Chapter

Organic Semiconductor for Hydrogen Production

Vikram Rama Uttam Pandit, Shivaji Tulsa Sandu Pandit, Ganesh Punjaba Dawange, Aeed S. Al-Fahdawi, Nurlan Bakranov, Ganesh Kavita Parshuram Jadhav and Omkar Sadhna Arun Malusare

Abstract

The quest of conquering balanced environment for the ultimate search of "Who am I" furnished to pollution and energy crises. As the viable world development is dependent on effective utilization of available renewable energy resources. Hydrogen fuel as an energy source is the future for many upcoming generations as it never produces pollutants. 6, 13 Pentacenequinone (PENQ) is recently developed and reported organic photocatalyst for the generation of hydrogen from water as well as hydrogen sulfide. PENQ can be synthesized and characterized using different methods and techniques/approaches that are listed in this chapter. Green Solid state synthesis method of PENQ is the most promising one as it gives high yield at room temperature and without solvents. Structural characterization of this novel organic catalyst were done using powdered XRD. Cyclic voltammetry is used for the calculating the difference between valance and conduction band levels in the organic PENQ catalyst. After complete structural and morphological characterization, organic PENQ was explored for the hydrogen production from hydrogen sulfide. This photocatalytic nature was also being confirmed using its composites/ coupled systems (PENQ: TiO_2 and PENQ: MoS_2) using hydrogen sulfide and water.

Keywords: hydrogen, organic, photocatalysis, semiconductor

1. Introduction

Considering the utmost importance of Hydrogen (H_2) gas for energy fuel source, scientists has made efforts to find novel ways to get inexpensive H_2 production. Hydrogen generation is the one area of researchers are digging but the storage is the main issue [1]. In this context Titanium dioxide is the very first photocatalyst reported for the production of hydrogen by Gratzel et al. For the improvement in the rate of produced hydrogen there are so many effective improvements are reported like co-catalysts, composites, coupling of two catalyst systems. Metals sulfides and oxides with this type of modifications are also reported [2, 3]. In the category of metal sulfides some binary and ternary sulfides showed excellent result with photocatalytic hydrogen generation. Moreover, graphene based semiconductor photocatalyst materials are also proved best for both generation and storage. As compared to the bulk nanomaterial semiconductor materials are having more surface area, good optical absorption, tunable electronic properties, and lesser charge recombination rate [4–7].

On the other hand, the search of an organic semiconductors for the hydrogen generation is still in progress. Organic five ring system Pentacene (PEN) is well studied semiconductor material in electronic applications. PEN and its derivatives are well utilized in mainly flexible and advanced electronic devices. Recently, it is also showed some very important uses in battery based devices as well as in catalysis [8]. On the other side, PEN and its derivatives are not much stable in air as well as in presence of light [9]. So, unwanted efforts were needed to save it from both light and air. Normally, PEN when come in contact with atmospheric air get oxidize to produce PENQ. This oxidized form of PEN is lately reported as a very important organic semiconductor photocatalyst. As like PEN this oxidized form is also has five aromatic rings with Quinone functional group in the center ring. Interestingly, this PENQ is again reported mostly as a starting compound to get substituted PENQ with fascinating properties [10].

Because of two extra oxygen atoms it gets stabilized and found very effective stability in both air and light. Overall molecular mass, melting point and resistivity towards the acids and other solvents increases. PENQ is with light yellow color and having absorption band edge well in visible region makes it a promising candidate for the photocatalysis applications. Keeping in mind this PENQ was reported for hydrogen generation from hydrogen sulfide gas as well as for the MB dye degradation. After this individual report, it is also found more effective when coupled with inorganic semiconductor materials like TiO2 and ZnO [10–14]. When it combined with other semiconducting materials it produces more hydrogen than the individual one. Yuan et al. very recently proved the effectiveness of this system for the generation of hydrogen from water. These all the modifications on PENQ catalyst is discussed in the present chapter.

By considering the utmost importance of hydrogen energy many attempts were done to produce it using different approaches. Hydrogen energy can be generating from biological, electrolytical, photocatalytical, steam reforming. Out of these photocatalytic method is the simplest and useful to get hydrogen from water and H_2S gas [15–17]. In photocatalysis, photocatalyst is the main hero which alter the rate of hydrogen generation. Plenty of inorganic and organic materials were reported for the production of hydrogen using photocatalysis method.

Also, after the individual organic or inorganic catalysts reports their combinations (composites/hybrid materials) were also reported with enhanced hydrogen production rates. Herein, PENQ and composites synthesis, characterization and photocatalytic activity towards hydrogen production using both water and H_2S were discussed. Enhancement in catalytic activity with the addition of inorganic materials and their effects were also discussed. During the photocatalysis reactions the main role of organic photocatalyst material is to provide necessary charges to complete the reduction reactions. Herein, this main process light is used to stimulate an organic semiconductor material termed as a catalyst which improves the rate of the process [18–20]. Generally, electrons and hole are produced when light absorbed by the semiconductor material.

The photocatalysis mechanism for the organic and inorganic material is the same [21, 22]. In short light is responsible for the traveling electrons from VB to CB [19, 23–26]. Main advantage of organic semiconductors over inorganic semiconductor is that they have high molar absorption coefficient [20, 27].

2. Experimental methods

2.1 Solution synthesis method of PENQ

For the solution method synthesis ortho-phthalaldehyde and cyclohexanedione were mixed thoroughly in an appropriate quantity of ethanol. To this mixture KOH is added dropwise and all the reaction mixture was refluxed till the reddish yellow precipitate get formed. After further purification and drying 40-45% of yield is recorded. In this method elevated temperature is used with organic solvents which is not in accordance to the green chemistry principles and not acceptable.

2.2 Solid-state method synthesis of PENQ

In a typical solid-state synthesis process, phthalaldehyde and cyclohexanedione were ground neatly in a clean mortar and pestle till gel like mass seen. Dropwise addition of KOH is done. During the addition, the brownish solution alters in yellow ppt. After the complete synthesis it was washed with water followed by acetone to remove unwanted products. The formation of PENQ was confirmed by NMR.

2.3 High pressure method synthesis of PENQ

Above aldehyde and ketone were mixed and heated at high pressure using a special autoclave type of reactor. In this method there were no need of any solvent as the reaction products tends to aromaticity and high stability of five membered ring system. As compared to above two methods this present method is found to be more economical and safe.

3. Results and discussion

3.1 PENQ characterization

After complete synthesis of PENQ its structural and morphological characterization were done using these techniques. **Figure 1** depicts the XRD of crystal-line monoclinic PENQ. The XRD diffraction peaks at 9.80, 12.00, 15.01, 23.60 and 27.70° matches with (002), (011), (012), (112) & (104) reflection planes, respectively. For the study of optical properties of PENQ, UV-Visible & Photoluminescence spectra as shown in **Figure 1**. The band gap of PENQ found near 3 eV. Cyclic voltammetry was used for finding the possible band structure of PENQ semiconductor.

A FE-SEM photos in the UV image shows the plate like structure with thickness around 60 nm. There is a stacking of uneven shaped plates and seems to be highly crystalline.

3.2 Photocatalytic hydrogen generation using PENQ

After the possible optical and morphological characterization this PENQ system was utilized for the generation of hydrogen.

Figure 2 depicts the rate of hydrogen production from fresh H_2S gas. Highest produced hydrogen was seen 4848 μmole/h/0.1gm. Same catalyst after proper cleaning and drying were subjected for the same type of experiments showed the almost equal hydrogen generation under the same conditions.

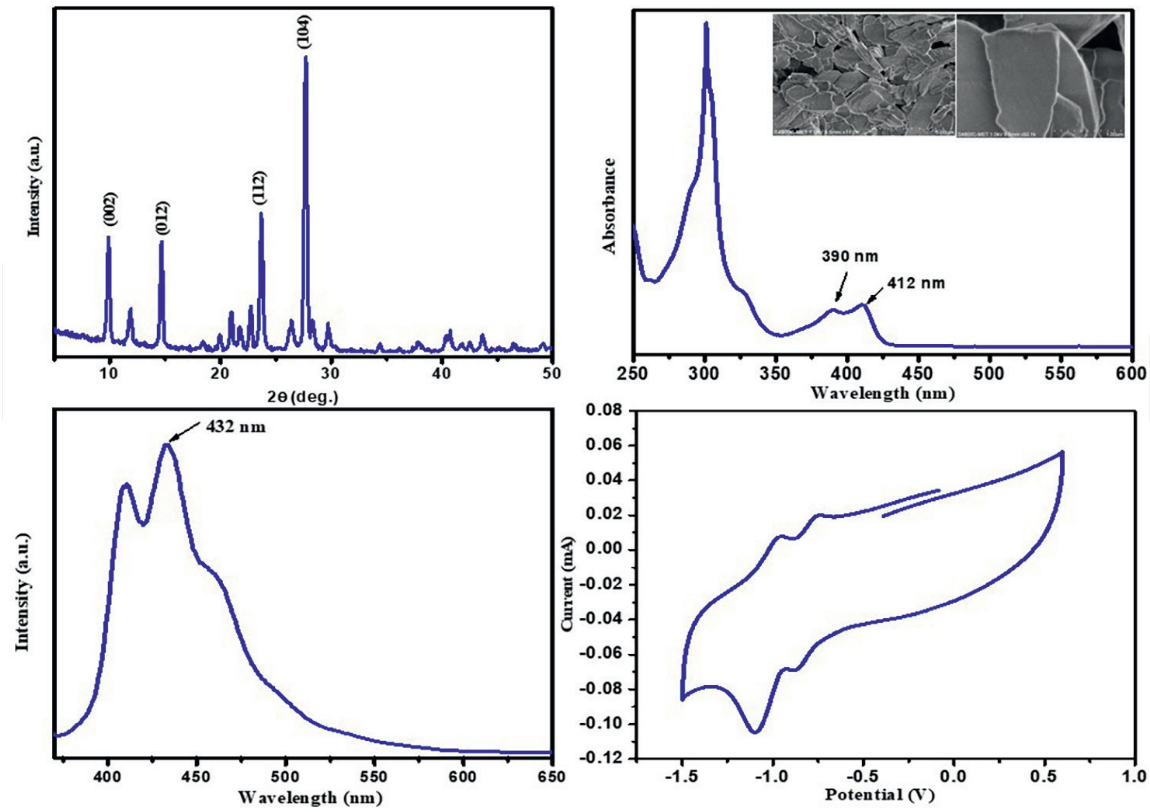

Figure 1.
XRD, UV, PL and CV study of PENQ. Reproduced with copyright permission from American Chemical Society.

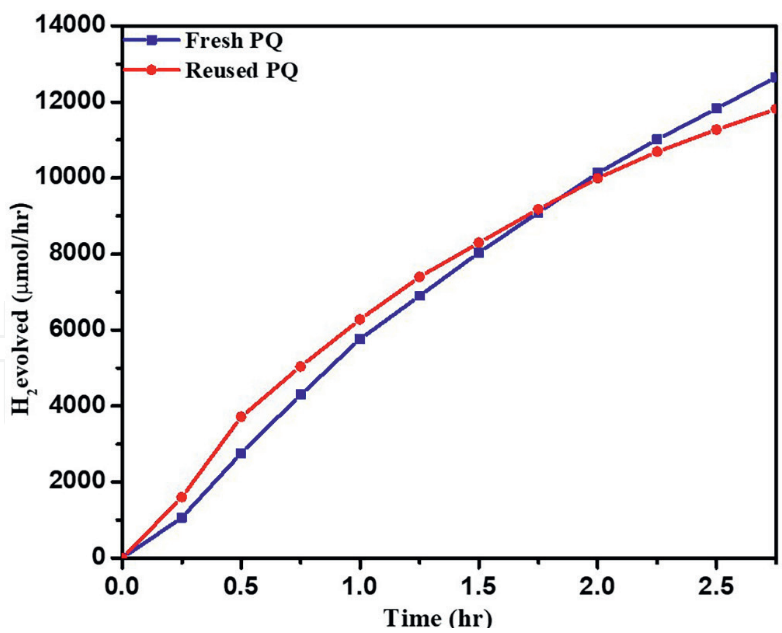

Figure 2.
Photocatalytic Hydrogen generation for PENQ. Reproduced with copyright permission from American Chemical Society.

4. Modification on PENQ with the help of inorganic nanomaterials

After the synthesis and photocatalysis experiments, loan PENQ an organic semiconductor material and by considering photostability and fascinating properties of inorganic TiO_2 an effective and novel organo-inorganic (PENQ: TiO_2) nanosystems is made. All the nanosystems were checked for visible light hydrogen generation experiments. As the stable PENQ has a band gap around 3 eV, it is selected for one of the composite member. In past this PENQ already synthesized using simple methods and it is also having a good molar absorption coefficient. In the present chapter this new organo-inorganic coupled photocatalyst system is prepared using solvothermal reaction method. Along with this characterization of these photosystems were done with the help of UV, PL, SEM, TEM and XRD analysis. Herein, during the individual synthesis of TiO_2 the PENQ is introduced as 5 (PT-5), 10 (PT-10) and 17 mmol (PT-17) of TIP (titanium tetra-isopropoxide) reactant.

4.1 Procedure for the PENQ: TiO_2 nanosystems synthesis

During the solvothermal synthesis method in a clean and dry beaker appropriate amount of titanium tetra-isopropoxide is stirred in methanol and minimum amount of hydrazine hydrate. To the another dry beaker guanidine carbonate is dissolved in acetic acid and added to the first beaker dropwise with continuous stirring for next 30 min. The PENQ which is taken for all the above compositions were taken from earlier reported methods. Further, all the solution is added to the Teflon coated autoclave reactor and kept at 145–150°C around 15-hour reaction time. Lastly, the solids were filtered and dried in vacuum oven. All the photocatalysts systems are well grinded in pestle mortar before the actual photocatalysis experiments.

4.2 Characterization of PENQ: TiO_2 nanosystems

This unique and hybrid nanosystems has been characterized further for phase identification. Powdered X-ray diffractometry (PXRD) tells the story about phase and crystal structure of given materials **Figure 3**. Highlights the PXRD of novel PENQ: TiO_2 photocatalyst nanosystems materials. As the concentration of TiO2 over the surface of PENQ increases the peak intensity is also increases. Both the peaks are highlighted with the help of different shapes in the figure. Diffraction peaks which are present at θ = 25.28, 38.01, 47.9, 54.01 and 54.89 are can be indexed for (101), (004), (200), (105) & (211) planes by corresponding to JCPDS card No. 21-1272 which confirms the Anatase TiO_2. Furthermore, the PXRD peaks θ =14.4, 23.3 & 27.9° are due to the following planes (012), (112) & (104) which matches with the monoclinic crystal structure phase of PENQ. The JCPDS card No.47-2123 is corresponds to monoclinic PENQ in previous reports.

Also, PXRD width in the peaks of inorganic material (TiO_2) highlights the reduction of particle sized to nano level, these sizes are in the range from 5 to 10 nm. After PXRD study same powdered samples were also analyzed using SEM analysis which is shown in the **Figure 2** (a and b). From the SEM pictures it can be clearly seen that these clear PENQ images are having size in the range of 60–250 nm thickness.

Further, SEM pictures of first nanocomposite system for 5 mmol showed the formation very tiny nanoparticles of 5 nm TiO_2 on all over the flakes of organic PENQ sheets. On the other hand, for 10 and 17 mmol nanocomposites systems are showing 6–10 nm sizes, respectively (2 e-h). All the above SEM micrographs shows the uniform stacking of nanoparticles on the surface of sheet like PENQ photocatalyst material. From these images it is observed that the comparative density of nanomaterials is increases as the concentration of TiO_2 is increases.

After the morphological analysis using SEM study nanosystems were subjected to for TEM characterization and SAED pattern analysis as shown in the **Figure 3**. From

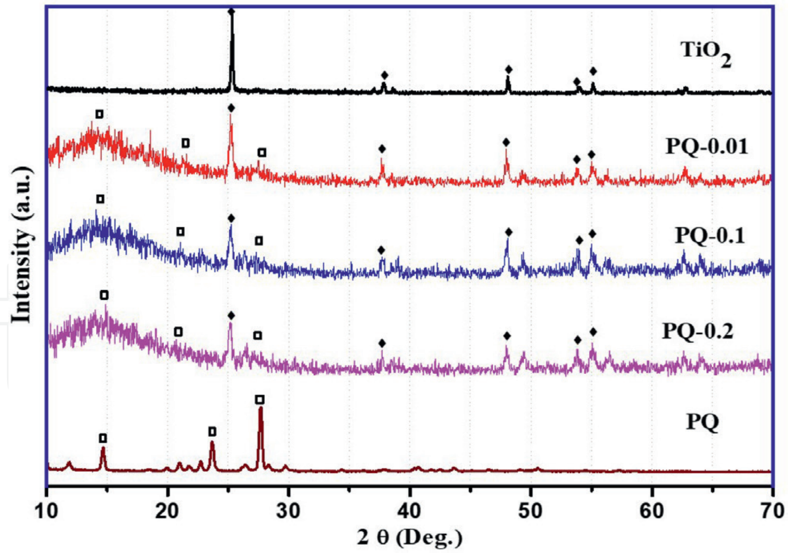

Figure 3.
XRD and UV diffraction analysis. Reproduced with copyright permission from Royal Society of Chemistry.

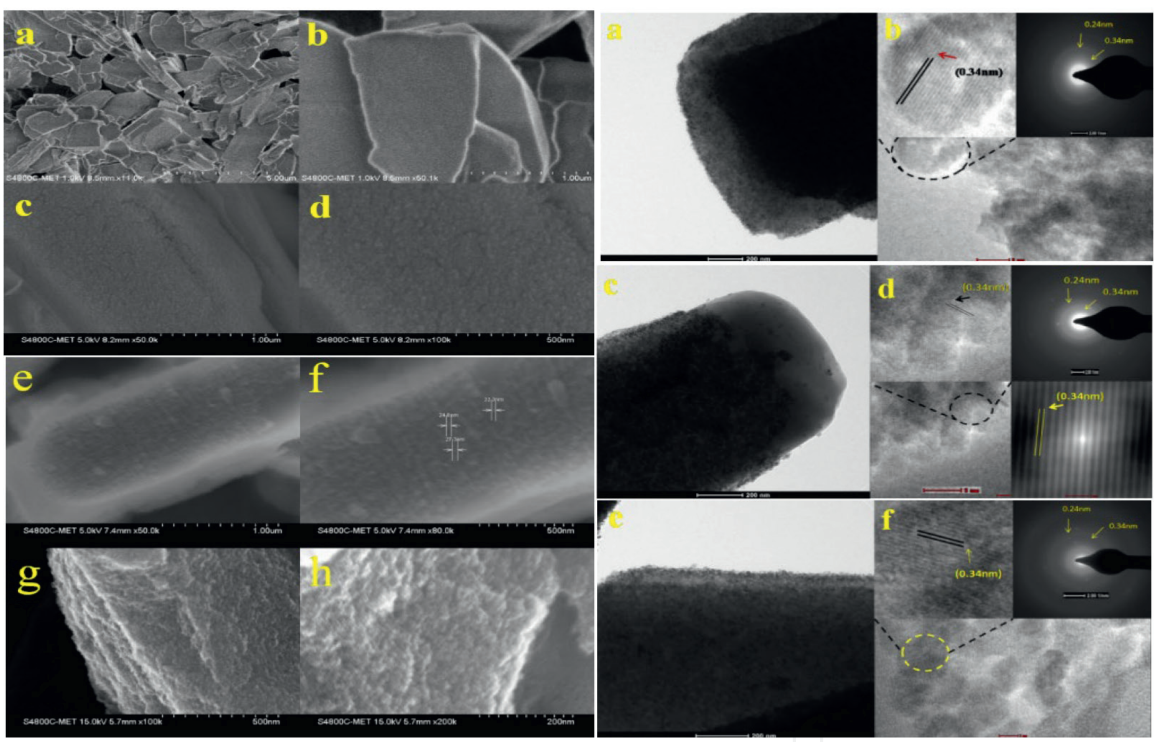

Figure 4.
FESEM and TEM analysis. Reproduced with copyright permission from Royal Society of Chemistry.

the TEM photos it is clear that the nano sized round particles of TiO2 are responsible for the covering of all the sheets of PENQ with 3 nm size. It is observed that at higher concentration of mmol the size of TiO2 is also increases from 3 to 10 nm and covers the sheets like surface of PENQ. Clear and prominent lattice fringes can be seen in high resolution TEM photos (in the **Figure 3b, d & f**) with 0.33 nm of inter-planer distance in between the planes corresponds to (101) crystal planes of inorganic nano TiO_2. The ED (Energy Dispersive) patterns clearly shows the high intense rings which also increases from 5 mmol to 17 mmol. When these round particles showed the close connection over the surface gives idea about the effective charge migration mechanism during the catalytic reactions (**Figure 4**).

For optical study diffuse reflectance UV-Visible (UV-DRS) absorbance spectra of PENQ and TiO_2 is given in **Figure 3**. The pure PENQ takes the absorbance edge at 450, 451 attributed the band gap around 2.9 and 2.7 eV. Band gap of TiO_2 in 10 mmol and 17 mmol is high because of blue shift in nano particle.

4.3 Photocatalytic study of PENQ: TiO_2 nanosystem

Semiconductor photocatalysis experiments were performed by manufactured PENQ: TiO_2 systems i.e. PT 5, 10 & 17 mmol from freshly prepared H_2S gas. **Figure 5** shows the band structure and of H_2S gas splitting in presence of UV light. Total hydrogen produced is 36,456 μmol/h/g for PT-5 nanosystem which is higher than PT-10 and 17 catalysts. As compared to TiO2 which is the best photocatalyst, this system produces four times higher hydrogen. 0.25 M KOH at pH 12.5, H_2S splitting follows the as showed mechanism, hydrosulfide HS^- ions (1). This system absorbs the light and produces electron and holes (2). Here holes (h^+_{VB}) are responsible for oxidation HS^- ion in to disulfide ion (S_2^{2-}), taking a proton from HS^- ion (3). Reduction faiths by using electrons to give hydrogen (4).

$$H_2S\,\text{gas} + OH^- \leftrightarrow HS^- + \text{Water}\,(H_2O) \tag{1}$$

$$\text{Semiconductor photocatalyst PENQ}: TiO_2 \leftrightarrow h^+VB + e^-CB \tag{2}$$

$$\text{Oxidation process}: 2HS^- + 2\,h^+VB \leftrightarrow S_2^{2-} + 2H^+ \tag{3}$$

$$\text{Reduction process}: 2H^+ + 2e^-CB \leftrightarrow H_2 \tag{4}$$

There is no any hydrogen generation was observed without catalyst and without light experiment; this proves that the hydrogen produced is because of PENQ: TiO_2 photocatalyst.

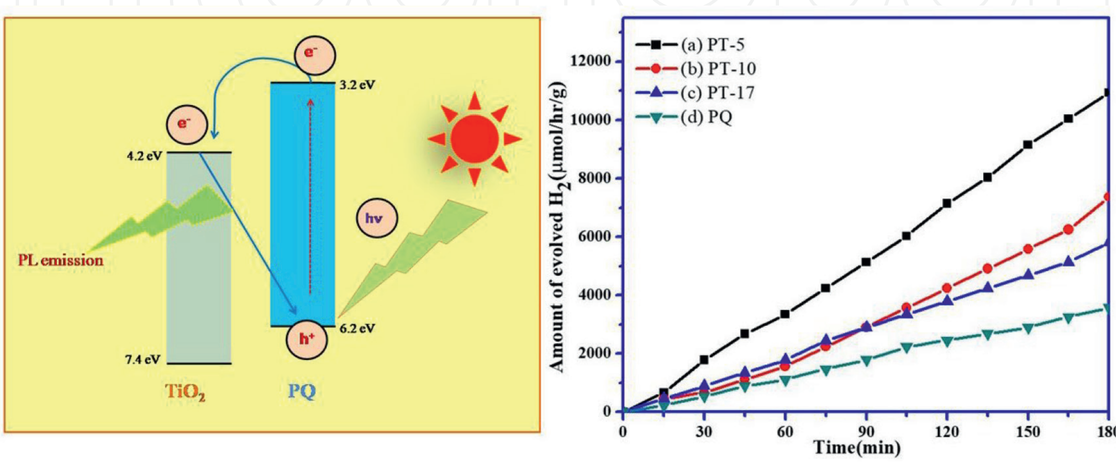

Figure 5.
The band structures and photocatalytic activity of PENQ: TiO_2 hybrid nanosystem. Reproduced by copyright permission from the Royal Society of Chemistry.

5. PENQ: MoS_2 nanosystems for Hydrogen production using water

Lately, PENQ is also used for the production of hydrogen using MoS_2 as a cocatalyst from water. This novel composite system is fully characterized using XRD, Raman spectroscopy, HRTEM, X-ray photoelectron spectroscopy and UV-vis. Here, the role of MoS_2 for the enhancement of PENQ activity was demonstrated effectively towards the water splitting for the faith of hydrogen. Also, the role of MoS_2 (cocatalyst) and TEOA (sacrificial agent) loading effect for the donation of electron was also demonstrated. Precisely, MoS_2 is more effective than Pt as a cocatalyst when combined on PENQ for water splitting.

6. Conclusions

In nutshell, the novel organic PENQ is a very suitable candidate in the race of inorganic semiconductor photocatalysts. PENQ is also showed good agreement in photocatalytical activity towards the degradation of other complex dyes which confirms its activity. The nanosystems is used for the H_2S splitting experiments to get hydrogen using UV-visible light. Highest hydrogen i.e. 36,456 μmol/h/g is seen in absence of cocatalyst. These results give a solid evidence that it can be used with other inorganic nanomaterials to produce hydrogen. It is noteworthy that other hybrid nanosystems with other semiconductor oxide can be synthesized with the present technique. As like PENQ other organic semiconductors may be useful for the construction of novel composite systems. Also, these systems are might have other photocatalytic applications like dye degradation, hydrogen generation and solar cell applications.

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Conflict of interest

Not applicable.

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Author details

Vikram Rama Uttam Pandit[1]*, Shivaji Tulsa Sandu Pandit[2], Ganesh Punjaba Dawange[3], Aeed S. Al-Fahdawi[4], Nurlan Bakranov[5], Ganesh Kavita Parshuram Jadhav[1] and Omkar Sadhna Arun Malusare[1]

1 Department of Chemistry, The Poona Gujarati Kelvani Mandal's Haribhai V. Desai College, Pune, India

2 Department of Chemistry, Arts, Commerce and Science College, Satral, Ahmednagar, India

3 Sanjivani College of Engineering, Kopargaon, India

4 Department of Chemistry, University of Anbar, Education College for Women, Iraq

5 Research Group AltAir Nanolab, Kazakhstan

*Address all correspondence to: vikramupandit@gmail.com; vikram.pandit@hvdesaicollege.edu.in

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