Converting CO_2 into fuels by graphitic carbon nitride based photocatalysts

Lingxia Zhang*, Mengli Li, Min Wang, Jianlin Shi

Shanghai Institute of Ceramics, Chinese Academy of Science, Shanghai, 200050, P.R. China

**Lingxia Zhang: +86 21 52413122 zhlingxia@mail.sic.ac.cn*

Abstract: CO_2 catalytic conversion using solar energy to high-value chemicals is a promising strategy to close the carbon cycle and a great challenge to achieve satisfying solar-to fuel conversion for practical application. Graphitic carbon nitride (g-C_3N_4) has attracted considerable attention owing to its excellent chemical and thermal stability, appealing electronic structure, and environmentally friendly features. However, its photocatalytic efficiency is still moderate because of the fast recombination of its photo-generated charge carriers and the mismatch between its band gap and solar radiation spectrum. In order to inhibit the recombination of charge carriers, we designed and synthesized g-C_3N_4 based heterostructure with other semiconductors (e.g. mesostructured m-CeO_2/g-C_3N_4, Bi_2WO_6/g-C_3N_4, 1D core-shell nanowire $LaPO_4$/g-C_3N_4, MnO_x/g-C_3N_4) for photocatalytic reduction of CO_2 into CO, CH_4 etc. After the combination of hetero-components, the light adsorption, conductivity, and separation of charge carriers have been greatly enhanced, thus the CO or CH_4 evolution by CO_2 reduction have been remarkably improved. And the synergetic effect between the two components in these catalyst systems played key roles in the enhancement of the photocatalytic activity of carbon nitride.

Keywords: graphitic carbon nitride, CO_2 reduction, photocatalysis.

1. Introduction

Energy shortage and air pollution caused by the use of fossil fuels are among the most serious problems we are now facing. The conversion of solar energy to chemical energy by photocatalytic CO_2 reduction to other valuable chemicals or fuels (such as CO, CH_4, HCOOH, and so on) using semiconductor materials is an increasingly important issue, which is one of the most promising methods to simultaneously solve both energy and environmental problems. Graphitic carbon nitride (g-C_3N_4) has attracted considerable attention owing to its excellent chemical and thermal stability, appealing electronic structure, and environmentally friendly features. However, its photocatalytic efficiency is still moderate because of the fast recombination of its photo-generated charge carriers and the mismatch between its band gap and solar radiation spectrum. In order to inhibit the recombination, we designed and synthesized g-C_3N_4 based heterostructure with other semiconductors (e.g. mesostructured m-CeO_2/g-C_3N_4, Bi_2WO_6/g-C_3N_4, 1D core-shell nanowire $LaPO_4$/g-C_3N_4, MnO_x/g-C_3N_4) for photocatalytic reduction of CO_2 into CO, CH_4 etc.

2. Experimental (or Theoretical)

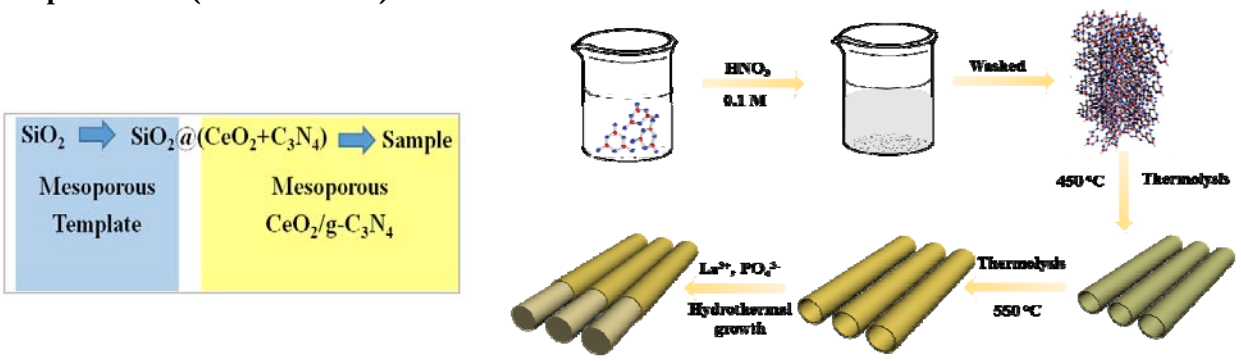

Figure 1. Synthesis of mesostructured m-CeO_2/g-C_3N_4 and 1D core-shell nanowire $LaPO_4$/g-C_3N_4.

3. Results and discussion

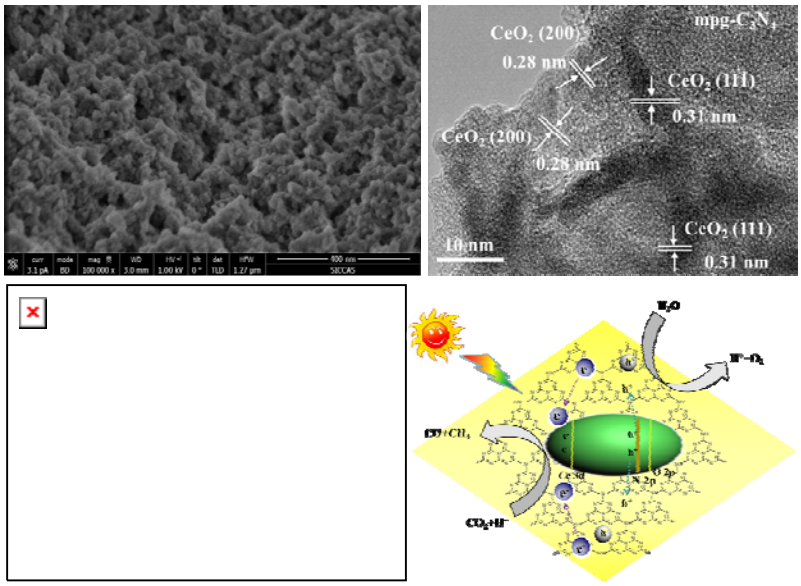

Figure 2. The figure shows the schematic illustrations of the proposed mechanism in the m-CeO_2/g-C_3N_4 heterostructures: electron and hole pairs generated in g-C_3N_4 and CeO_2 under light irradiation; the electrons on the conduction band of g-C_3N_4 migrate to that of CeO_2, while the holes generated on the valence band of CeO_2 migrate to that of g-C_3N_4. At the VB of g-C_3N_4, H_2O molecules are oxidized by h^+ to generate O_2 and H^+, meanwhile, at the VB of CeO_2, CO_2 molecules are reduced to CO and CH_4 by e- with the assistance of H^+.

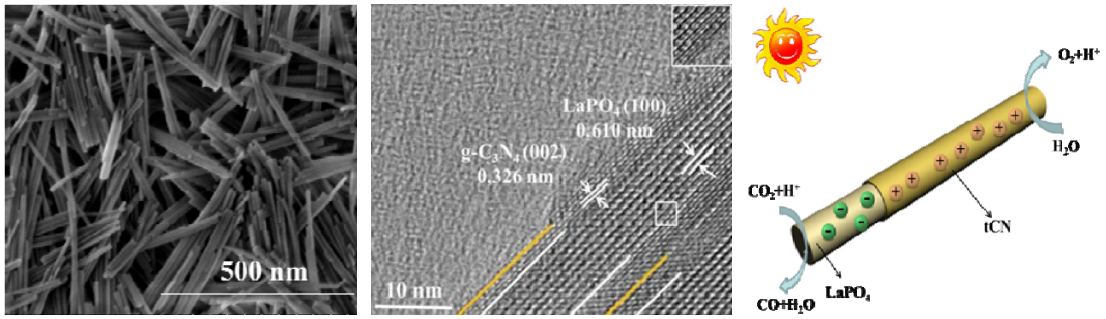

Figure 3. Once irradiated by simulated sunlight, both tCN and $LaPO_4$ can produce electrons and holes. Because of the well-matched and overlapping band structure and the extensive interface in close contact, electrons on the CB of tCN will directly transfer to that of LaPO4, meanwhile, holes on the VB of $LaPO_4$ transfer to that of tCN spontaneously. This results in an efficient space separation between h^+ and e^-, and thus reduces the probability of charge recombination. In this process, both tCN and $LaPO_4$ are activated. At the VB of tCN, H_2O molecules are oxidized by h^+, generating O_2 and protons. At the same time, CO_2 molecules can be reduced to CO by e^- at the CB of $LaPO_4$ with the assistance of protons.

4. Conclusions

After the combination of hetero-components, the light adsorption, conductivity, and separation of charge carriers have been greatly enhanced, thus the CO or CH_4 evolution by CO_2 reduction have been remarkably improved. And the synergetic effect between the two components in these catalyst systems played key roles in the enhancement of the photocatalytic activity of carbon nitride.

References

1. M. Wang, M. Shen, L.X. Zhang, J.J. Tian, X.X. Jin, Y.J. Zhou, J.L. Shi, Carbon 120 (2017) 23.
2. M.L. Li, L.X. Zhang, X.Q. Fan, M.Y. Wu, M. Wang, R.L. Cheng, L.L. Zhang, H.L. Yao, J.L. Shi, Appl Catal B Environ 201 (2017), 629.
3. M.L. Li, L.X. Zhang, X.Q. Fan, M.Y. Wu, Y.Y. Du, M. Wang, Q.L. Kong, L.L. Zhang, J.L. Shi, Appl Catal B Envrion 190(2016) 36.
4. M.L. Li, L.X. Zhang, M.Y. Wu, Y.Y. Du, X.Q. Fan, M. Wang, L.L. Zhang, Q.L. Kong, J.L. Shi, Nano Energy 19 (2016) 145.