

# Synthesis of Au Nanoparticles Supported on MnO<sub>2</sub> Nanowires for High Performances in the Silane Oxidation

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## Abstract

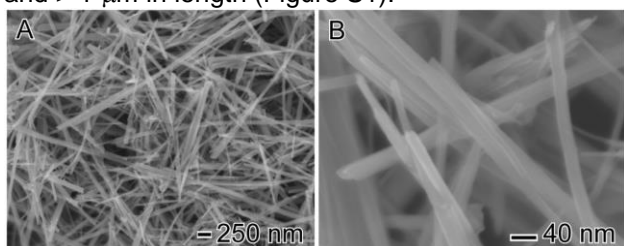
MnO<sub>2</sub> nanowires decorated with ultrasmall Au NPs showed high catalytic activities towards the green oxidation of silanes.

## Introduction

Gold (Au) nanoparticles are known to be highly active towards a wide variety of heterogeneous catalytic transformations, including oxidation, reduction, C-C coupling reactions, and others.<sup>1</sup> Among these transformations, silane oxidations are especially attractive as silanols are a key element in the production of silicon-containing materials.<sup>2</sup> However, conventional routes for the silane oxidation generally require the presence of strong and toxic oxidants such as permanganate and dichromate.<sup>2</sup> Here, we demonstrate that high catalytic performances (TOF = 590000 h<sup>-1</sup>) could be achieved towards the green oxidation of silanes and H<sub>2</sub> production under ultralow Au loadings (0.001 – 0.0002 mol % in terms of Au) employing H<sub>2</sub>O as the oxidant, 25 °C as the reaction temperature, and MnO<sub>2</sub> nanowires decorated with ultrasmall Au NPs (having diameters of 3 nm or less) as catalysts.

## Results and Discussion

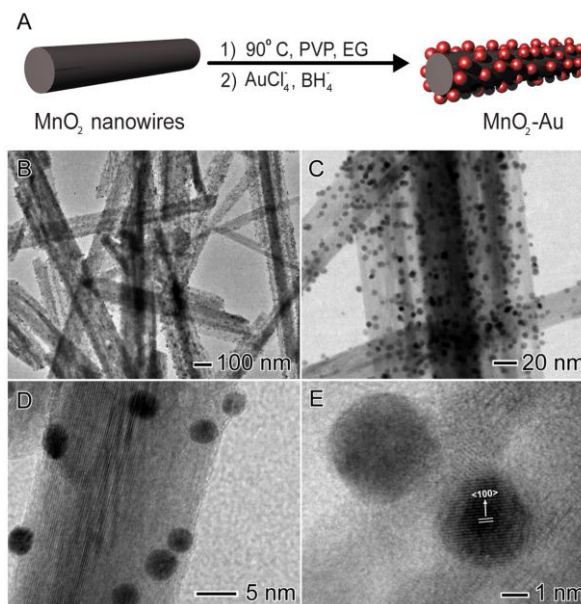
The investigations started with the synthesis of MnO<sub>2</sub> nanowires (Figure 1) obtained by the hydrothermal method.<sup>3</sup> The nanowires displayed well-defined shapes and uniform sizes, being 34 ± 5 nm in width and > 1 µm in length (Figure S1).



**Figure 1.** SEM images of MnO<sub>2</sub> nanowires employed as physical templates for Au deposition.

The MnO<sub>2</sub> nanowires could be directly employed as physical templates for the nucleation and growth of Au NPs over their surface without the need of any surface modification/functionalization steps as depicted in Figure 2.<sup>4</sup> Our approach employed AuCl<sub>4</sub><sup>-</sup> (aq) as the Au precursor, PVP as the stabilizer, BH<sub>4</sub><sup>-</sup> (aq) as the reducing agent, EG (ethylene glycol) as the solvent, and 90 °C as the reaction temperature. The uniform deposition (without agglomeration) of

monodisperse, spherical, and ultrasmall (3 ± 1 nm) Au NPs over the entire surface of the MnO<sub>2</sub> nanowires could be clearly detected.



**Figure 2.** (A) Strategy for the synthesis of MnO<sub>2</sub> nanowires decorated with ultrasmall Au NPs, (B–E) HRTEM images of MnO<sub>2</sub>-Au NPs.

In the next step, MnO<sub>2</sub> nanowires decorated with ultrasmall Au NPs were employed as heterogeneous catalysts towards the green oxidation of hydrosilanes and H<sub>2</sub> production. Surprisingly, high catalytic performances (TOF = 590000 h<sup>-1</sup>) could be achieved towards silane oxidations. The MnO<sub>2</sub>-Au NPs displayed good stability/recyclability, and no morphological changes or loss of activity were observed even after 10 reaction cycles.

## Conclusion

We described the catalytic activity of MnO<sub>2</sub> nanowires decorated with ultrasmall Au NPs (towards the green oxidation of hydrosilanes, which produces silanols and hydrogen gas (H<sub>2</sub>). Owing to their morphology comprised of ultrasmall Au NPs (3 nm), we found that the MnO<sub>2</sub>-Au NPs displayed high catalytic performances under ultralow Au loadings (0.001 - 0.0002 mol %).

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