Nanostructure rod-like TiO_2-reduced graphene oxide composite aerogels for highly-efficient visible-light photocatalytic CO_2 reduction

Sijia Liu [a,b,c], **Gang Tan** [a], Sheng Cui [b,c], **Xiaodong Shen** [b,c]

[a] *Department of Civil and Architectural Engineering, University of Wyoming, Laramie, WY 82071, USA*
[b] *College of Materials Science and Engineering, Nanjing Tech University, Nanjing 210009, China*
[c] *Jiangsu Collaborative Innovation Center for Advanced Inorganic Function Composites, Nanjing Tech University, Nanjing 210009, China*

Email address: njtechlsj@163.com (S. Liu), scui@njtech.edu.cn (S. Cui), gtan@uwyo.edu (G. Tan), xdshen@njtech.edu.cn (X. Shen)

Abstract

In response to the worldwide over-standard carbon dioxide emission problem [1, 2], this work synthesized a series of titanium dioxide/reduced graphene oxide composite aerogels (rGO-Ti) for photoconversion of CO_2 by a one-step hydrothermal and freeze-drying method. The microstructure, chemical composition, optical characteristics and photocatalytic reduction activity of samples have been tested and analyzed. The conclusions were summarized as follows: (1) The 3-D network structure rGO aerogel are introduced to rod-like TiO_2 with a diameter of 10-20 nm and length of 100-150 nm. The hydrothermal reaction between Ti^{4+} and graphene formed strong O=C-O-Ti group which is related to specific chemical bonding sites. (2) The surface area of rGO-25Ti aerogel is as high as 287.3 m^2/g and it also has high pore volume of 0.72cm^3/g, which is beneficial for more absorption of reactants and rapid transfer of products. (3) Under visible light irradiation, the rGO reinforced samples, especially in-situ rGO-Ti aerogel, exhibit much higher light absorption efficiency than pure P25, in which the graphene sheets play an important role in accelerating electron transfer. (4) According the Kubelka-Munk function, the calculated band gap value of rGO-25Ti (TiO_2-rGO with 25mmol Ti^{4+}, 2.9eV) is lower than that of commercial P25 (3.2eV), resulting in red shift in the absorption edge and contributing higher photocatalytic activity. (5) When the addition amount of $TiCl_4$ to graphene solution for hydrothermal was 25 mmol, the highest carbon conversion of TiO_2-rGO aerogel was 21.38 μmol/g, as much as 15.7 times of the conversion rate of pure P25. To sum up, the rGO aerogel-based photocatalyst composite synthesized with $TiCl_4$ as precursor was applied to photocatalytic CO_2 reduction for the first time. This work indicates that this sort of material could be used as a promising photocatalyst for the photoreduction of carbon dioxide [3, 4].

Keywords

Rod-like TiO_2; reduced graphene oxide; aerogel; nano composite; visible light photocatalysis; CO_2 conversion

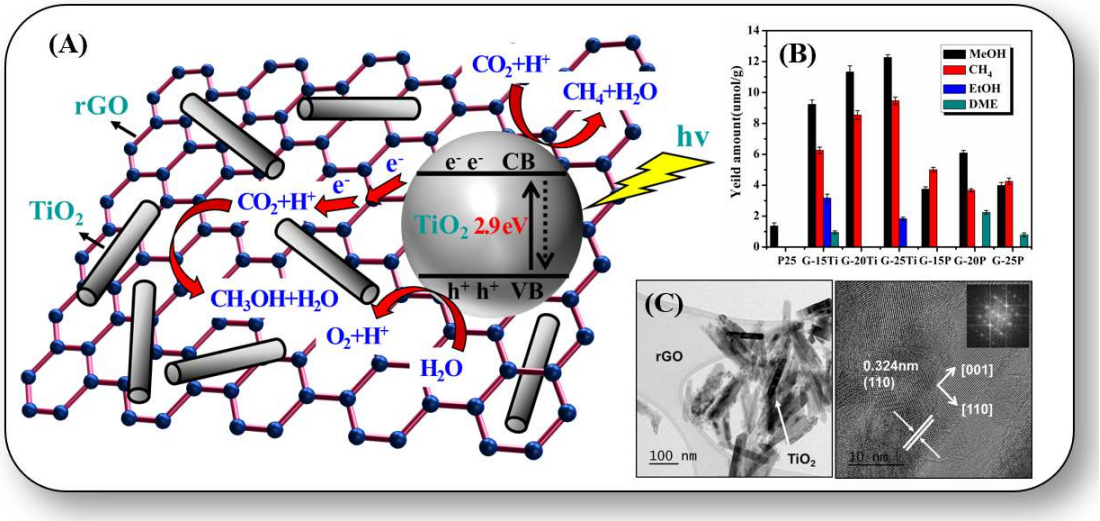

Fig.1 (A) Schematic illustration of the band structure and charge separation in TiO2-rGO, (B) MeOH, CH_4, EtOH and DME yields amount of photocatalytic conversion of CO_2 for different catalysts and (C) TEM micrographs of G-25Ti composite.

Reference

[1] B. Adeniran, R. Mokaya. Compactivation: A mechanochemical approach to carbons with superior porosity and exceptional performance for hydrogen and CO_2 storage. Nano Energy. 16 (2015) 173-85.

[2] G.G. Esquivel-Patino, M. Serna-Gonzalez, F. Napoles-Rivera. Thermal integration of natural gas combined cycle power plants with CO_2 capture systems and organic Rankine cycles. Energy Conversion And Management. 151 (2017) 334-42.

[3] Y. Wei, X. Wu, Y. Zhao, L. Wang, Z. Zhao, X. Huang, et al. Efficient photocatalysts of TiO_2 nanocrystals-supported PtRu alloy nanoparticles for CO_2 reduction with H_2O: Synergistic effect of Pt-Ru. Applied Catalysis B: Environmental. 236 (2018) 445-57.

[4] Bie C, Zhu B, Xu F, et al. In Situ Grown Monolayer N-Doped Graphene on CdS Hollow Spheres with Seamless Contact for Photocatalytic CO_2 Reduction[J]. Advanced Materials, 2019, 31(42).

Acknowledgements

This work was financially supported by the Wyoming State Legislator through the School of Energy Resources, University of Wyoming, USA. This project is also supported by the Industry Program of Science and Technology Support Project of Jiangsu Province (BE2016171), the Program for Changjiang Scholars and Innovative Research Team in University (No.IRT_15R35), the Major Program of Natural Science Fund in Colleges and Universities of Jiangsu Province (15KJA430005), the Priority Academic Program Development of Jiangsu Higher Education Institution (PAPD).