

Sulfur-doped carbon nitride hybrid materials tested under green light for photoelectrocatalytic benzylamine oxidation and oxygen evolution reactions

Maria Jerigova¹, Yevheniia Markushyna¹, Ivo F. Texeira^{1,2}, Bolortuya Badamdorj¹, Mark Isaacs^{3,4}, Daniel Cruz⁵, Iver Lauerman⁶, Miguel Ángel Muñoz-Márquez⁷, Nadezda V. Tarakina¹, Nieves Lopez Salas¹, Aleksandr Savateev¹, Pablo Jiménez-Calvo^{1,*}

¹ Department of Colloid Chemistry, Max-Planck-Institute of Colloids and Interfaces, Potsdam, Germany

² Department of Chemistry, Federal University of São Carlos, São Carlos, Brazil

³ HarwellXPS, Research Complex at Harwell, Rutherford Appleton Lab, Didcot, United Kingdom

⁴ Department of Chemistry, University College London, 20 Gower Street, London, United Kingdom

⁵ Department of Inorganic Chemistry, Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany

⁶ Helmholtz-Zentrum Berlin für Materialien und Energie, Department, Berlin, Germany

⁷ Chemistry Division, School of Science and Technology, University of Camerino, Camerino, Italy

*e-mail address: pablo.jimenez-calvo@mpikg.mpg.de

Keywords: carbon nitride, purpald, sulfur, benzylamine photooxidation, oxygen evolution

High-performing materials will dictate the pace of reinventing industrial chemical processes to achieve carbon neutrality^[1]. Visible-light photoelectrocatalysts from abundant resources will play a key role in exploiting solar irradiation^[2]. Anionic doping via pre-organization of precursors and further co-polymerization creates tuneable, extrinsic semiconductors. Triazole derivative-purpald, an unexplored precursor with sulfur (S) container, combined in different initial ratios with melamine during one solid-state polycondensation with two thermal steps yields hybrid S-doped carbon nitrides (C₃N₄).

The series of S-doped/C₃N₄-based materials showed enhanced optical, electronic, structural, textural, and morphological properties and exhibited higher performance in organic benzylamine photooxidation, oxygen evolution, and similar energy storage (capacitor brief investigation)^[3]. 50M-50P exhibited the highest photooxidation conversion yield (84±3%) of benzylamine to imine at 535 nm – green light for 48h (**Figure 1**), due to an extra discrete shoulder reaching ~700 nm, an unusual high sulfur content, preservation of crystal size, new intraband energy states, rare deep structural defects by layer distortion, hydrophobic surface, low porosity, and 10-16 nm pores. An in-depth analysis of S doping was investigated coupling x-ray photoelectron spectroscopy, transmission electron microscope, and elemental analysis, providing insights on bonds, distribution, and surface/bulk content. This work contributes to the development of disordered photocatalysts with long-visible-light range for solar energy conversion and storage.

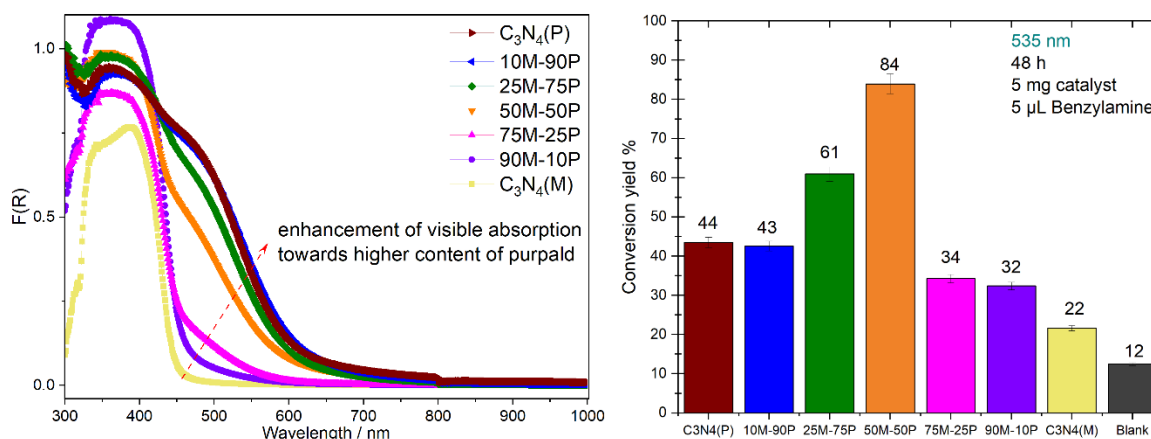


Figure 1. **Left)** Kubelka-Munk UV-vis spectra. **Right)** Photooxidation of benzylamine including the reaction conditions.

[1] Mark Isaacs, Julio Garcia-Navarro, Wee-Jun Ong, Pablo Jiménez-Calvo, Global Challenges, **2022**, production.

[2] Pablo Jiménez-Calvo, Valérie Caps, Valérie Keller, Renewable and Sustainable Energy Reviews, **2021**, 149, 111095

[3] Maria Jerigova, Yevheniia Markushyna, Ivo F. Texeira, Bolortuya Badamdorj, Mark Isaacs, Daniel Cruz, Iver Lauerman, Miguel Ángel Muñoz-Márquez, Nadezda V. Tarakina, Nieves Lopez Salas, Aleksandr Savateev, Pablo Jiménez-Calvo, ChemRxiv Cambridge Open Engage, **2022**