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## Understanding the Role of Gold Nanoparticles in Enhancing the Catalytic Activity of Manganese Oxides in Water Oxidation Reactions

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## Abstract:

The Earth-abundant and inexpensive manganese oxides  $(MnO_2)$  have emerged as an intriguing type of catalysts for the water oxidation reaction. However, the overall turnover frequencies of  $MnO_x$  catalysts are still much lower than that of nanostructured  $IrO_2$  and  $RuO_2$  catalysts. Herein, we demonstrate that doping  $MnO_x$  polymorphs with gold nanoparticles (AuNPs) can result in a strong enhancement of catalytic activity for the water oxidation reaction. It is observed that, for the first time, the catalytic activity of  $MnO_x/AuNP$  catalysts correlates strongly with the initial valence of the Mn centers. By promoting the formation of  $Mn^{3+}$  species, a small amount of AuNPs (<5%) in  $\alpha$ - $MnO_2/AuNP$  catalysts significantly improved the catalytic activity up to 8.2 times in the photochemical and 6 times in the electrochemical system, compared with the activity of pure  $\alpha$ - $MnO_2$ .

Key-words: manganese oxide, metal nanoparticles, oxygen evolution reaction, transition-metal oxides, water oxidation

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