

Synthesis and Catalytic Activity of Gold Nanoparticles Doped Anatase TiO₂ Mesocrystals

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Since the discovery that gold nanoparticles supported on transition metal oxides, such as titanium dioxide, is a catalyst with unique catalytic performances, gold catalysis has rapidly gained importance attracting many researchers [1–3].

The main aim of the work described here is the synthesis and characterization of catalysts based on anatase TiO₂ mesocrystals uniformly doped with Au nanoparticles, as well as the evaluation of its catalytic properties using as model the electron-transfer reaction between hexacyanoferrate (III) and borohydride ions.

The TiO₂ mesocrystals with a single-crystal like structure and tunable sizes were fabricated on a large scale through mesoscale assembly in the titanium (IV) butoxide-acetic acid system without any additives under solvothermal conditions [4].

The TiO₂@Au catalysts were prepared by the method of deposition-precipitation with urea developed by Zanella and co-workers [5]. TiO₂@Au catalysts with different sizes of gold NPs ranging from 1.4 to 4.5 nm were synthesized by varying the amount of TiO₂ added to the aqueous solution of HAuCl₄ and of urea (see Figure 1).

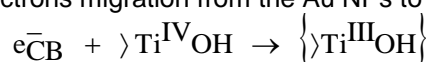
In order to test the catalysis activity of the TiO₂@Au, we employed a model electron-transfer reaction, such as the reduction of hexacyanoferrate (III) by borohydride ions in aqueous solution [6]. The time evolution of the reaction was monitored indirectly through the ultraviolet-visible UV-vis spectrum of hexacyanoferrate (III). As seen in the UV-Vis absorption spectra of the reduction of Fe(CN)₆³⁻ in the presence of TiO₂ or TiO₂@Au (Figure 2) the absorption peak of hexacyanoferrate (III) at 420 nm decreased revealing the occurrence of catalyzed reduction. Nevertheless, the presence of gold NPs strongly enhances the rate of Fe (III) reduction. The results clearly show that the reduction of Fe(CN)₆³⁻ by BH₄⁻ ions is catalyzed by the TiO₂ just when the oxide is doped with Au NPs.

The probable mechanism for the reduction of hexacyanoferrate (III) by BH₄⁻ ions, catalyzed by TiO₂@Au, involves:

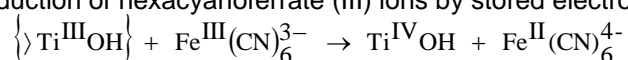
1. ° Oxidation of BH₄⁻ ions and injection of electrons onto the Au NPs



2. ° Electrons migration from the Au NPs to the conduction band of TiO₂



3. ° Reduction of hexacyanoferrate (III) ions by stored electrons on TiO₂



The recyclability of TiO₂@Au was also checked by repeating the reduction of hexacyanoferrate (III) through a sequential addition of K₃Fe(CN)₆ to the suspension containing excess of borohydride and a constant concentration of TiO₂@Au. The study revealed that the TiO₂@Au catalyst was reused six times without significant decrease of catalytic activity.

References

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Figures

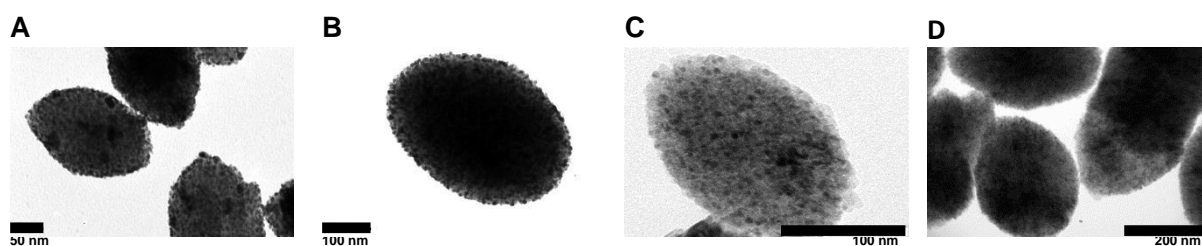


Figure 1. TEM images of anatase TiO_2 mesocrystals decorated with Au NPs of different size: (A) 4.5 ± 1.5 nm - $\text{TiO}_2@Au-1$, (B) 4.0 ± 1.4 nm - $\text{TiO}_2@Au-2$, (C) 2.0 ± 0.8 nm - $\text{TiO}_2@Au-3$, and (D) 1.4 ± 0.4 nm - $\text{TiO}_2@Au-4$.

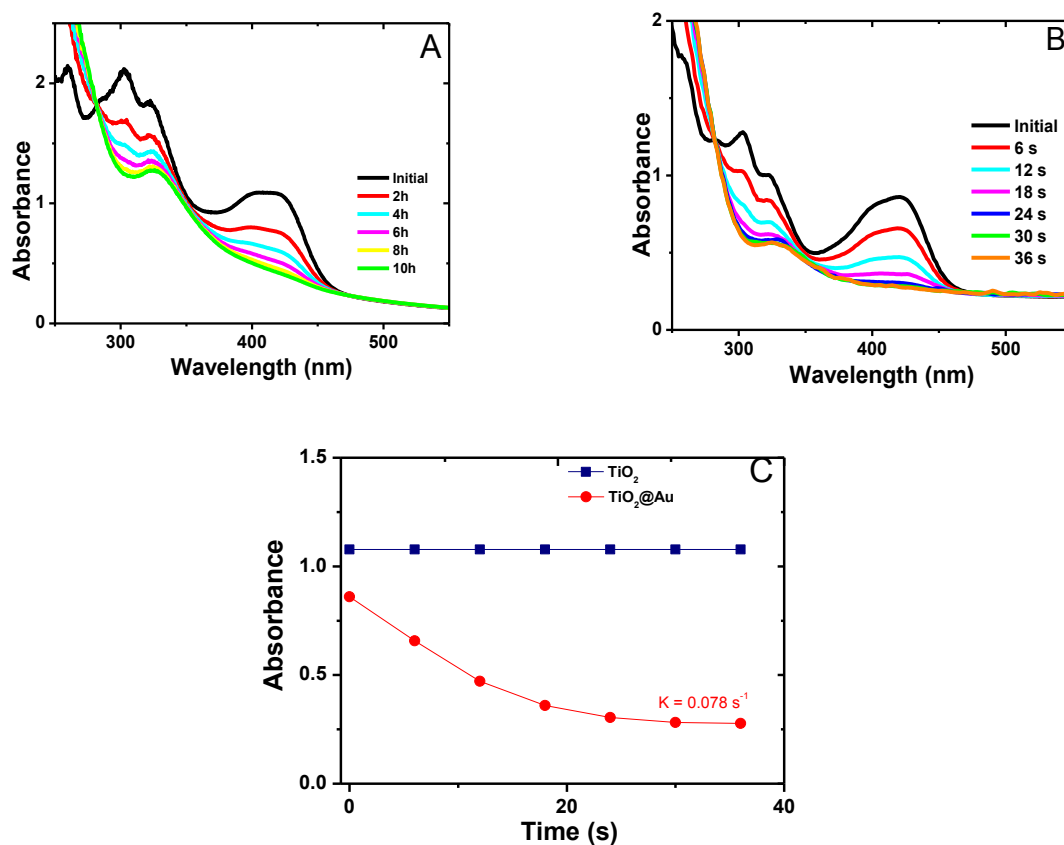


Figure 2A-B. Spectral evolution of a mixture of hexacyanoferrate (III) and (A) TiO_2 , (B) $\text{TiO}_2@Au$ upon borohydride addition. **Figure 2C.** Kinetic trace of the absorbance at 420 nm during the reduction of $\text{Fe}(\text{CN})_6^{3-}$ in the presence of TiO_2 (black) or $\text{TiO}_2@Au-1$.