

Fabrication and characterization of NiCu/GO and NiCu/rGO nanocomposites for fuel cell application

Aya Mohamed¹, Mohamed Shaban^{2*}, Mohamed G. M. Kordy^{1,3*}, Ghadah M. Al-Senani⁴, M. F. Eissa¹, Hany Hamdy¹

¹Nanophotonics and Applications Lab, Physics Department, Faculty of Science, Beni-Suef University, Beni-Suef, 62514, Egypt; ayaelkhatib22@gmail.com (A.M.); m.kordybio@science.bsu.edu.eg (M.G.M.K); mostafa.eisa@science.bsu.edu.eg ((M.F.E.); hshamdy@hotmail.com (H.H.)

²Department of Physics, Faculty of Science, Islamic University of Madinah, Madinah, 42351, Saudi Arabia; mssfadel@aucegypt.edu (M.S.)

³Biochemistry Department, Faculty of Science, Beni-Suef University, Beni-Suef 62521, Egypt

⁴Department of Chemistry, College of Science, Princess Nourah bint Abdulrahman University, P.O. Box 84428, Riyadh 11671, Saudi Arabia; gmalnany@pnu.edu.sa (G.M.A.)

*Corresponding authors: mssfadel@aucegypt.edu (M.S.) and m.kordybio@science.bsu.edu.eg (M.G.M.K)

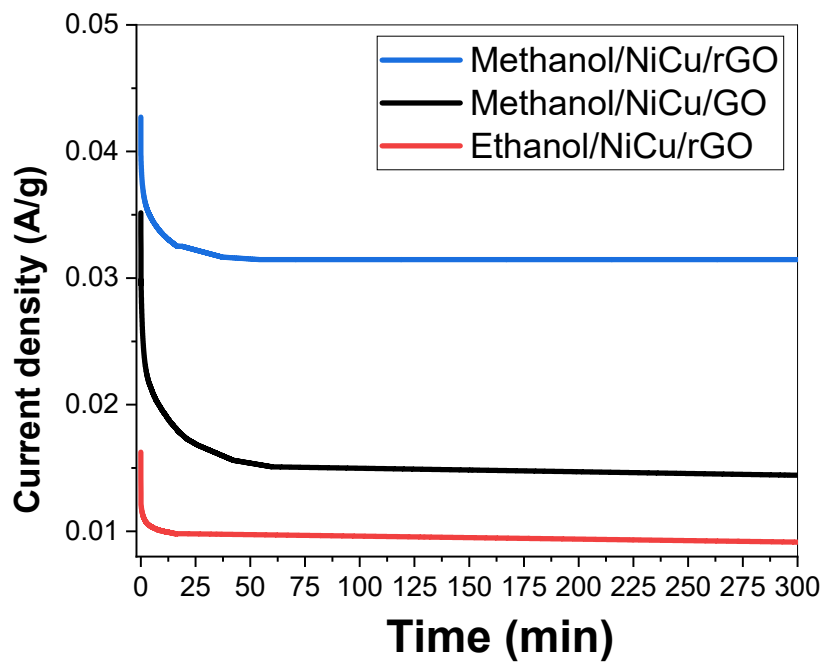


Figure S1. The variation of the current density versus time, long-term CAM measurements, in ethanol and methanol at optimized concentrations.

1. Electrochemical oxidation, adsorption mechanisms and adsorption energy

The electrochemical oxidation of methanol and ethanol is a process that involves the transfer of electrons from these alcohols to an electrode, usually made of a metal catalyst. Adsorption mechanism refer to how molecules or atoms adhere to solid surfaces. I.e., the adsorption mechanism is the way that the alcohol molecules interact with the surface of the catalyst, which affects the rate and selectivity of the reaction. Adsorption can be classified into two types: physisorption and chemisorption. Physisorption uses weak van der Waals forces, whereas chemisorption uses strong covalent bonds [1]. Adsorption energy measures the adsorbate-adsorbent interaction strength. The difference between the system's total energy before and after adsorption is commonly used to calculate the adsorption energy. I.e, the adsorption energy is the amount of energy released or consumed when the alcohol molecules bind to the catalyst surface, which reflects the strength and stability of the adsorption. Electronic and geometric features of adsorbates and substrates affect adsorption energy. The adsorption energy of a composite depends on several factors, such as the size and shape of the nanostructure, the type and amount of the support, the temperature and pressure of the reaction, and the nature of the adsorbate. Nørskov et al.'s d-band center model [2,3], effective in explaining adsorption patterns on transition metals and alloys, identifies the top border of the d-band as a reliable descriptor for most pure transition metals. This model serves as a fundamental basis for understanding the link between adsorption energies and reaction energetics in both experimental and theoretical settings.

This is why Gao et al. [4] proposed a predictive model for the quantification of the adsorption energies of small molecules on metallic materials and oxides. The model utilizes a linear combination of the valence and electronegativity of surface atoms and the coordination of active sites, with the corresponding pre-factors determined by the valence of adsorbates. This approach captures the impact of adsorbate and substrate properties on bonding, naturally deriving well-known adsorption-energy scaling relations. The model also addresses the efficiency and limitations of manipulating adsorption and reaction energy, enabling rapid, predictable design of materials with optimal adsorption properties.

The adsorption energy indicates how strongly the adsorbate binds to the adsorbent surface. It is computed by subtracting the total energy of the system before adsorption from the total energy after adsorption [5]. Previous studies have demonstrated that NiCu bimetallic alloys are effective

catalysts for methanol and ethanol oxidation, because of the cooperative effects of Ni and Cu atoms and the favorable hydrogen adsorption energy of NiCu [6,7]. NiCu/GO and NiCu/rGO are hybrid materials that integrate the benefits of NiCu alloys and graphene oxide (GO) or reduced graphene oxide (rGO) as supports. GO and rGO can enhance the distribution and stability of NiCu nanoparticles and also offer high electrical conductivity and large surface area [6]. The adsorption processes of NiCu, NiCu/GO, and NiCu/rGO for methanol and ethanol oxidation are complicated and influenced by the surface structure, composition, and morphology of the catalysts, as well as the reaction conditions. Some potential steps involved are (a) adsorption of methanol or ethanol molecules on the catalyst surface, (b) dehydrogenation of methanol or ethanol to produce CO and H₂, (c) oxidation of CO to CO₂, and (d) desorption of CO₂ and H₂O from the catalyst surface [6,7].

Zhao et al. observed hydrogen adsorption/desorption in the range of -1.0 to -0.7 V for all catalysts, noting that Ni and Pd (1:1 ratio) supported on multiwalled carbon nanotubes (Ni₁Pd₁/MWCNTs) showed slightly more negative potentials than Pd on the surface of MWCNTs (Pd/MWCNTs). The current peak for palladium oxide reduction in Ni₁Pd₁/MWCNTs shifted over 50 mV toward negative potential compared to pure Pd particles. Ni₁Pd₁/MWCNTs demonstrated that the synergistic effect enhanced electrocatalytic activity and stability compared to Pd/MWCNTs, indicating its promise for portable applications in alkaline solution-based direct methanol fuel cells (DMFC). The study by Liu et al. [8] revealed that nanocomposites of 5% MgH₂ with NiCu/rGO exhibit enhanced hydrogen sorption/desorption kinetics measurements compared to nanocomposite of 5% MgH₂ with NiCu. MgH₂/NiCu/rGO has superior hydrogen sorption kinetics over MgH₂/NiCu. MgH₂/NiCu/rGO manifests also a substantially diminished apparent activation energy for hydrogen desorption relative to MgH₂/NiCu. Therefore, we guess that our electrocatalyst, NiCu/rGO, can demonstrate superior efficiency compared to other electrocatalysts. This can be attributed to the synergistic effect arising from the interaction between rGO and NiCu nanoparticles and the ability of Ni/Cu to oxidize methanol molecules into active intermediates as the same as Pt/Pd [9,10].

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