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Anti-fouling response of gold–carbon nanotubes composite for enhanced ethanol electrooxidation

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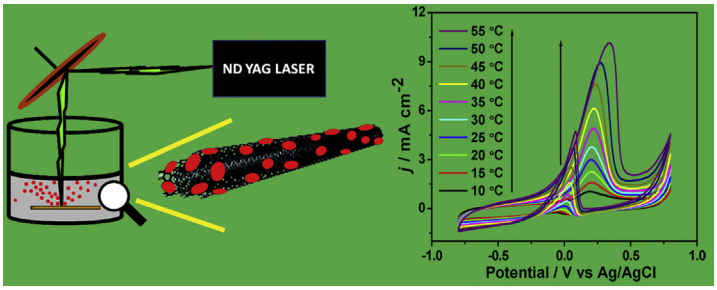
HIGHLIGHTS

- Surfactant free laser ablation synthesis of gold–carbon nanotubes nanocomposite.
- Catalytic modification of carbon paste electrode for ethanol electrooxidation.
- Remarkable stability of the catalyst towards electrooxidation.
- Low Arrhenius energy for electrooxidation of ethanol (~28 kJ mol^{-1}).
- Auto depassivation effect on intermediates by the electrocatalyst.

GRAPHICAL ABSTRACT



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ABSTRACT

We report the synthesis of gold carbon nanotubes composite through a one-pot surfactant free approach and its utility for ethanol electrooxidation reaction (EOR). The method involves the application of laser ablation for nanoparticle synthesis and simultaneous assembly of these on carbon nanotubes. The catalyst has been characterized by field emission scanning electron microscopy (FESEM), energy dispersive X-ray analysis (EDAX) and UV–vis spectroscopic techniques. A systematic study of gold carbon nanotubes modified carbon paste electrode for EOR has been pursued. The kinetic study revealed the excellent stability of the modified electrode even after 200 cycles of EOR and with an Arrhenius energy as low as ~28 kJ mol^{-1}. Tafel slopes that are the measure of electrode activity have been monitored as a function of temperature of the electrolyte. The results indicate that despite an increase in the reaction rate with temperature, the electrode surface has not been significantly passivated by carbonaceous species produced at high temperatures.

1. Introduction

Kinetics of ethanol oxidation reaction (EOR) has been widely studied on platinum in alkaline medium [1–4]. The two main reasons for this extensive research in EOR are: (i) Ethanol is a safer substitute to hydrogen in fuel cell applications and (ii) Active catalytic behaviour of platinum [5]. Although platinum has been the preferred catalytic material, the search for newer anode catalysts is still ongoing, since Pt is expensive and its surface gets poisoned by carbonaceous species produced during EOR [3]. Therefore, the quest for studying EOR on different metal surfaces and nanocomposites with less poisoning & superior catalytic activity is desirable [6]. Gold nanoparticles (AuNPs) in this context, when

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loaded over heterogeneous supports, have wide applications pertaining to catalysis and electro catalysis [7,8]. The reports on the kinetics of EOR on AuNPs supported composites have however been sparse. One such study pursued by Rodriguez et al. describes the superior activity of gold in alkaline medium owing to the crucial role of CO [9,10]. More recently, Pandey et al. have studied the electrocatalytic activity of AuNPs on conducting polymers (Au-CPs) like polyaniline (PANI), polypyrrole (PPY), polythiophene (PTP) and poly(3,4-ethylenedioxythiophene) (PEDOT) [11]. These studies have broadened the scope for pursuing the kinetics of EOR with AuNPs based catalytic composites. There are several reports on the use of carbon nanotubes as ideal supports, on account of their high electrical conductivity; surface area; mechanical strength; and chemical stability [12]. An extension to this has been the synergistic use of AuNPs supported on carbon nanotube (CNT) scaffolds, having the dual properties of the individual entities [13].

Of the several routes available for AuNPs synthesis, the bottom up route is very well known. This approach gives precise control over the size and shape of the synthesized particles [14,15]. Nevertheless, the capping agents may mask the catalytic performance of the nanoparticle by hindering the approach of the reactant species towards the metal surface and reduce the efficiency of the catalysis [16]. Therefore, an alternative top down route for synthesis has already been explored by a number of researchers. These methods involve electrochemical [17], microwave [18], sonochemical [19] and ball-milling techniques [20], in sequel to the earlier work that involves the synthesis of AuNPs in water through laser ablation (LA). In the present study we have employed LA approach not only to synthesize AuNPs, but also to decorate them over multi walled CNTs (MwCNTs). In this study, Au-CNT composite is synthesized in a single step one-pot reaction without the use of any surfactants. To attain an appreciable loading of AuNPs over MwCNTs, the MwCNTs must be homogeneously dispersed in water. This dispersion has been made possible due to the uniform functionalization of CNTs achieved through a microwave induced reaction [3]. In the recent past, we have loaded NPs over functionalized hydrogen exfoliated graphene using LA and used it as a catalyst for EOR and environmental remediation involving the reduction of coloured dyes [21]. In the present study, carbon paste electrode (CPE) has been modified using Au-CNT and has shown excellent catalytic performance for ethanol electrooxidation in alkaline medium. A high rate of electro–catalytic activity has been observed using Au-CNTs with a decreased activation energy (AE) barrier. The AE for EOR with Au-CNTs is ~28 kJ mol^{-1}. The electrode has shown excellent stability even after 200 cycles of ethanol oxidation. These properties make the composite a plausible contender for direct ethanol fuel cell (DEFC) and other analogous applications. The hybrid catalyst material has been characterized by field emission scanning electron microscopy (FESEM), energy dispersive X-ray analysis (EDAX) and UV–vis spectroscopy.

2. Experimental section

2.1. Reagents

MwCNTs (OD 20–30 nm, purity 95%) were purchased from Cheap tubes Inc. All the other chemical reagents used in this study were of analytical grade. All the aqueous solutions in this study were prepared with Millipore water having resistivity of 18.2 Ω-cm.

2.2. Instruments

The UV–vis spectra were recorded using a shimadzu 2450 PC UV–vis spectrophotometer equipped with a quartz cuvette holder for liquid samples. FESEM and EDAX were obtained from FESEM (Zeiss). Functionalization of CNTs was done using microwave accelerated reaction system (mode: CEM Mars) with internal temperature and pressure controls. A high power nanosecond Nd:

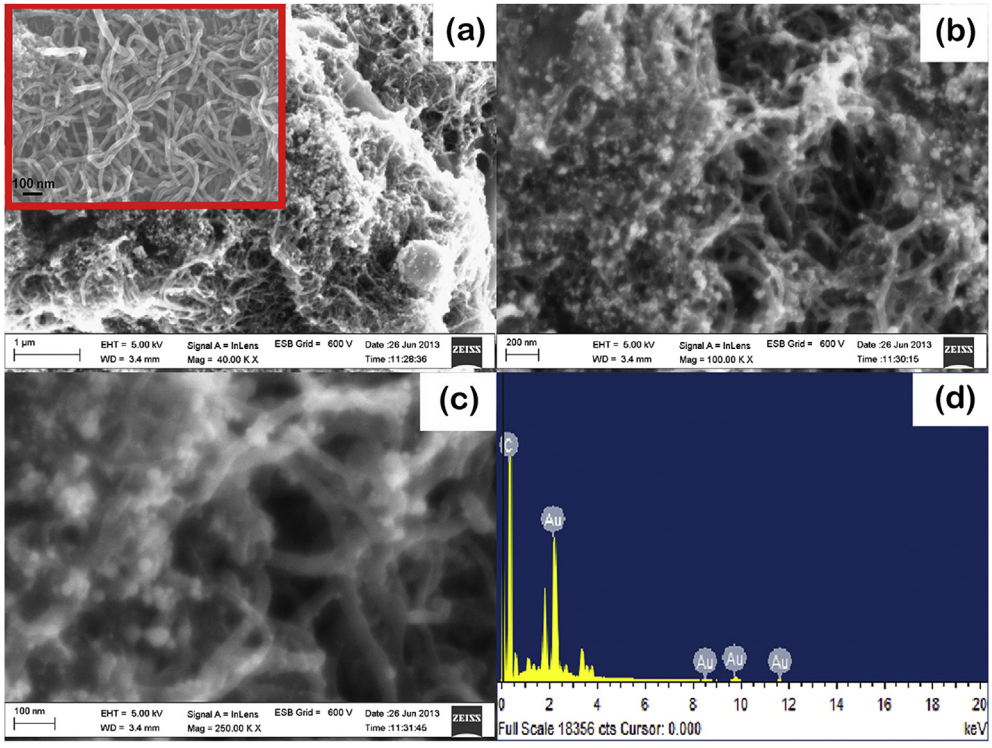

Fig. 1. (a) to (c) FESEM images of Au-CNT under different magnifications. (d) shows the EDAX Spectrum of Au-CNT. Inset in (a) shows FESEM image of pristine MwCNT.