

Rising Star on the Horizon of Green Hydrogen Generation! (Graphitic C₃N₄-NSs And Related Composites)

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Introduction

Knowing well the world's limited fossil-fuel reserves vis-a-vis growing environmental pollutions, hydrogen-based energy systems have been attracting our extensive considerations because of their environmentally clean nature. Hydrogen is a clean energy carrier because the chemical energy stored in the H-H bond is easily released when it combines with oxygen and ultimately forms water as the reaction product. Accordingly, making an effort to establish a future energy infrastructure based on hydrogen has, thus, been perceived as an ideal long-term solution to energy-related environmental problems. Hydrogen has also been produced from a variety of primary sources, such as natural gas, naphtha, heavy oil, methanol, biomass, wastes, coal, and solar, wind, and nuclear power. Currently, large-scale hydrogen production is achieved by reforming or gasifying fossil fuels. For many decades, steam reforming of hydrocarbon feedstocks (SMR) has been the preferred method for the industrial production of hydrogen, either as a pure gas or as a reactant for the production of ammonia or methanol. The main drawback of SMR is that it produces massive amounts of carbon dioxide (CO₂). Owing to the long-term environmental uncertainties of the CO₂ capture approach, there have been proposals to decarbonize fossil fuels by recovering and sequestering gaseous CO₂, or by employing carbon-free energy precursors [1].

In accelerating the rate of chemical reactions under milder conditions several types of catalysts are continuously being evolved to make the related processes more cost effective. A group of photocatalysts are being examined to enhance the chemical reactions under the influence of optical irradiation that act either directly or by exciting a substance that in turn catalyzes the main reaction. In the context of hydrogen evolution using optical irradiation (abundantly available from solar radiation falling on Earth) it is imperative to consider exploring the possibilities of redox reactions. Here, the catalytic activity involves oxidation-reduction chemical reactions by changing the oxidation states of the reactants. All the redox reactions deploy reduction and oxidation reactions simultaneously. The primary reason for considering the use of photocatalytic in hydrogen generation is the natural access to the solar energy in abundance. For instance, in one hour more solar energy strikes the Earth from the Sun than the annual consumption of the planet annually (14 TW). This extremely large and diffuse solar energy must be captured, converted, and stored in the form of an energy carrier such as hydrogen to overcome the daily cycle and the intermittency of the solar radiation. Solar energy can be used to produce hydrogen from water in the form of heat, light, or electricity. Among these, the solar energy used as light is the most efficient solar path to hydrogen because it does not have the inefficiencies associated with thermal transformation or with the

conversion of solar energy into electricity followed by electrolysis. Water decomposition by means of sunlight mimics photosynthesis by converting water into H_2 and O_2 using inorganic photo-semiconductors that catalyze the water-splitting reaction [1]. Water decomposition using sunlight on semiconductor photocatalysts has been as the priority area of research since the pioneering work on a photo-electrochemical cell conducted by Honda and Fujishima in 1972. This work stimulated the researchers to try water splitting reaction using particulate photocatalysts that was first realized in 1980 via stoichiometric evolution of hydrogen and oxygen. Since these ground-breaking works, many papers have been published on the impact of different semiconductor materials on photocatalytic water splitting performance. These studies clearly prove that the energy conversion efficiency of water splitting is principally determined by the properties of the semiconductors used as photocatalysts. Significant progress towards the development of efficient photocatalysts under visible light has been made during recent years, but the maximum efficiency achieved so far in the overall water splitting using particulate photocatalysts (5.9%) is still far from practical application (10%). Consequently, progress in materials science and engineering applied to the development of efficient semiconductors used as photocatalysts is still one of the most important scientific challenges for scientists [1].

Since the discovery of the Honda–Fujishima effect, over 130 semiconductor systems have been developed and explored for the photochemical water-splitting reaction or either water oxidation or reduction in the presence of sacrificial agents. These studies have made it amply clear that the energy conversion efficiency of water splitting is principally determined by the properties of the semiconductors used as photocatalysts. In spite of these comprehensive search for better photocatalyst, current results still record lower efficiencies for visible-light-to-hydrogen conversion (5.9% QY). Improving the efficiency of photocatalysts being essential for success it makes essential to understand the whole process of redox reactions leading to water-splitting reactions involved in the oxidation and reduction of water on photocatalyst surfaces, structure and defect chemistry, and charge-transfer mechanisms between semiconductor surfaces and co-catalysts. These factors have not yet been examined in sufficient detail and should be investigated as a means of refining the materials to maximize efficiency. On the other hand, the search for new photocatalytic materials with improved semiconducting and electrochemical properties would be necessary. High-throughput screening or combinational chemistry-based approaches, as well as a more rational search based on fundamental calculations/predictions would help in accelerating the progress of developing the new photocatalytic materials. The effect of variable material preparations and surface impurities on the catalytic activity of semiconductors such as sulphur and oxide on CdS has not yet been fully understood. These areas, once understood better, would offer significant opportunities for improving the qualities of water-splitting photocatalysts. The tailoring of both electronic structure and the reactivity of the nanostructures as well as their synthetic routes must be considered jointly for controlling

the morphology of catalysts down to the nanoscale. In combination with advanced analytical tools for material characterization, these advances will help to further raise the efficiency of photochemical water-splitting catalysts [1].

Rise of g-C₃N₄ as Photocatalyst of Future?

Perusal of the research publications appearing on photocatalytic hydrogen evolution using robust and simple to synthesize graphitic carbon nitride (g-C₃N₄) clearly shows as one of the important methods of cost-effective hydrogen productions as a source of clean energy of future. Its environmental friendliness, efficient performance and non-polluting nature as compared to numerous others photocatalysts are being examined extensively to produce green energy. The phenomenon of photocatalytic water splitting into hydrogen and oxygen would ultimately turn out to have the potential for commercial production of hydrogen on large scale. However, the commercial production of low-cost and high efficiency photocatalysts for hydrogen production has not yet been translated into the practical applications due to overall material costs [2-6]. While searching for the suitable photocatalyst for H_2 production, a family of Polyoxometalates (POMs) were found noteworthy supramolecular metal-oxide clusters based on Mo, W, V, Nb and Ta elements. A sub-class of POMs with the unique electronic characteristics of high charge density and rapid electron transfer rate, known as Polyoxoniobates (PONbs) were noted possessing promising photocatalytic properties when combined with other semiconductor species. Polyoxometalates (POMs) belong to a special group of inorganic redox active materials consisting of the multiple metal-oxide ions linked together by oxygen atoms to form nanoclusters within an ordered three-dimensional framework. These oxide quantum dots were noted to possessing a very high surface to volume ratio. Their rapid and highly reversible redox activity facilitated them with excellent electrochemical properties. This is the prime motivation for an increasing amount of research into POMs for energy materials and other related applications [7].

It was further noted that the $K_7HNb_6O_{19}$ turned out to be a favorite candidate of PONbs to investigate the construction of PONb-based hydrogen-evolution photocatalysts, for its easy preparation and higher stability. However, immobilization and reusability were some of the challenges faced during implementation for such materials because of the water solubility, higher alkalinity, and confined working pH range [7-11]. Another promising polymeric photocatalyst for hydrogen evolution was noted in the form of graphitic carbon nitride (g-C₃N₄) as it has the appropriate band gap and energy structure capable of performing water reduction reaction. However, the major concern in this process is how to increase the recombination lifetime that finally lowers the photocatalytic activity. A number of propositions were made to explore deploying controlled morphology, elemental doping, dye sensitization, heterojunction construction, and loading of different noble metals like Pt and Au besides other methods of improving the photocatalytic activity of g-C₃N₄. Among several options, two strategies of loading noble metals and constructing heterojunctions have been explored more

extensively to boost the catalytic property of $g\text{-C}_3\text{N}_4$. Alternately, fabricating heterojunctions by combining with other semiconductors turned out to be a preferred choice of fabricating $g\text{-C}_3\text{N}_4$ -based photocatalysts on account of the high scarcity and cost of noble metals. It was proven that the combination of $g\text{-C}_3\text{N}_4$ and POMs would be an effective strategy to obtain heterojunctions with improved photoactivity, which would not only offer a large specific surface along with a reduced band gap, but also could accelerate the photoinduced interfacial charge transfer and delay the recombination of the electrons and holes in the process. For example, a series of type II heterojunction composites (POMs/ C_3N_4) were reported using polyoxoanions $\text{SiW}_{12}\text{O}_{40}^{4-}$, $\text{PW}_{12}\text{O}_{40}^{3-}$ and $\text{PMo}_{12}\text{O}_{40}^{3-}$. Up to now, the reported POM-based $g\text{-C}_3\text{N}_4$ hybrid materials such as $\text{Co}_4\text{PW}_9\text{O}_{34}/g\text{-C}_3\text{N}_4$, $\text{FePW}_4\text{O}_{24}/g\text{-C}_3\text{N}_4$ and $\text{PMo}_{10}\text{V}_2\text{O}_{40}/g\text{-C}_3\text{N}_4$ have mainly been based on acidic POMs. As for the highly basic PONbs, there have only been a few examples reported, such as $\text{Mg}_3\text{Al-LDH-Nb}_6$, $\text{CdS}/\text{K}_7\text{HNb}_6\text{O}_{19}/\text{NiS}$, $\text{K}_8\text{Nb}_6\text{O}_{19}/g\text{-C}_3\text{N}_4$ and $\text{K}_4\text{Nb}_6\text{O}_{17}/g\text{-C}_3\text{N}_4$. Of late, another series of $\text{K}_7\text{HNb}_6\text{O}_{19}/g\text{-C}_3\text{N}_4$ photocatalysts was fabricated via hydrothermal method for effective H_2 generation without any co-catalyst. This turned out to be the first study of preparing a binary $\text{K}_7\text{HNb}_6\text{O}_{19}/g\text{-C}_3\text{N}_4$ type-II heterojunction photocatalyst, and it was found possessing outstanding photocatalytic H_2 evolution properties under ultraviolet light driving. Various salient points observed in this context have already been discussed in the cited publications [12-23].

Since the report of Fujishima and Honda about photoelectrochemical hydrogen evolution, many photocatalytic and photoelectrochemical systems have been developed. However, their practical applications are still not ready to translate into industrial process because of the relatively high cost of the photocatalyst. Accordingly, the development of various sustainable semiconducting materials, especially those comprising of earth-abundant elements, is still being pursued. Among these, recently developed polymeric $g\text{-C}_3\text{N}_4$ is a novel metal-free visible-light-induced organic semiconductor photocatalyst and is considered especially attractive in this context. It offers a promising high performance due to its better hardness, lighter weight, easy preparation from available starting materials, excellent stability at ambient conditions and as it has suitable band gap energy of 2.7eV and can absorb blue light up to 450nm. This novel nanostructured material was found to have many potential applications, such as energy conversion, the purification of contaminated water, good performance in the photo-oxidation of dyes, as a base metal-free catalyst for NO decomposition, <https://pubs.rsc.org/en/content/articlelanding/2016/ra/c5ra26702a> - cit2 as a reference material in differentiating oxygen activation sites for oxidation reactions, as a functional material to synthesize nanosized metal particles and as a stable photocatalyst for H_2 evolution from water under visible light irradiation and also in fuel cells [2-6]. Various theoretical simulations like molecular dynamics, first principal pseudopotentials, Hartree-Fock and local density approximations used in studying the $g\text{-C}_3\text{N}_4$ favor its potential application in splitting water and decomposing organic pollutants under visible light. However, its photocatalytic activity is non-satisfactory due to lower

quantum efficiency in presence of fast recombination of the photo-generated the electron-hole pairs; pure $g\text{-C}_3\text{N}_4$ absorbing only blue light in the solar spectrum (450nm), which limits the utilization of a broad spectrum of solar light; high degree of condensation of the monomers rendering the materials with a low surface area ($\sim 10\text{m}^2/\text{g}$) and without forming textured pores; and the presence of grain boundary effect disrupting the delocalization of electrons from the surface of a photocatalyst through the interface.

To take better advantage of $g\text{-C}_3\text{N}_4$, it is important to optimize the material to explore more efficient photocatalytic reactivity. The design of high-performance $g\text{-C}_3\text{N}_4$ is highly dependent on the size, morphology, surface area, abundant surface-active sites and even extended light harvesting capacity. Some of the important strategies to improve the photocatalytic hydrogen production of $g\text{-C}_3\text{N}_4$ are listed as [24].

- Preparation of mesoporous and ordered mesoporous $g\text{-C}_3\text{N}_4$;
- Preparing texturally and morphologically controlled $g\text{-C}_3\text{N}_4$;
- Doping with non-metals, such as B, S, P, F, I, and similar others;
- Loading co-catalysts (noble metals, such as Ag, Pt, Au, and like that);
- Preparing heterojunction/composites with transitional metal-/metal oxides

Some of the methods with special reference to the processes like heteroatom doping, loading a co-catalyst, designing composites/heterojunctions, and other combinations appear worth examining in detail to alter the electronic band structure as well as the redox potential of $g\text{-C}_3\text{N}_4$ for extending the light absorption and to promote photocatalytic hydrogen generation in the visible region [24]. Heteroatom doping involves the substitution of atoms or ions into a crystalline lattice to modify the structure of the crystallites. Doping with non-metals reduces the energy gap to enhance the visible light absorption of $g\text{-C}_3\text{N}_4$. The increased dispersion of the contour distribution of the HOMO and LUMO brought about by doping facilitates the charge carrier mobility and favors the charge separation. The wider the VB, the higher the mobility of the generated holes, and this improves the photo-oxidation efficiency of the holes accordingly. To increase the VB width by non-metal doping, the dopant atom must have a lower electronegativity than the substituted atom and there must be a homogeneous distribution of the dopant. The mechanism behind the enhanced activity is explained in the photocatalytic Scheme 2, taking the example of S-doped $g\text{-C}_3\text{N}_4$. S-doped $g\text{-C}_3\text{N}_4$ with a unique electronic structure that showed an increased VB width along with an elevated CB minimum and a slightly reduced absorbance, and its photo reactivity for H_2 evolution increased 7.2 to 8.0-fold. Whereas an upliftment of VB was reported causing bandgap to 2.61eV by in situ S-doping for increased activity (H_2 evolution increased 30-fold). Semiconductor hybridization and the creation of heterojunctions/composites with an appropriate semiconducting material is another strategy to broaden the utilization of $g\text{-C}_3\text{N}_4$ for visible light photocatalytic

hydrogen generation. This is based on the band alignment between $g\text{-C}_3\text{N}_4$ and the other semiconductors to achieve a better efficiency for photogenerated charge separation and to promote photocatalytic activity. This promotion effect was explained by creating heterojunctions by using three different mechanisms, as described below. In the process of sensitization, the electrons generated by visible light irradiation in $g\text{-C}_3\text{N}_4$ migrate to a wider bandgap semiconductor with a VB and CB at a higher potential (such as in ZnO, and TiO_2), while the photogenerated electrons from the CB of $g\text{-C}_3\text{N}_4$ are transferred to the CB of wider bandgap semiconductors and help in photoreduction and the holes are transferred to the CB of $g\text{-C}_3\text{N}_4$, thus resulting in effective charge separation.

Future Prospects

It is expected that the development of $g\text{-C}_3\text{N}_4$ based composite NSs doped with appropriate inorganic and organic material species, modified by co-catalysts and noble metals with adequate defect engineering combined with the realization of heterostructures having optimally located valence and conduction bands supported by the theoretical simulations and experimental syntheses would be able to change the photo response of the resultant catalyst for economically viable commercial production. Combination of QDs and 2D-NSs is ultimately expected to provide a robust photocatalyst system responding to the entire solar spectrum resulting into viable system of water splitting based hydrogen generation.

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