# Development of heterometallic nanoparticles by polyoxometalate protection

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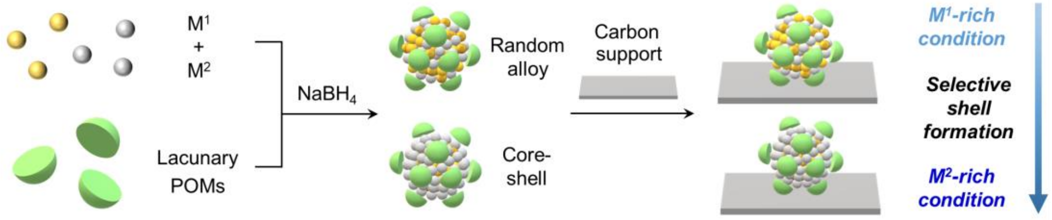
Metal nanoparticles have been widely employed in diverse research fields and can be precisely designed with desired properties for various applications through varying factors such as sizes and electronic states.[1] Heterometallic nanoparticles offer an additional degree of freedom for property modulation by incorporating two and more metals within a single particle.[2] However, conventional synthesis of heterometallic nanoparticles often involves complex, multiple-step procedures and faces with challenges in controlling the hybrid structures.[2] Recently, we demonstrated that lacunary polyoxometalates (POMs), a family of molecular metal oxides, can be used to prepare ultrastable and highly reactive monometallic nanoparticle catalysts, whose catalysis can be further modulated by varying the POM structure.[3] Our group also previously reported the synthesis of heterometallic nanoclusters by utilizing selective affinity of lacunary POMs toward different metals.[4] Considering these findings, we envisioned that heterometallic nanoparticles with controlled structures could be feasibly prepared by utilizing both the protection effects and selective affinity of lacunary POMs.

In this work, we reported a facile co-reduction method for developing heterometallic nanoparticles in aqueous solution. Specifically, through selecting metals ($M^1$ and $M^2$) with differing affinity to lacunary POMs, either random alloy or core–shell structures can be controlled simply by adjusting the molar ratio of two types of metals. A series of characterization and control experiments confirmed the unique role of lacunary POMs compared to conventional protecting ligands. Furthermore, these heterometallic nanoparticles were immobilized on the carbon support and exhibited superior catalytic activity compared to their monometallic counterparts.



(1) *Nat. Nanotechnol.* **2021**, *16*, 129. (2) *Adv. Sci.* **2022**, *9*, 2104054. (3) a) *Angew. Chem. Int. Ed.* **2022**, *61*, e202205873. b) *Nat. Commun.* **2024**, *15*, 851. c) *Dalton Trans.* **2024**, *53*, 11088. (4) a) *J. Am. Chem. Soc.* **2019**, *143*, 12809. b) *Angew. Chem. Int. Ed.* **2024**, *63*, e202408358.