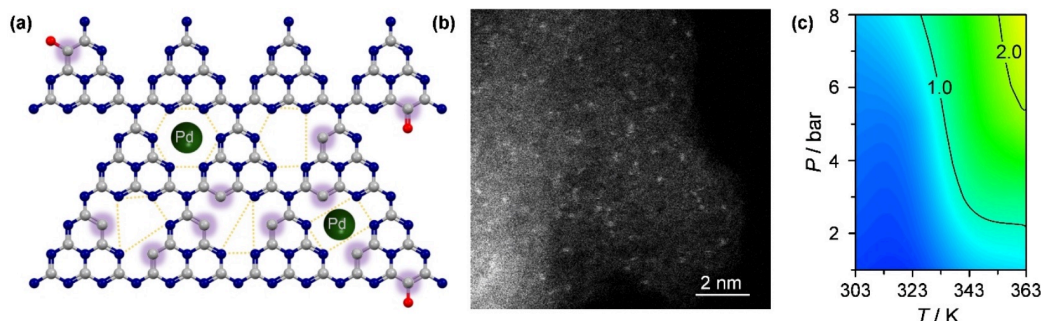


## Stabilization of single metal atoms on graphitic carbon nitride

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Graphitic carbon nitride (g-C<sub>3</sub>N<sub>4</sub>) exhibits unique properties for the preparation of single-atom heterogeneous catalysts (SAHCs) due to the presence of six-fold nitrogen-based coordination sites in the lattice.<sup>1</sup> Understanding how the synthesis method, carrier properties, and metal identity impact the isolation of metal centers is essential to guide their design (**Figure 1**). This study compares the effectiveness of direct and post-synthetic routes to prepare SAHCs incorporating different metals (Pd, Pt, Ag, Ir) in g-C<sub>3</sub>N<sub>4</sub> carriers of distinct morphology (bulk, mesoporous and exfoliated) and composition (C/N ratio). The speciation (single atoms, dimers, clusters, or nanoparticles), distribution, and oxidation state of the supported metals are characterized by multiple techniques. SAHCs are most readily attained via direct approaches applying copolymerizable metal precursors and employing high surface area carriers. In contrast, although post-synthetic routes enable improved control over the metal loading, nanoparticle formation is more prevalent. Comparison of the impact of carrier morphology also points toward the involvement of defects in stabilizing single atoms, while tailoring the carrier composition through the introduction of carbon-rich heterocycles during the synthesis visibly affects the interaction with the metal. The distinct metal dispersions and chemical states are rationalized by density functional theory and kinetic Monte Carlo simulations, highlighting the interplay between the adsorption energetics and diffusion kinetics. Evaluation in the continuous three-phase semihydrogenation of 1-hexyne or 2-methyl-3-butyn-2-ol identifies controlling the metal-carrier interaction and exposing the metal sites at the surface layer as key challenges in designing efficient SAHCs.



**Figure 1** (a) Schematic of Pd atoms stabilized in the g-C<sub>3</sub>N<sub>4</sub> structure. Doped C atoms are highlighted by a purple glow. Yellow dashed lines connect N atoms within the coordination sites. (b) AC-STEM image of the Pd dispersion on g-C<sub>3</sub>N<sub>4</sub>. (c) Reaction rate (in 10<sup>3</sup> mol<sub>product</sub> mol<sub>Pd</sub><sup>-1</sup> h<sup>-1</sup>) of 2-methyl-3-butyn-2-ol hydrogenation at different temperatures and pressures.

[1] G. Vilé, D. Albani, M. Nachtegaal, Z. Chen, D. Dontsova, M. Antonietti, N. López, J. Pérez-Ramírez, *Angew. Chem. Int. Ed.* **2015**, 54, 11265.

[2] Z. Chen, S. Mitchell, E. Vorobyeva, R. K. Leary, R. Hauert, T. Furnival, Q. M. Ramasse, J. M. Thomas, P. A. Midgley, D. Dontsova, M. Antonietti, S. Pogodin, N. López, J. Pérez-Ramírez, *Adv. Funct. Mater.* **2017**, 27, 1605785.