Nitrite reduction on a multimetallic porphyrin-polyoxotungstate layer-by-layer modified electrodes

García, M., Honores, J., Quezada, D., Díaz, C., Dreyse, P., Celis, F., ... & Isaacs, M. (2016). Nitrite reduction on a multimetallic porphyrin/polyoxotungstate layer-by-layer modified electrodes. Electrochimica Acta, 192, 61-71. <10.1016/j.electacta.2016.01.132> Accessed 31 Dec 2020.

Abstract

Electro and photoelectrochemical reduction of nitrite in aqueous solution was studied using a multielectrocatalysts modified ITO electrode. ITO modification was carried out using the layer-by-layer (LBL) method, where sequential electrostatic assemblies were formed using a μ-(meso-5,10,15,20-tetra(pirydil)porphyrin)tetrakis{bis(bipyridine)chloride ruthenium (II)} [MTRP]n+, coordinated in its central cavity with Mn(III), Zn(II) or Ni(II) as a cationic layer, and polyoxotungstate [SiW12O40]4− as the anionic layer. Electrochemical measurements and UV–vis spectroscopy were used to monitor the modification process. Optimal results were obtained when three layers were deposited onto the ITO surface and were stable in aqueous solution. The order of the multilayer formation was explored by comparing a modified electrode where [Zn(II)TRP]4+ was the outermost layer with an electrode where [SiW12O40]4− was the outer layer. Results show that the best performing electrode is one with [SiW12O40]4− as the outer layer. Nitrite reduction on these electrode surfaces was studied in dark conditions and under light irradiation. Potential controlled electrolysis experiments were also performed, finding hydroxylamine, hydrazine and ammonia as the reduction products in dark conditions. Under light irradiation, only hydrazine and ammonia were found and, we observed an increase in the amount of obtained product. In this case, the electrolysis was carried out 150 mV less and half of time than in dark conditions. These results show that the combination of light and potential give rise to an improvement in the electrocatalytic properties of the modified electrodes. Continuous photolysis and IR spectroelectrochemical experiments were carried out to determinate the nature of this phenomena, evidencing the formation of an intermediary species between nitrite and [Mn(III)TRP]5+..

Keywords

Layer-by-Layer, Modified electrode, Nitrite reduction, Photo-electrochemistry, IR Spectro-electrochemistry.