

Synthesis and Catalytic Activity of Gold Nanoparticles Doped Anatase TiO₂ Nanoparticles

Ana Cláudia Lobão-Nascimento, Jorge Pérez-Juste, Isabel Pastoriza-Santos

Departamento de Química Física, Universidade de Vigo, Lagoas-Marcosende, 36310 Vigo, Spain
aclobao@gmail.com

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 a catalyst based on anatase TiO₂ nanoparticles 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 (fig.1 a) 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 mesoporous channels offer larger surface area and a connect pore system which can help to concentrate molecules for the electron-transfer reactions. It is known that chemical reactions are most effective when the transport paths through which molecules move into or out of the nanostructured materials are included as an integral part of the architectural design.

The TiO₂@Au catalysts were prepared by the method of deposition-precipitation with urea developed by Zanella and co-workers [5]. TiO₂ is decorated with homogeneously distributed gold nanoparticles with 4.5 nm of size (Fig. 1b). The close contact between Au nanoparticles and TiO₂ allows an effective transfer of electrons from Au nanoparticles to TiO₂ core.

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]. In an initial step, the gold nanoparticles surface is rapidly charged by the addition of borohydride. The double-layer charging around the metal nanoparticle facilitates the storage of the electrons on the gold. The electrons migration of the electrons from Au to the conduction band of TiO₂ occurs until the equilibration of Fermi level in the entire system is reached. Then, the ferricyanide ions reach the surface of gold and are reduced by excess surface electrons. The progression of the reaction was monitored indirectly through the ultraviolet-visible UV-vis spectrum of hexacyanoferrate (III). The characteristic absorption peak of hexacyanoferrate (III) is located at 420 nm, and its intensity was continuously decreased immediately after the addition of TiO₂-Au, revealing the occurrence of catalyzed reduction (Fig. 2).

References

- [1] Haruta, M., *Catal. Today*, **36** (1997) 153.
- [2] Haruta, M., *Catal. Surv. Jpn*, **1** (1997) 61.
- [3] Bond, G.C.; Thompson, D.T., *Catal. Rev. Sci. Eng.*, **41** (1999) 319.
- [4] Ye, Jianfeng; Liu, Wen; Cai, Jinguang; Chen, Shuai; Zhao, Xiaowei; Zhou, Henghui; Qi, Limin, *J. Am. Chem. Soc.*, **133** (2011) 933.
- [5] Zanella, Rodolfo; Giorgio, Suzanne; Henry, C. R.; Louis, C., *J. Phys. Chem. B*, **106** (2002) 7634.
- [6] Hervés, P.; Pérez-Lorenzo, M.; Liz-Marzán, L. M.; Dzubielia, J.; Lu, Y.; Ballauff, M., *Chem. Soc. Rev.*, **41** (2012) 5577.

Figures

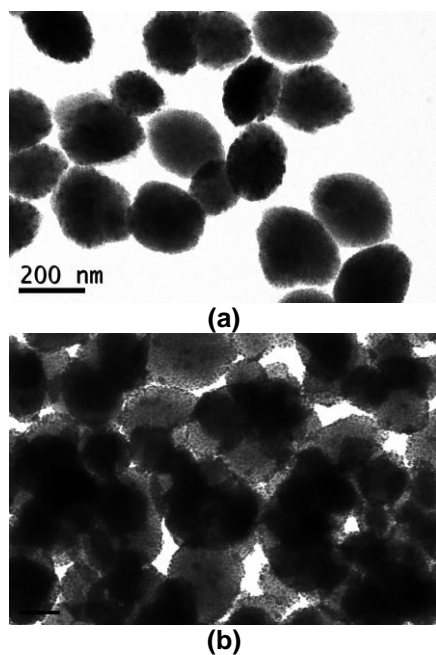


Figure 1. TEM images of (a) spindle-shaped nanoporous anatase TiO₂ mesocrystals and (b) TiO₂ mesocrystals decorated with 4.5 nm gold nanoparticles.

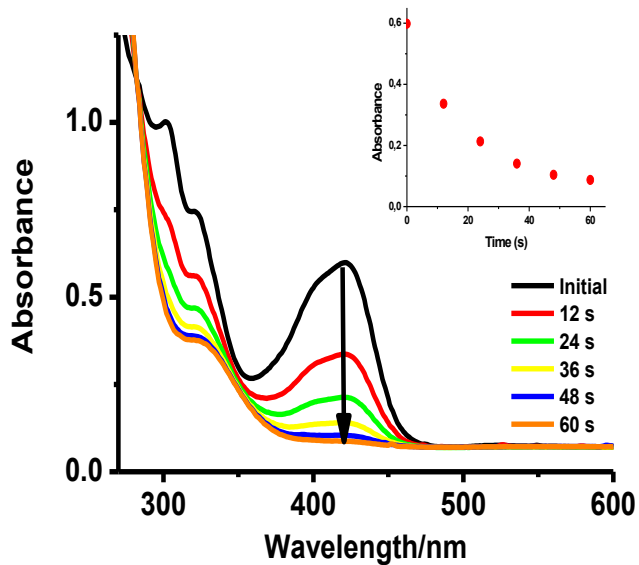


Figure 2. Spectral evolution of a mixture of hexacyanoferrate (III) and TiO₂-Au nanoparticles upon borohydride addition ([Fe(CN)₆³⁻]=8.33×10⁻⁴ M, [BH₄⁻]=8.33×10⁻³ M, [TiO₂-Au]=2.27×10⁻⁵ g/mL, T= 25°C, pH=11.5). Inset: Kinetic trace of the absorbance at 420 nm during Fe(CN)₆³⁻ reduction.