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Title: In-situ preparation of Au(111) oriented nanoparticles trapped carbon nanofiber-chitosan modified electrode for enhanced bifunctional electrocatalysis and sensing of formaldehyde and hydrogen peroxide in neutral pH solution

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## **ACCEPTED MANUSCRIPT**

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peroxide; EQCM; Bipotentiostat-flow injection analysis

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Abstract: A unique gold(111) oriented nanoparticles trapped carbon nanofiber-chitosan modified electrocatalyst coated glassy carbon electrode(GCE/CNF-CHIT@Aunano) was prepared by an in-situ electrochemical procedure for efficient bifunctional electrocatalytic oxidation and reduction of formaldehyde and hydrogen peroxide in neutral pH solution. In the typical preparation, a microliter quantity of Au3+ solution was drop-casted on GCE/CNF-CHIT surface and potential cycled in pH 7 PBS. The GCE/CNF-CHIT@Aunano showed well-defined electrochemical response of gold nanoparticles of calculated electrochemically active surface area, 0.1347 cm2, which is about 3-3000 times higher than that of the surface area of the respective unmodified electrodes such as polycrystalline Au (0.0407 cm2), GCE/CNF@Aunano (0.0034 cm2) and GCE@Aunano (0.0005 cm2). Physicochemical characterizations such as FESEM, EDAX, TEM, XRD, Raman, FTIR and XPS spectroscopic techniques revealed stabilization of  $10\pm5$  nm sized Au(111) phase oriented nanoparticles by the amino functional group of chitosan in the composite matrix. The detailed electrochemical characterization by cyclic voltammetry (CV), rotating disk electrode (RDE) and in-situ CV-electrochemical quartz crystal microbalance (EQCM; Mw = 44±1g mol-1 species was identified) techniques showed direct oxidation of formaldehyde to formate as an intermediate (45 g mol-1) without any CO poisoning, unlike the conventional Pt and Au based electrodes. Using a bipotentiostat, selective and simultaneous flow injection analyses of formaldehyde and hydrogen peroxide in a mixture at discreet applied potentials (Eapp = 0.5 V/0.15 V and -0.15 V vs Ag/AgCl) were demonstrated. The applicability of the GCE/CNF-CHIT@Aunano was tested by detecting formaldehyde and hydrogen peroxide in a commercial hair dye formulation with about 100% recovery values.

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