics. The first one has a layer of Plasmonic nanometals on the top of the absorbing layer. The light scattering increases the effective optical; path through the absorbing layer. The second one has nanometals implanted into the absorbing layer. The light absorbance increases due to Plasmonic near field. The third one has a back layer of rough metal surfaces. This generates propagating plasmons which enhances photon trapping. [25]

- *Tuneability of the characteristics :*

An important characteristics of plasmonic metal nanostructures is that the near field and the localised surface plasmon resonance can be effectively tuned in terms of spectrum, enhancement, spatial profile, frequency and the quality of the LSPR mode [26][27].

The LSPR response can be tuned by changing the shape of the nanostructure alone from say a sphere to a rod. The rod shaped nanoparticle has two different resonances by the virtue of Plasmonic oscillations along the long and the short axis. The nature of metal is also vital to the determination of the LSPR quality. For instance, silver, being the most conductive metal, has a higher plasmon quality than other noble metals such as gold [28]. The LSPR frequency can also be tuned with changes in the dielectric properties of the medium surrounding the nanostructures [29].

## IV. QUANTUM DOTS FOR ENHANCEMENT OF PHOTOCATALYSIS

Quantum Dots are semiconductor nanoparticles whose electron motions are confined in all the three dimensions of space. Thus, there is a quantisation in energy levels. This facilitates the modulation of electronic properties. The electronic properties of the quantum dots lie in between those of bulk semiconductors and those of discrete molecules of comparable size, and electronic properties such as band gap, can be tuned as a function of particle size and shape for a given composition.
Benevolent utilization of Quantum Dots is considered promising due to the following characteristics -
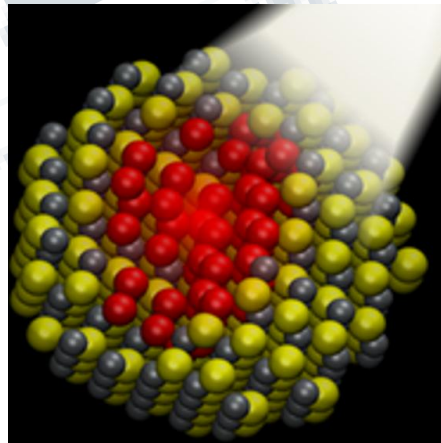


*Fig 2: Quantum Dot [B]*

- *Enhanced light absorption :*

QDs have high visible light absorption coefficient and enriched stability, thus replacing costly noble metals. Lot of potential remains unutilized in bulk semiconductors. But, small quantities of QD Semiconductor can utilize the maximum flux of photons

due to enhanced surface area and quantum size effect. They allow a tuneablity of band gap with respect to size and shape, which in turn allows building a multi gap system harvesting the whole solar spectrum [30].With a decrease in size of QDs, there is an increase in the band gap with which the colour varies from red to violet. The energetics regarding electron transfer from the conduction band of QD to the conduction band of semiconductor can also be modulated, to attain thermodynamic feasibility.

- *Charge carrier utilisation :*

 Recently QDs are remarkably noted for featuring multiple ion generation, a process by which an absorbed photon generates multiple excitons [31]. This process could generate hot electrons that can amplify the incoming photons in addition to a near 100% quantum energy yield. Also QDs provide charge carrier separation which is critical in determining efficiency. When the size of QDs is less than that of excitonic Bohr radius, the charge carrier diffusion lengths being smaller than Bohr radius facilitate charge carrier separation.

- *Photo catalytic Applications:*

 Photo catalysis of QDs sensitized semiconductors is promoted by interfacial charge transfer from QD to semiconductor via the heterojunction. With QDs, a high photon conversion efficiency is obtained. Chen et al demonstrated photo-electrochemical water splitting by Cd-Te sensitized ZnO nanowire under visible light radiation. The photo current density obtained to be three times more than that of ZnO alone. Lee et al demonstrates mesoporous TiO2 photo-electrode, co-sensitized by CdS showed very good hydrogen production due to cascade electronic structure obtained for TiO2/CdS assembly.

## V. PLASMONIC SEMICONDUCTOR QUANTUM DOTS FOR ENHANCEMENT OF PHOTOCATALYSIS

 The localised surface plasmon resonance is no longer seen as an attribute of nano-metals, but as an optical property of any nanoscale collection of charge carriers. Thus Plasmonic resonance is also found in nano sized semiconductors, with appreciable charge carrier density. Metal-like LSPRs are found in semiconductor nano-crystal systems, including copper selenide, tungsten oxide, indium oxide, copper telluride, germanium telluride, and zinc oxide [32][33][34][35][36].
Following are the properties exhibited by plasmonic quantum dots –

- *Enhanced absorption :*

Similar to the metal nanostructures, as resonance frequency, these doped quantum dots also display *enhanced absorption* and emission, Raman scattering, and nonlinear optical properties [37].

- *Charge carrier utilisation :*

 The charge carrier concentration of about $10^{21}$ electrons cm$^{-3}$ allows a harvesting of near infrared and infrared range of the spectrum, hence allowing the utilisation of the red end of the solar energy [38]. The intentional doping of the colloidal semiconductor is however limited due to the phenomenon of self-purification during the crystal growth, expelling the dopants too the outer layer of the semiconductor [39].

- *Photo catalytic applications :*

 The semiconductors such as $Cu_{2-x}S$ exhibits numerous copper deficiencies, and as a result is p type self-doped. It has been synthesized [40] [41] [42] and studied due to its near ideal band gap for solar harvesting and abundance [43]. It shows an absorption onset of 1.1 to 1.4 eV, compatible with Silicon. There is also a hint of possibility of self-doping in other semiconductors like GeTe and SnTe [44]

- *Tuneability :*

 The LSPR of quantum dots can be tuned similar to the metal nanostructures. The charge concentration of semiconductor nano crystals, can be tuned even after the completion of synthesis, by redox doping or electrochemical means. [45]

## VI. CONCLUSION

 Hydrogen energy from solar water splitting is a clean and sustainable technology, however has a limited feasibility with respect to the current scenario. After about three decades of research, the development is still confined to laboratory stage. Apparently many challenges and issues pertaining to the practicality and economic feasibility seem to be associated with this technology but that doesn't diminish the potential of this new sustainable approach. The successful implementation of this technology is sure to pave the way for the planet's green and sustainable future.

## REFERENCES

[1] R. Pike and P. Earis, "Powering the World with Sunlight," Energy & Enviromental Science, Vol. 3, No. 2, 2010, p. 173. DOI:10.1039/b924940k

[2]

[3] S. Raja Ambal, K. Sivaranjani And C. S. Gopinath, Journal of Chemical Science., 127, 33 - 47 (2015)

[4]

[5] Michael Bowker Green Chem., 2011,13, 2235-2246 DOI: 10.1039/C1GC00022E

[6] Kudo A and Miseki Y 2009 Chem Soc Rev 38 253.

[7] Linic S, Christopher P and Ingrum DB Nat Mater. 2011 Nov 23;10(12):911-21. doi: 10.1038/nmat3151.

[8] S. Link, M.A. El-Sayed, Int. Rev. Phys. Chem. 19 (2000) 409

[9] P.K. Jain, X. Huang, I.H. El-Sayed, M.A. El-Sayed, Acc. Chem. Res. 41 (2008)1578

[10] Warren SC and Thimsen 2012 Energy Environ. Sci. 5 5133

[11] Qi Hao, Chenxi Wang et al Sci Rep. 2015; 5: 15288 DOI: 10.1038/srep15288

[12] K.L. Kelly, E. Coronado, L.L. Zhao, G.C. Schatz, J. Phys. Chem. B 107 (2003) 668.M.A. El-Sayed, Acc. Chem. Res. 37 (2004) 326

[13] U. Kreibig, M. Vollmer, Optical Properties of Metal Clusters, Springer, Berlin,1995.

[14] Keisuke Nakayama, Katsua Kitanabe and Harry A Atwater App. Phy. Lett. 93 121904 2008

[15] Sivaranjani K , Raja Ambal S, Das T, Roy K, Bhattacharya, Gopinath CS 2014 Chem. Cat 6 522

[16] P.K. Jain, M.A. El-Sayed, Chem. Phys. Lett. 487 (2010) 153

[17] K.O. Aruda, M. Tagliazucchi, C.M. Sweeney, D.C. Hannah, E.A.Weiss, Phys. Chem. Chem. Phys. 15 (2013) 7441

[18] C. Sönnichsen, T. Franzl, T. Wilk, G. von Plessen, J. Feldmann,Phys. Rev. Lett. 88 (2002) 077402

I.  Zori´c, M. Zach, B. Kasemo, C. Langhammer, ACS Nano 5 (2011)2535

[19] J.A. Dieringer, A.D. McFarland, N.C. Shah, D.A. Stuart, A.V. Whitney, C.R. Yonzon, et al., Faraday Disc. 132 (2006) 9

[20] S. Nie, S.R. Emory, Science 275 (1997) 1102

[21] Hisotomi T, Maedo K, Takanake K, Kubota J, Domen K 2009 J Phys.Chem c113 21458

[22] X. Huang, P.K. Jain, I.H. El-Sayed, M.A. El-Sayed, Photochem.Photobiol. 82 (2006) 412.

[23] C.-W. Yen, M.A. Mahmoud, M.A. El-Sayed, J. Phys. Chem. A 113(2009) 4340

[24] Kongkanand A, Turdy K, Takechi K, Kuno M, Kamat PV 2008 aj Am. Chem. Soc. 130 4007

[25] C.J. Corcoran, S. Kang, L. Li, X. Guo, D. Chanda, R.G. Nuzzo,Appl. Mater. Interfaces 5 (2013) 4239

[26] Kelly, K.L., Coronado,E,Zhao,L.L. and Schatz, G. C. (2003) J. Phys. Chem. B, 107, pp. 668-677

[27] Jain, P. K., Lee, K.S.,El-Sayed, I. H. and El-Sayed, M.A. J. Phys. Chem. B,110 pp. 7238-7248

[28] Huang,W Jain, P.K and El-Sayed, M. A., Nano Lett.,7 pp.2080-2088

[29] Jain, P.K., Huang,W and El-Sayed, M. A., Nano Lett.,7 pp.2080-2088

[30] Nozik A 2008 J Chem Phys. Zett 457 3

[31] Chen HM, Chen UK, Chang Y, Chang WS ,Chen KH 2010 Angew. Chem. Int. Ed. 49 5966

[32] Dorfs, D.; Härtling, T.; Miszta, K.; Bigall, N. C.; Kim, M. R.;Genovese, A.; Falqui, A.; Povia, M.; Manna, L.  J. Am. Chem. Soc. 2011, 133, 11175−11180

[33] Manthiram, K.; Alivisatos, A. P.  J. Am. Chem.Soc. 2012, 134, 3995−3998.

[34] Kriegel, I.; Rodríguez-Fernández, J.; Wisnet, A.; Zhang, H.;Waurisch, C.; Eychmüller, A.; Dubavik, A.; Govorov, A. O.; ACS Nano 2013, 7, 4367−4377.

[35] Polking, M. J.; Jain, P. K.; Bekenstein, Y.; Banin, U.; Millo, O.;Ramesh, R.; Alivisatos, Phys. Rev. Lett. 2013, 111, 037401

[36] Buonsanti, R.; Llordes, A.; Aloni, S.; Helms, B. A.; Milliron, D. J. Nano Lett. 2011, 11,4706−4710.

[37] Kneipp, K. et al. . Phys. Rev. Lett. 78, 1667_1670 (1997)

[38] Kundu, J., Le, F., Nordlander, P. & Halas, N. J. Chem. Phys. Lett. 452, 115_119 (2008).

[39] Norris, D. J., Efros, A. L. & Erwin, S. C. Doped nanocrystals. Science 319, 1776_1779 (2008).

[40] Du, X. et al Cryst. Growth Des. 8, 2032_2035 (2008)

[41] Ghezelbash, A. & Korgel, B. A. Langmuir 21, 9451_9456 (2005)

[42] Han, W. et al. J. Am. Chem. Soc. 130, 13152_13161 (2008).

[43] Wu, Y., Wadia, C., Ma, W. L., Sadtler, B. & Alivisatos, A. P. Nano Lett. 8,2551_2555 (2008)

[44] Jain P.K., Luther J.M., Ewers T., Alivisatos A.P. Nat. Mat. (2011)

[45] Jain, P. K.; Manthiram, K.; Engel, J. H.; White, S. L.; Faucheaux,J. A.; Alivisatos, A. P. Angew. Chem., Int. Ed. 2013, 52, 13671−13675

[46] SMITH J.A., FAUCHEAU J. A., JAIN P.K. NANO TODAY (2015) 10, 67—80

[47] Faucheaux J. A., Stanton A. L. D., Jain P.K. J. Phys. Chem. Lett. 2014, 5, 976−985