Stabilizing Nanogold with Cerium-modified Titania Nanotubes

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Background

Nanostructured titania is a versatile material with unique optical and photocatalytic properties and has been active in industry and research frontiers for decades. When used as a catalytic support, it enables unusually high catalytic activity of gold nanoparticles for reactions such as CO oxidation and water-gas-shift reaction by triggering oxygen activation on the metal-support interface.

Small gold nanoparticles have demonstrated excellent catalytic activity in many reactions including CO oxidation at low temperatures. One drawback is their high potential to aggregate to decrease the reactivity, esp. at elevated temperatures. In our research, cerium species (Ce^{4+}/Ce^{3+}) are introduced as a chemical stabilizer for Au nanoparticles supported by titania nanotubes for enhanced thermal stability.

Objectives

1. Study the Au-Titania interaction in the titania nanotubes with different Au contents;
2. Understand the surface chemistry of the cerium-modified titania nanotubes;
3. Study the Au stabilization in the modified titania materials.

Material Synthesis

Stage 1: Anatase nanotubes (ANT)

1. Hydrothermal synthesis of sodium titanate nanotubes and ion exchange with mild acids to hydrated titania nanotubes;
2. Phase transformation to anatase by slow annealing in air up to 500 °C.

Stage 2: Au-doped ANTs (Au-ANT)

Various Au concentration is loaded using the deposition-precipitation method;

Stage 3: Ce-modified titania (Ce-TiO_x)

Stage 4: Au supported by Ce-modified titania (Au-Ce-TiO_x) (in process)

Anatase Nanotubes

The as-synthesized titanate nanotubes have show nanotubular structures with diameter about 6-8 nm. After annealing up to 500˚C, the nanotubular structures maintain, and the surface area decreased from 515 to a still impressive 383 m^2/g.

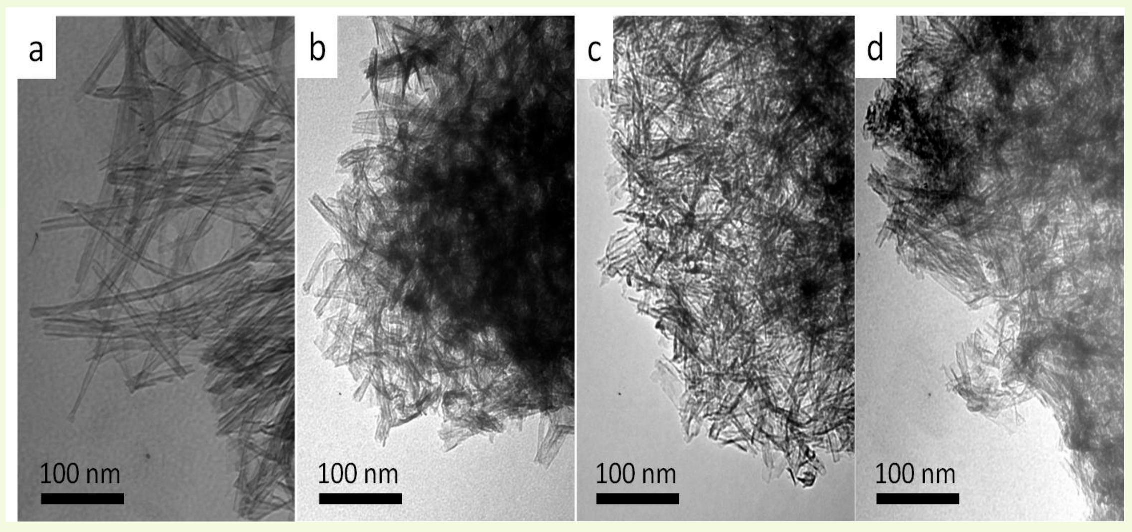

Figure 1. The TEM images of (a) the as-synthesized titanate nanotubes and the nanotubes after annealing at (b) 300, (c) 400, and (d) 500˚C.

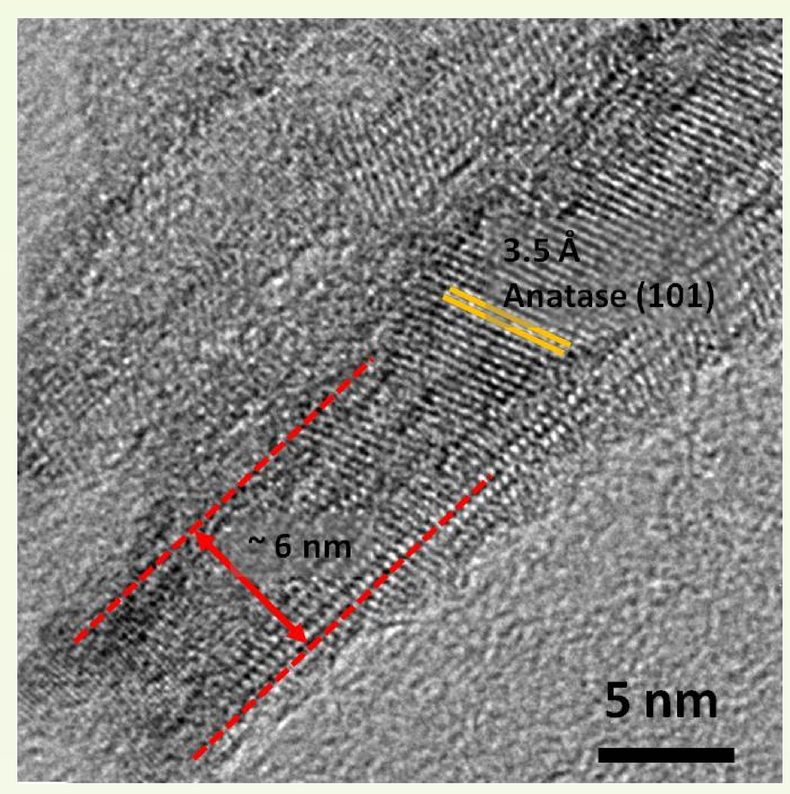

Figure 2. The HRTEM image of anatase nanotube.

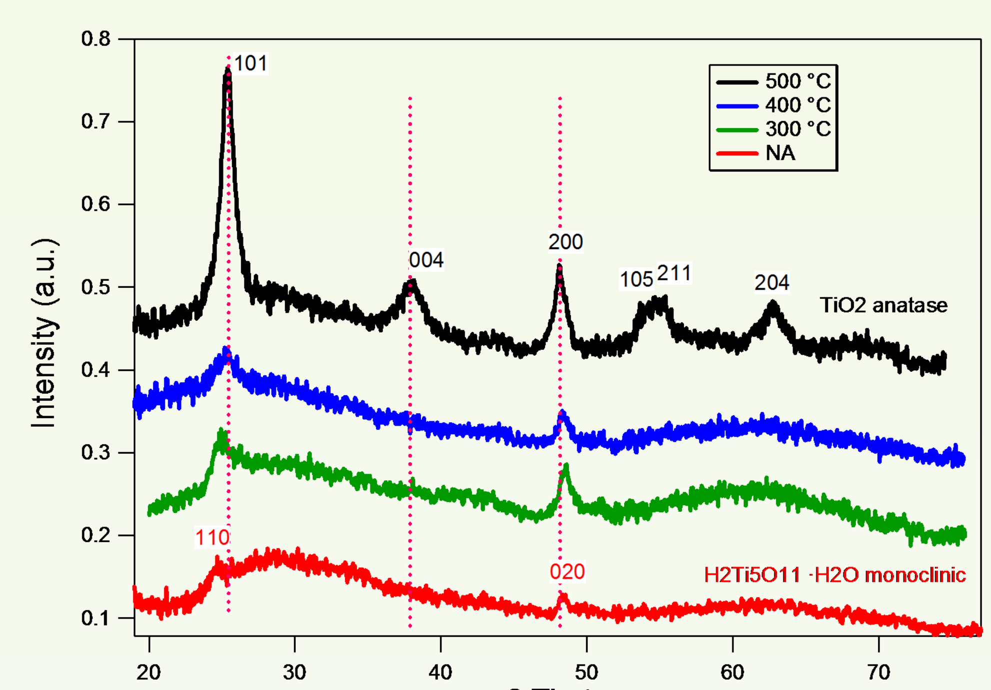

Figure 3. The XRD patterns of the as-synthesized titanate nanotubes and the nanotubes after annealing at 300, 400, and 500˚C.

Au-doped ANTs

The Au nanoparticles (3-5 nm in diameter) are uniformed dispersed in titanate nanotubes. The catalysts show excellent catalytic activities for CO oxidation at low temperatures. One limitation is the relative large size of Au nanoparticles, which easily lead to the deactivation of catalysts.

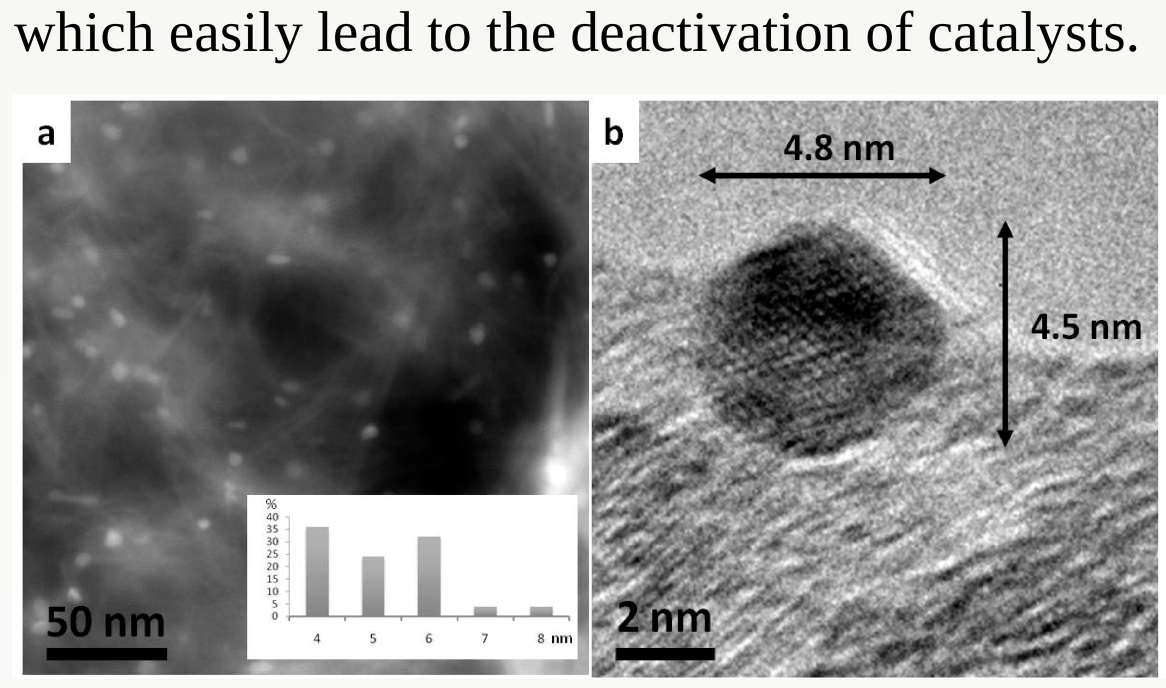

Figure 4. The TEM images of 1at%Au/HTNT. (a) HAADF image shows the Au nanoparticles are uniformed dispersed in titanate nanotubes, the size is 5.1±1.3 nm, and the inset shows a statistical size distribution; (b) one Au nanoparticle.

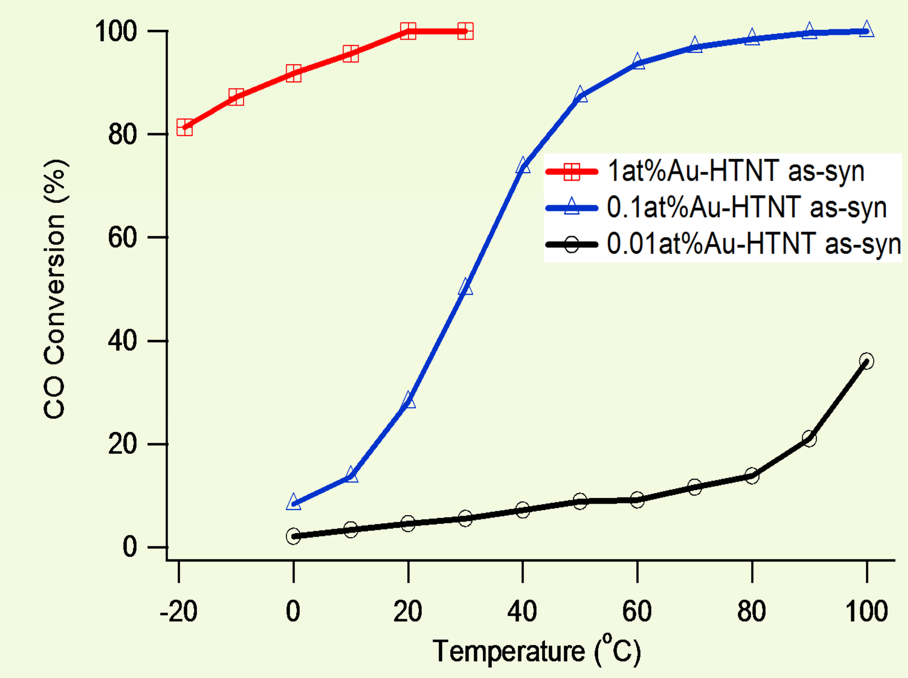

Figure 5. The catalytic behavior of Au/HTNT with different Au loading on catalytic CO oxidation.

Ce-modified Titania

The cerium-modified P25 samples have shown enhanced catalytic activity than bare ceria or titania. Optimized Ce content was found to be 5 at%.

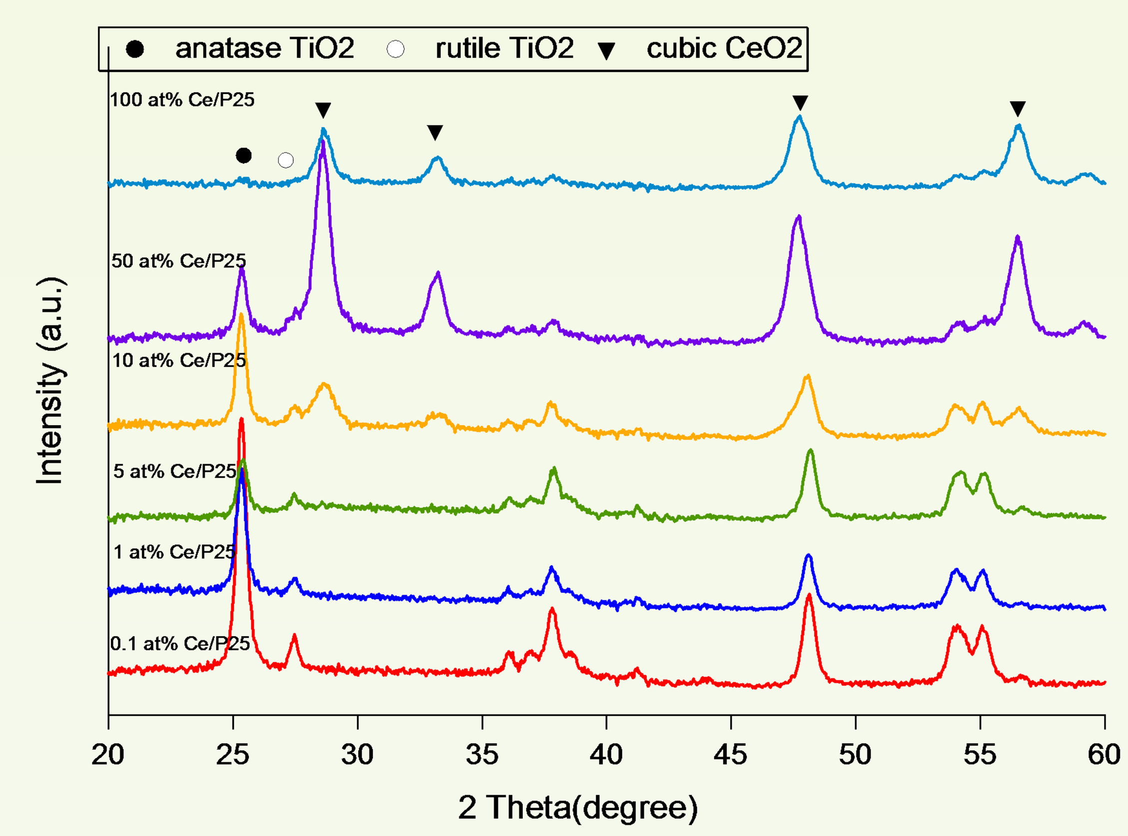

Figure 6. XRD patterns of Ce/TiO_2 with different Ce content.

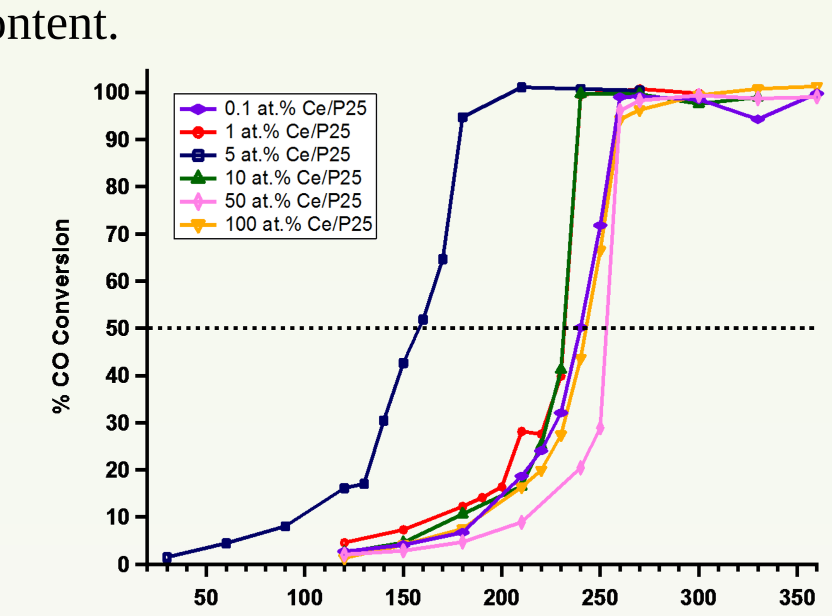

Figure 7. Catalytic performance of Ce/TiO_2.

Conclusion

1. Au nanoparticles supported by titanate and anatase nanotubes have high catalytic activity for CO oxidation.
2. Ce-modified titania exhibits interesting surface chemistry with increasing Ce species, leading to the enhanced catalytic performance.
3. Future effort will be dedicated to the understanding of how the Ce-modified titania stabilize the interfacial Au species.

Acknowledgment

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