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Effect of Electropolymerization Method in the Charge Transfer Properties and Photoactivity of Polyaniline Photoelectrodes

Authors : Alberto Enrique Molina Lozano, María Teresa Cortés Montañez

Abstract : Polyaniline (PANI) photoelectrodes were electrochemically synthesized through electrodeposition employing three techniques: chronoamperometry (CA), cyclic voltammetry (CV), and potential pulse (PP) methods. The substrate used for electrodeposition was a fluorine-doped tin oxide (FTO) glass with dimensions of 2.5 cm x 1.3 cm. Subsequently, structural and optical characterization was conducted utilizing Fourier-transform infrared (FTIR) spectroscopy and UV-visible (UV-vis) spectroscopy, respectively. The FTIR analysis revealed variations in the molar ratio of benzenoid to quinonoid rings within the PANI polymer matrix, indicative of differing oxidation states arising from the distinct electropolymerization methodologies employed. In the optical characterization, differences in the energy band gap (Eg) values and positions of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) were observed, attributable to variations in doping levels and structural irregularities introduced during the electropolymerization procedures. To assess the charge transfer properties of the PANI photoelectrodes, electrochemical impedance spectroscopy (EIS) experiments were carried out within a 0.1 M sodium sulfate (Na_2SO_4) electrolyte. The results displayed a substantial decrease in charge transfer resistance with the PANI coatings compared to uncoated substrates, with PANI obtained through cyclic voltammetry (CV) presenting the lowest charge transfer resistance, contrasting PANI obtained via chronoamperometry (CA) and potential pulses (PP). Subsequently, the photoactive response of the PANI photoelectrodes was measured through linear sweep voltammetry (LSV) and chronoamperometry. The photoelectrochemical measurements revealed a discernible photoactivity in all PANI-coated electrodes. However, PANI electropolymerized through CV displayed the highest photocurrent. Interestingly, PANI derived from chronoamperometry (CA) exhibited the highest degree of stable photocurrent over an extended temporal interval.

Keywords : PANI, photocurrent, photoresponse, charge separation, recombination
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