

Metal–Organic Frameworks for Photocatalytic CO₂ Conversion Under Visible Light

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Molecular catalysts are typically used as a discrete unit having free-motion in solvents, so it has been challenging to design the spacial condition that the catalytic reactions are taking place. In this talk, we show how covalently attached photoactive centers within metal-organic framework (MOF) interior can be spatially localized and subjected to the enhanced electromagnetic field surrounding plasmonic silver nanocubes to significantly increase their photocatalytic activity. Specifically, we covalently attached ReI(CO)₃(BPYDC)Cl, BPYDC = 2,2'-bipyridine-5,5'-dicarboxylate, into a zirconium MOF, UiO-67, and controlled its density in the pores in increments (0, 1, 2, 3, 5, 11, 16, and 24 complexes per unit cell), finding the highest activity for 3 complexes. Placing this construct on silver nanocubes resulted in seven-fold enhancement of carbon dioxide conversion to carbon monoxide under visible light.