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Induction of oxygen vacancies in $CuWO_4$ films used as photoanodes to improve the photocurrent and progesterone degradation efficiency

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Abstract

One of the biggest problems faced by humanity is the pollution of water resources by pollutants such as organic compounds such as polymers, herbicides, pesticides, dyes and medicines.[1] Studies show that several medications with estrogen and progesterone hormones pose risks to male fish and other aquatic organisms. The main problems caused by these hormones are decreased fertility, feminization of male organisms and hermaphroditism. Similar adverse effects are caused by these hormones also in humans, and these aqueous pollutants can alter the endocrine system and increase the risk of cancer.[2] Photoelectrocatalytic technologies using metallic oxide semiconductors have received great attention owing to their potential and effectiveness in wastewater treatment. However, rapid recombination of the photogenerated electrons/holes **(e^-/h^+)** is the major drawback for this methodology.[3] Copper tungstate ($CuWO_4$) is considered a semiconductor oxide with relatively short bandgap energy, ranging from 2.2 to 2.4 eV with excellent chemical stability over a wide pH range. However, $CuWO_4$ presents a rapid recombination of photogenerated charges. Our research group has investigated strategies to improve charge transfer in $CuWO_4$ films [4,5]. Oxygen vacancies (OVcs) in $CuWO_4$ have also been induced as a way of altering the properties of this material.[6] In our study, OVcs were achieved through thermal treatment of the material in a gaseous atmosphere formed by a mixture of air/N_2, in proportions of 0-100%. $CuWO_4$ films with triclinic structure (Fig.1) were obtained by the drop-casting method on FTO-glass from a suspension prepared by polymer precursor method. The electrode thermally treated with an air/N_2 ratio of 75% was the one with the highest photocurrent value. Photoelectrochemical measurements (Fig.2) carried out under polychromatic irradiation (100 mW cm^{-2}) show that the $CuWO_4$-75% films achieved a photocurrent of 40 µA cm^{-2}. This value is approximately four times higher than the current observed for the unmodified $CuWO_4$ film. This result indicates that N_2 induces OVcs (Fig.3), due to the lower concentration of O_2 during heat treatment and the growth of $CuWO_4$ crystals. Thus, it can improve photocatalytic activity in the degradation of progesterone.

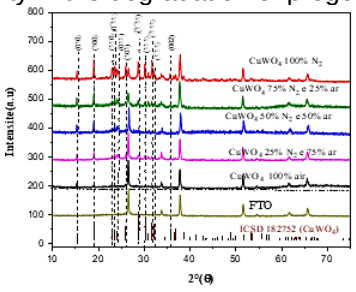

Fig.1. X-ray diffractograms of $CuWO_4$ films deposited on FTO in air and in controlled atmospheres of atmospheric air and pure N_2, in pure N_2 proportions of (0, 25, 50, 75 and 100%) in heat treatment at 500°C for 2h

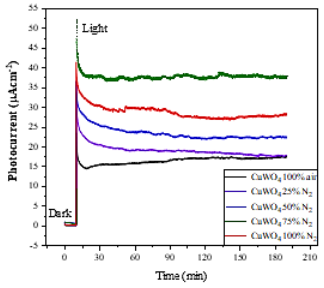

Fig 2. Stability of $CuWO_4$ films in air and pure N_2 atmospheres (0, 25, 50, 75 and 100%) in 1molL^{-1} Na_2SO_4 solution and potential of 0.8V Ag/AgCl for 3h(180min) irradiated in solar simulator

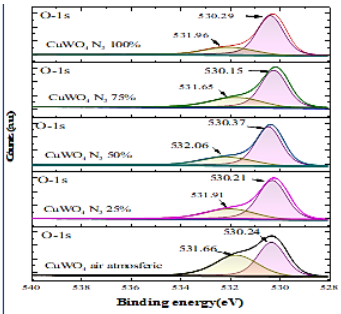

Fig 3. XPS spectrum of O 1s and of $CuWO_4$ films in various air and N_2 atmospheres

Palavras-chave:CuWO4, Oxigen Vacacie, Progesterone

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