Assembling Ni$^{2+}$ complexes and gold nanoparticles on γ-Al$_2$O$_3$ as visible light photocatalysts for hydrogenolysis of lignin model compounds

Pengfei Han$^1$, Sarina Sarina$^1$, HuaiYong Zhu$^1$*

$^1$School of Chemistry, Physics and Mechanical Engineering, Faculty of Science and Technology, Queensland University of Technology, Brisbane, QLD 4001, Australia

Lignin is a main constituent (15-30% by weight, 40% by energy) of lignocellulosic biomass, which refers to the most abundantly available raw material on the earth for the production of bio-fuels. Besides, a large volume of lignin waste is produced annually by the paper industry. However, the aryl ether bonds of lignin are relatively unreactive, depolymerisation of lignin into small molecules is challenging, so more than 98% of lignin is currently simply burned to provide heat for other industrial processes.

The major repeating units of lignin are orthomethoxy-substituted C$_9$ phenolic moieties, which are cross-linked by relatively unreactive C-O bonds, contributed by β-O-4 (45-62%), α-O-4 (3-12%), and 4-O-5 (4-9%) linkages. The conversion of lignin into high-volume and low-molecular weight aromatic molecules has become the center of interest for scientists worldwide.

Nickel has been found as an effective element in catalyzing C-O bond cleavage of lignin models by hydrogenolysis, but the operating temperature (>150 °C) is still high that over-reduction could easily happen and by-products like saturated cycloalkanols would be obtained inevitably.

Herein, the photocatalytic performance of the Au-Ni$^{2+}$ system for the cleavage of benzyl phenyl ether and 2-phenyl phenyl ether that have α-O-4 and β-O-4 linkages, respectively, is investigated. The catalytic activity of Ni complexes can be enhanced by the localized surface plasmon resonance (LSPR) effect of nearby Au nanoparticles under visible light irradiation, thus making the reactions happened at a mild condition (90°C).

Figure 1. The Schematic illustration of the synthesized nAu@Al$_2$O$_3$-silane-NH$_2$-Ni$^{2+}$ photocatalyst, A) TEM image and B) EDS mapping of the photocatalyst, C) Comparison of the catalytic performance of the Au-Ni$^{2+}$ composite catalyst with the monometallic catalysts (supported Au NPs and immobilized Ni$^{2+}$) and the mixture (supported Au NPs mixed with Ni salt) for C-O bond cleavage of lignin model compounds under visible light irradiation (blue) and in the dark (black). Reaction conditions: lignin model compounds (0.05 mmol), KOH (0.15 mmol), 2 mL of IPA solvent, 1 atm argon atmosphere, 20 mg of catalysts, under 90 °C for 24 h, halogen light intensity: 0.96 and 1.11 W cm$^{-2}$ in α-O-4 and β-O-4 reaction respectively.

References

Corresponding author email: hy.zhu@qut.edu.au