Crucible-Dependent Modulation of Graphitic Carbon Nitride Properties for Enhanced Photon-Assisted CO2 Reduction: A Comprehensive Structure-Activity Correlation Study

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This study investigates the impact of crucible materials on the properties and photon-assisted catalytic performance of graphitic carbon nitride (g-C_3N_4) for CO_2 reduction. Our findings reveal that crucible choice significantly influences g-C_3N_4's crystallinity, surface area, pore structure, and defect chemistry. g-C_3N_4 synthesized in aluminum (Al-gCN) and zirconium (Zr-gCN) crucibles demonstrated superior performance in photon-assisted CO_2 reduction to methane and methanol. Notably, photon-assisted catalytic activity for CO_2 reduction depends on a complex interplay of factors beyond conventional parameters like bandgap and band edge positions. Surface functionalities, light absorption characteristics, and adsorption properties emerged as crucial determinants of catalytic performance. To address this complexity, we introduce two key parameters correlating with catalytic activity: the normalized surface concentration (NSC%) from XPS analysis and surface area measurements and the D.P/S.A ratio from derivative UV-DRS and surface area measurements. These findings provide valuable insights into structure-property-performance relationships in g-C_3N_4 materials and offer guidance for optimizing their synthesis for CO_2 reduction applications. Our study emphasizes the importance of crucible selection in designing efficient g-C_3N_4 catalysts for photon-assisted processes, paving the way for advancements in CO_2 reduction technologies.

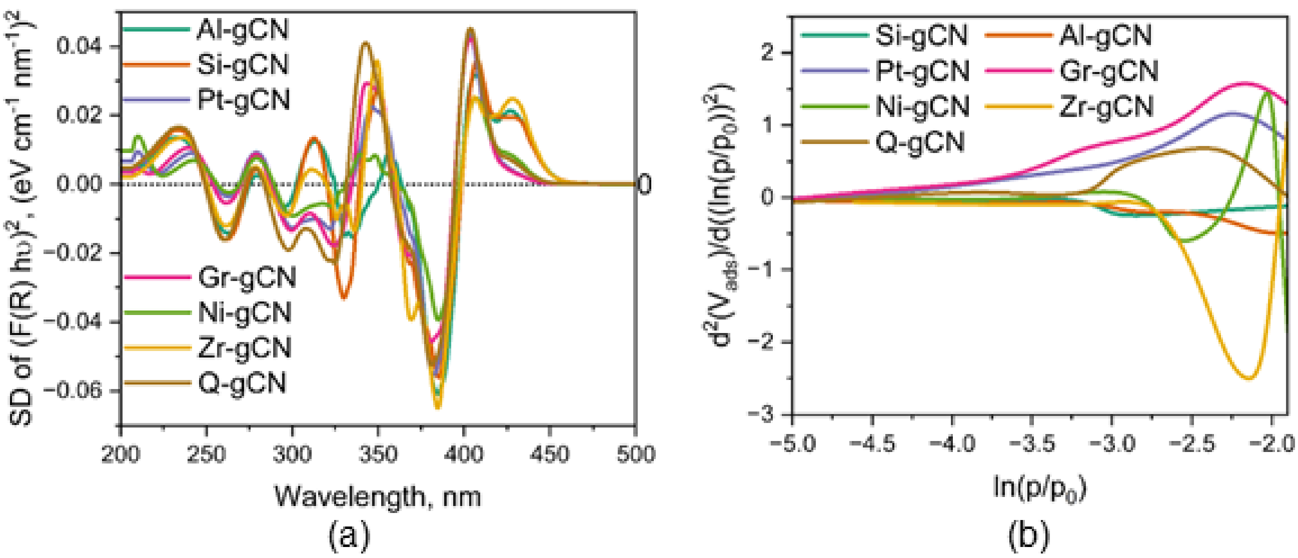

Figure 1. Second derivative analysis of (a) UV-Visible Diffuse Reflectance Spectra (UV-DRS) and (b) Derivative Isotherm Summation (DIS) for g-C3N4 systems synthesized using various crucibles

References:

[1] Dubrovkin, J., Derivative Spectroscopy; Cambridge Scholars Publishing: 2020.

[2] Villieras, F.; Michot, L. J.; Bardot, F.; Cases, J. M.; Francois, M.; Rudzinski, W. An Improved Derivative Isotherm Summation Method to Study Surface Heterogeneity of Clay Minerals. Langmuir 1997, 13, 1104–1117.

[3] Scheinost, A. C.; Chavernas, A.; Barron, V.; Torrent, J. Use and Limitations of Second-Derivative Diffuse Reflectance Spectroscopy in the Visible to Near-Infrared Range to Identify and Quantify Fe Oxide Minerals in Soils. Clays and Clay Minerals 1998, 46, 528–536.