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Enhanced hydrogen production by the protonated, sulfur doped and Pt-loaded g-C_3N_4 nanolayers

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Chemically modified graphitic carbon nitride (g-C_3N_4) nanolayers have been developed with simultaneous modifications through protonation, sulfur-doping and Pt-loading. The obtained materials have been extensively studied for their structural, morphological, optical, surface area, photocurrent density, impedance and photocatalytic hydrogen production properties under solar light irradiations. The synergistic effect of these modifications is found to increase their photocatalytic efficiencies into many folds. From the obtained results, the mechanism of the observed efficiency can be proposed as follows; (i) the protonation led to a stronger exfoliation of g-C_3N_4 from its bulk-structure to nanolayers, while (ii) the sulfur doping reduces the band gap energy through altering their band edge positions and (iii) the Pt-loading enhances the charge separation, which facilitated more number of electrons to reduce H^+ ions into H_2 molecules.

1. Introduction

The demand for sustainable and renewable energy resources has gained a significant attention due to the increasing global population and environmental issues [1]. Among the various energy sources, solar-energy has been considered as the ultimate source of energy, which can be harnessed, converted and stored as electrical and chemical fuels. Unfortunately, the utilization of sunlight is still limited because of the inefficient solar conversion strategies [1]. However, the photocatalysis technique has been realized to be one of the effective strategies to convert the solar energy into useful applications [2]. In this direction, graphitic carbon nitride (g-C_3N_4), which is a metal-free polymeric photocatalyst, has been received a great interest due to its properties such as excellent chemical-stability, cost-effectiveness and environmental-benignity [3]. However, the photocatalytic performance of the conventional bulk g-C_3N_4 is still limited due to its rapid carrier-recombination and insufficient solar light absorption efficiencies [3–5]. The current developments in g-C_3N_4 have been focused on two main strategies in order to address these limitations. These include (i) reducing the layer-thickness of g-C_3N_4 thereby to increase the surface area and to decrease the carrier-recombination and (ii) improving the visible-light absorption. To achieve this goal, g-C_3N_4 has been modified in their morphological and band gap structures through chemical treatments, doping of non-metal atoms, compositing with other visible-light-driven photocatalysts and plasmonic nanoparticles to promote the visible light absorption in g-C_3N_4 [6,7]. Interestingly, the doping process in g-C_3N_4 modifies its band gap energy via two main hypotheses: (i) the formation of localized states in the band gap structure and (ii) elevation of VB or lowering of CB position [3]. Among the various doping elements, sulfur has been considered as an effective dopant to narrow-down the band gap structure and to improve the overall photocatalytic activity in g-C_3N_4 [3].

In this context, our strategy is (i) to increase the surface area by exfoliating the bulk g-C_3N_4 into nanolayers through acid treatments and (ii) to obtain the tunable band gap energy through S doping. Thereby, the synergistic effects due to these modifications are expected to enhance the visible light absorption and photocatalytic activity of g-C_3N_4.

2. Results and discussion

Briefly, in this study, we have synthesized bare g-C_3N_4 (GCN), protonated g-C_3N_4 (PGCN), sulfur-doped protonated g-C_3N_4 (S:PGCN) and Pt-deposited sulfur-doped protonated g-C_3N_4 (Pt-S:PGCN) and studied their synergistic enhancements in the solar light driven photocatalytic hydrogen generation and associated properties. The details of experiments and characterizations can be found in the Electronic Supporting Information (ESI).

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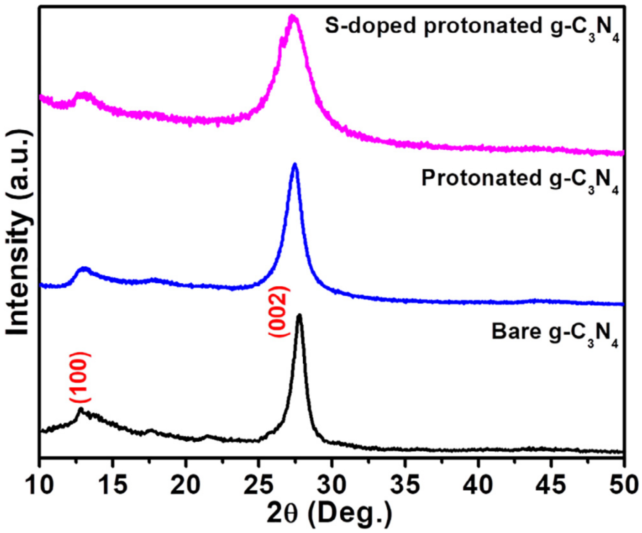

Fig. 1. XRD pattern of the various chemically-modified g-C_3N_4 photocatalyst.

Fig. 1 shows the XRD pattern of the synthesized GCN, PGCN and S:PGCN. The XRD patterns are well matched with the standard JCPDS #87-1526, where it revealed that the synthesized materials found to possess hexagonal crystal structure and belong to $P\bar{6}m2$ space-group. It is known that the peak corresponding to (1 0 0) is attributed to the in-plane structural packing of tri-s-triazine motifs, while the other peak corresponding to (0 0 2) plane is attributed to the repeated inter-planar stacking of the conjugated aromatic systems [8]. Accordingly, the decreased intensity of (1 0 0) plane indicates the stronger exfoliation of bulk-GCN to nano-GCN, which resulted from the protonation process [9] and the observed slight shift in the (0 0 2) plane for S:PGCN as compared to other samples indicates the successful doping of sulfur atoms into the lattices of PGCN [10].

The obtained TEM images showed the bulk-structure of bare-GCN (Fig. 2(a)), while it is significantly reduced into few-layer-thickness after the protonation process as shown in Fig. 2(b). Similarly, it can be observed that the S-doping transformed the surface morphology of PGCN into more crumbled-structure (Fig. 2(c)), which helps enhancing the surface active sites and facilitates the catalytic activity as well as the surface-deposition of Pt onto the PGCN layers [9,10]. Accordingly, Fig. 2(d) shows the crumpled-PGCN nanolayers that deposited with Pt nanoparticles of size around 5 nm. These subsequent changes in the morphological structures of g-C_3N_4 also found to influence their surface energy as evidenced from their BET surface analysis as shown in Fig. S1 in the ESI.

The successive chemical modifications from bare-GCN to Pt-S:PGCN nanolayers clearly demonstrate the synergistic enhancement in their photocatalytic hydrogen production as shown in Fig. 3(a) and (b). The PGCN gives rise to the enhanced adsorption of the water and sacrificial molecules and facilitates the reduction of H^+ ions into H_2 molecules [11]. The further modification of PGCN through S-doping enhances the visible light absorption, which resulted from the reduced band gap energy of S:PGCN as shown in Fig. S2(a) and (b) in ESI. The subsequent deposition of Pt further

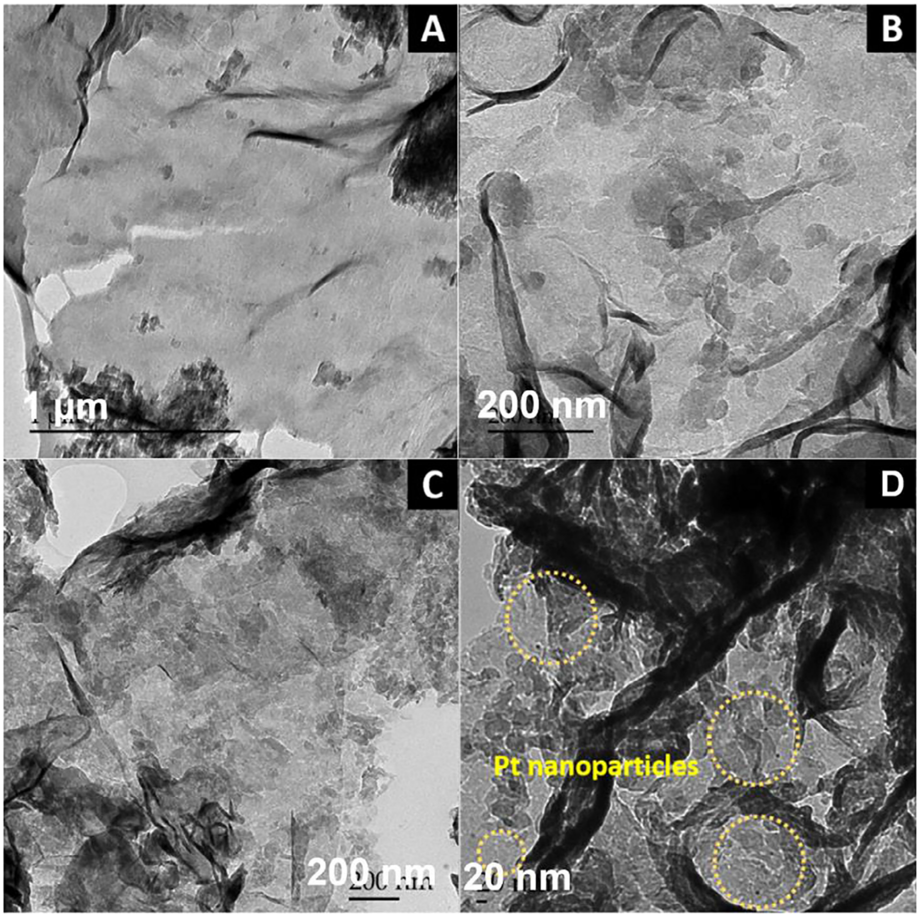

Fig. 2. TEM image of (a) bare, (b) protonated, (c) S-doped protonated and (d) Pt-loaded S-doped-protonated g-C_3N_4.

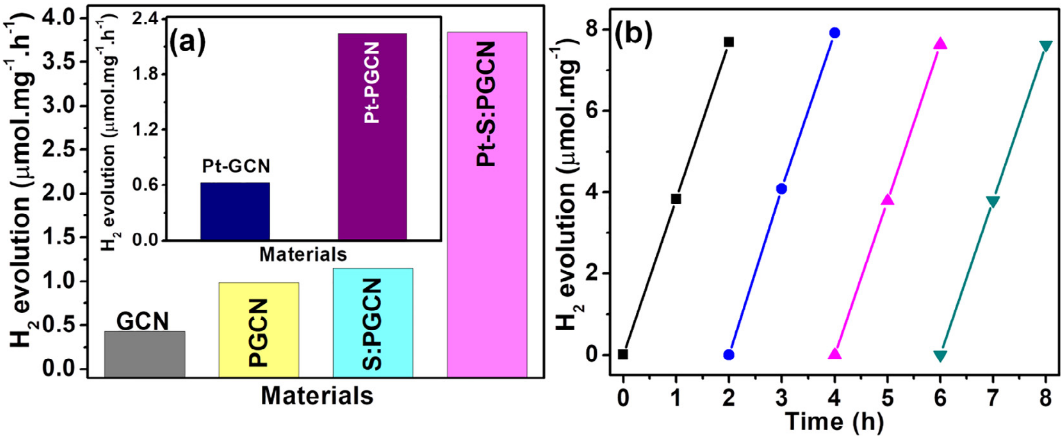

Fig. 3. (a)-(insert) Amount of hydrogen produced by various chemically modified g-C_3N_4 and (b) recyclable hydrogen production by Pt:S-PGCN.

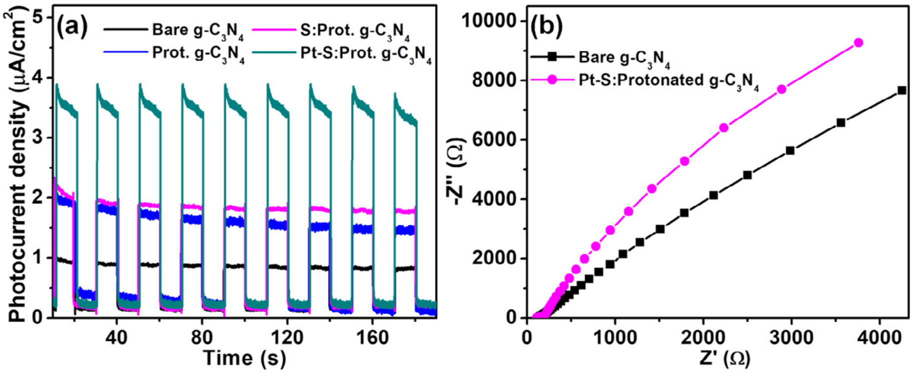

Fig. 4. (a) Photocurrent density and (b) impedance properties (Nyquist plot) of the bare and modified g-C_3N_4.

improves the photocatalytic properties rapidly by enhancing the charge separation in the system, which facilitates the rapid generation and reduction of H^+ ions into H_2 molecules [12]. In addition, the amount of hydrogen produced by Pt-deposited GCN and PGCN is also obtained and given in the insert of Fig. 3(a). These results also showed that the Pt deposition enhances the photocatalytic properties of GCN and PGCN. However, the synergistic effect of protonation, sulfur-doping and Pt disposition drastically enhances the overall photocatalytic efficiency of the system. The recycle experiment (Fig. 3(b)) showed a consistent hydrogen production efficiency of Pt-S:PGCN, which demonstrates their excellent chemical and photo-stability for a prolonged utilization of the photocatalyst.

The photocurrent measurements (Fig. 4(a)) demonstrated a significant enhancement in the photocurrent density of Pt-S:PGCN nanolayers as compared to the other samples. This could be attributed to the presence of Pt NPs, which facilitated the enhanced charge separation and transportation of electrons in the conduction band of S:PGCN [13]. Similarly, the observed slight enhancement for S:PGCN as compared to PGCN may be attributed to their reduced band gap energy in addition to the effective charge separation in the system. It is noteworthy that the observed gradual decrement in the (damping) photocurrent density of PGCN with increasing time may be due to the intercalated protons in PGCN layers that enhanced the photocurrent density, which further stabilized with time. This essentially signifies that the intercalated protons facilitated the stronger exfoliation and conductivity of the Pt-S:PGCN nanolayers [9,14]. Further, as it is observed from the Nyquist plots (Fig. 4(b)), the recombination resistance is considerably decreased for Pt-S:PGCN as compared to GCN, which in-lines with the observed improved photocurrent density of Pt-S:PGCN.

4. Conclusion

Pt-deposited sulfur-doped protonated g-C_3N_4 nanolayers were synthesized via a wet-chemical process. The obtained results showed that the Pt-S:PGCN could be a promising photocatalyst towards the effective production of hydrogen under sunlight. From the obtained results, the observed synergistic enhancements in the properties of Pt-S:PGCN could be attributed to (i) the improved active sites due to the intercalated H^+ ions and the resulted effective layer separations, (ii) the reduced band gap energy due to S-doping and the effective adsorption of surrounding molecules and (iii) the effective charge separation and transportation of electrons for the rapid reduction of H^+ ions into H_2 molecules.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.matlet.2018.02.013.

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