

Development of semiconductor catalysts for enzyme mimic based on CeO₂ nanoparticles system.

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Palavras Chave: nanoparticles, enzyme mimic, biosensors, semiconductor

Abstract

In this work, we study the catalytic activity of CeO₂ nanoparticles supported on SBA-15 silica as enzyme mimetic systems.

Introduction

The creation of artificial enzymes that mimics the complexity and function of natural systems has been a major challenge for the past two decades. The use of nanomaterials as peroxidase mimetic systems have recently been of great importance since it has been shown the intrinsic peroxidase activity of Fe₂O₃ magnetic nanoparticles. Recently, it was found that the CeO₂ nanoparticles (CeNPs) have an antioxidant activity at physiological pH values and, in this context; several studies have reported the biomedical application of these systems. In this sense, it is emphasized the catalytic activity of CeNPs as enzyme mimetic systems which was the main objective of this work. The materials were synthesized by the impregnation-decomposition cycles methodology (IDC), allowing a good size control and an uniform distribution of the precursor in the host silica^{1,2}. A detailed study of particle size control and synergistic effects were held in order to understand how these effects will be able to modify its biosensing performance.

Results and Discussion

Well-ordered hexagonal mesoporous silica (SBA-15) with tunable large uniform pores sizes (up to 300Å) is obtained as described by Zhao et al.³. According to N₂ adsorption-desorption analysis and transmission electron microscopy, the SBA-15 mesoporous silica presents a hexagonal array of pores in range of 7.93 nm. Nanometric ceria-decorated SBA-15 was prepared by the impregnation of SBA-15 pores by a solution of cerium (III) 2-ethylhexanoate (0.5 mol.L⁻¹), followed by its thermal decomposition at 700°C. The number of successive IDC was monitored by nanoparticle size using X-ray diffraction (XRD), Small-angle X-ray scattering (SAXS), Raman and UV-vis absorption spectroscopy techniques, being set as 4, 6 and 8. XRD patterns indicated the formation of CeO₂ fluorite phase with *Fm3m* space group. The calculate crystallite sizes for 4, 6 and 8 IDC cycles

were 1.90, 1.95 and 2.22 nm, respectively, indicating that all systems are under nanometric regime. SAXS patterns also indicated a decrease of pore diameter as function of IDC number, suggesting formation of these nanoparticles inside SBA-15 mesopores. These data are in accordance with N₂ desorption-adsorption analysis, where a decrease in mean pore size of SBA-15 was observed.

The resulting systems exhibit a peroxidase-like activity and catalyses the H₂O₂-mediated oxidation of 3,3', 5, 5'-tetramethylbenzidine (TMB) to produce a blue coloured product. The kinetics of the catalytic reaction was monitored by UV-Vis absorption band at 650 nm as function of time. We examined several factors to optimize this colorimetric system including pH, H₂O₂, TMB and catalyst concentration. All results indicated that this catalytic system accelerate the electron-transfer process and facilitate radical generation at the surface of the CeNPs. These results also indicated that particle size also affects its catalytic performance, and it was observed that catalyst the maximum catalytic performance was observed for 8 IDC.

Conclusions

In summary, ceria nanoparticles supported on SBA-15 with tunable particle size were prepared by IDC methodology. Textural properties showed that CeNPs are formed inside SBA-15 pores and increase in size upon IDC number. From the obtained results, we find that CeO₂ supported on SBA-15 silica are effective as catalyst and possess a peroxidase-like activity. The catalytic performance also showed that these systems potential materials in biosensing of biological molecules.

Aknowlegments

FAPESP, CNPq, CAPES, IQ-UNICAMP, LNNano.

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