Title: Nanostructured graphitic carbon nitrides and their composites for photocatalytic hydrogen evaluation and sending applications

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Abstract: The acceleration of globalization since 18th century has witnessed a precipitous increase in the fossil fuel consumption in order to meet the continuous increasing requirement of global energy supply. But this increased consumption resulting in the increased CO2 emissions, the major culprit for global warming. Henceforth, the global energy supply should be independent of fossil fuels. The H2 is a clean energy carrier and best alternative for the replacement of fossil fuels. Hence, it is highly encouraged to develop a stable photocatalyst with suitable band gap to effectively harvest visible light for the large scale H2 production. Important breakthrough is achieved when an organic polymer, carbon nitride was reported in 2009 with the semiconducting property to split water under visible light. Graphitic carbon nitride (g-CN, mostly known as g-C3N4) is proven to be a highly robust and synthesized from commercially low cost precursors. However, the fast recombination of photogenerated electron and hole restrict its solar energy to fuel conversion efficiency. In this context, photosensitization has been used as powerful tool to enhance the fuel conversion efficiency of the photocatalysts. The charge recombination could be reduced if these photo-generated charge carriers from sensitizer molecules could be transferred to low lying conduction band (CB) of a g-CN and thereby improving the photocatalytic property of g-CN. Very recently, S, N co-doped graphene quantum dots are discussed as rising photosensitizer and have attracted a wide range of interest in the fields of sensing, bioimaging and photocatalysis. Especially, S, N-GQDs (S, N co-doped Graphene Quantum Dots) sensitized g-CN systems for H2 production has not been studied so far. In the first study, we have synthesized one-pot quantum dot sensitized g-CN/S,N-GQDs heterostructure photocatalyst for the first time and studied their H2 generation performance under simulated solar light. To our astonishment, we found that g-CN/S,N-GQDs heterostructure photocatalyst produces H2 which is about 4.34 mmol h-1 g-1 under visible light which is 4.5 times higher than that of pristine/bench mark g-CN with an AQY of 23.2 % measured at 400 nm. More interestingly, under natural sunlight, the same catalyst produced H2 at a rate of 5.24 mmol h-1 g-1. These studies may open plenty of opportunities to explore the different quantum dots as photosensitizer and wider the possibility of large scale H2 evolution. Recently, we have developed an oxygen-linked heptazine polymer (OLHP) and it showed a better photocatalytic performance for H2 generation when compared to nitrogen-linked g-CN. Further to enhance the performance of OLHP for H2 generation, we have focused on the photosensitization of OLHP and its effect on the photocatalytic activity. Thus, we have developed S,N-GQDs decorated OLHP photocatalyst for the first time using simple hydrothermal method and studied the water splitting activity for hydrogen generation in the presence of sacrificial agent. We found that S, N-GQDs decorated OLHP photocatalyst showed metal-free, visible light assisted photocatalytic H2 evolution about 23.9 µmol g-1 h-1 (□ > 420 nm, Xe-lamp, 90 mW cm-2). Herein, we achieved noble metal free H2 evolution as a result of tethering photosensitization and photocatalytic properties of S, N-GQDs and OLHP semiconductors, respectively. After the use of graphitic carbon nitride-based materials for photocatalytic H2 evolution, we applied these materials in chemi-resistive sensing applications which is an emerging field of nanotechnology for energy and environment purpose. With the increasing demand over IoT-based applications, high-performance gas/vapor sensors with a good figure of merits are highly essential for environmental monitoring, exhaled breath analysis, food quality control and industrial safety applications. In this context, conventional chemiresistive sensors based on metal and metal oxides suffer from the higher operating temperature, and the selectivity drift depends on the analyte detection. In this background, our group is the first to explore graphitic carbon nitrides (g-CN) in the recent years, where g-CN and their composite materials serves as a promising material for probing different VOCs and humidity with better sensing characteristics through chemiresistive sensing. However, it is seldom to find any reports on metal/metal oxide-free g-CN for ethanol sensing despite few sensors reported for NO2 and relative humidity sensing. Hence it is highly essential and imperative to fabricate g-CN sensor operating at room temperature for selective detection of Volatile Organic Compounds (VOCs), which is still elusive. Keeping this in view, we report the room temperature ethanol sensing characteristics using metal-free mesoporous g-CN for the first time with an appreciable figure of merits in different %RH levels. The mesoporous metal-free g-CN showed a maximum sensing response of S=182.4@ 46 %RH towards 50 ppm of ethanol vapor with the lowest detection limit of 500 ppb at room temperature (RT). The response and recovery times of the mesoporous g-CN were 115 and 121 s, respectively. Though there is relatively longer transient time, the room temperature sensing with such figure of merits opens a new venue for the heterogeneous metal-free polymeric materials for sensing in an ambient atmosphere with its rich chemical diversity. In the next project, we have synthesized Ru quantum dots modified g-CN (Ru@g-CN) for sensing of 3-methyl-1-butanol. 3-methyl-1-butanol is an important bio-marker for the contaminated food caused by the bacterial pathogen Salmonella typhimurium, which leads to foodborne disease and health-disorder. The Ru@g-CN effectively shows the maximum sensing response of 55.8 @48% RH toward 100 ppm of 3-methyle-1-butanol at room temperature. The response and recovery time were measured with the corresponding values of 61 s and 147 s, respectively. Ru@g-CN as such can sense lowest detection range up to 1 ppm of 3-methyl-1-butanol. Thus, here the Ru quantum dots modification causing decrease of grain-boundary resistance which helps to improve charge mobility and better sensing response towards 3-methyle-1-butanol. The development of Ru@g-CN as chemiresistive sensor opens a new pathway for the selective identification of 3-methyle-1-butanol at room temperature for food quality control. In summary, we have successfully synthesized quantum dots modified g-CN and mesoporous g-CN. We established the role of S,N-GQDs as photosensitizer to improve the photocatalytic H2 evolution. Herein, we achieved noble metal free H2 evolution which is a result of tethering photosensitization and photocatalysis properties of S,N-GQDs and OLHP semiconductor, respectively. The progress on the g-CN and its hybrid-based chemo-sensors pave a way in further fabricating different forms of g-CN based sensors for the challenges ahead in the field of energy and environment, especially IoT based futuristic sensing platforms.

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