



The activation of C—H bonds using an EmimAc/MWCNTs composite: a comparison of the composite used as electrolyte and electrode in aqueous media



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ARTICLE INFO

Article history:

Received 23 March 2016

Received in revised form 21 April 2016

Accepted 22 April 2016

Available online 30 April 2016

Keywords:

EmimAc/MWCNTs composite
activation of C—H bond
electro-oxidation

ABSTRACT

An EmimAc/MWCNTs composite was prepared and characterized through SEM and TEM. The MWCNTs were well dispersed after combining with alkaline EmimAc. The activity of the composite was demonstrated by CV and controlled potential electrolysis. The composite could be used independently as electrolyte or electrode and showed excellent activity toward the electro-oxidation of the C—H bond of benzylic systems, and did so at a lower oxidation potential than when using EmimAc or MWCNTs. After modification, the pH value of the composite was adjusted to the acid range, and the yield of aldehyde adducts obtained through electro-oxidation improved.

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1. Introduction

The activation of unreactive C—H bonds serves as an important step in many synthetic transformations [1,2]. Over the past century, reports have appeared describing the role of inductive effects, conjugation, steric hindrance, and the introduction of directing groups to improve the selective activation of C—H bonds [3]. One attraction to this area of investigation focuses upon the electro-oxidative activation of a C—H bond to form a carbonyl unit [4–9]. Of course, the success of the chemistry requires optimization in order to determine a suitable solvent, electrolyte and electrode.

Room temperature ionic liquids (RTILs) and carbon nanotubes (CNTs) have attracted much interest [10,11]. RTILs are promising solvents and electrolytes in electrochemical applications because of their low volatility, high conductivities, and wide potential windows relative to conventional electrolytes [12]. While their high price and high viscosity limits widespread application, CNTs do offer significant advantages in electrochemical systems because of their unique structure and properties including, for example, large specific surface area, strong mechanical moduli and excellent

chemical stability. Recently it was shown that some ILs exhibit unexpectedly strong interactions with CNTs through the formation of gels after the two have been ground together [13–15]. The resulting ILs/CNTs composites material were used as capacitors [16], sensors [17] and as a lubricant additive [18]. However few reports exist concerning their application to the electro-oxidation of C—H bonds to form aldehydes, a focal point of the present investigation.

In our previous work, ILs, especially imidazole ILs wherein the pH values ranged between 2 and 6, were shown to be a suitable solvent-electrolyte combination for the electro-oxidation of methyl-substituted aromatic compounds to the corresponding aldehydes. On the other hand, alkaline imidazole ILs such as 1-ethyl-3-methylimidazolium acetate (EmimAc), led preferentially to the formation of *p*-methoxybenzylalcohol (*p*-MeOBzOH) without further oxidation [9]. In an effort to expand the scope of the chemistry, we have explored the immobilization of the alkaline ILs with an objective being to decrease the amount of IL used and also facilitate the electro-oxidation of a C—H bond to a carbonyl unit. Greatly encouraged by the effectiveness of a recently reported composite dispersion reaction medium in eliminating the need to use large amounts of a supporting electrolyte in organic solvents [19], we chose to form a new composite, one consisting of EmimAc as the IL in combination with multi-walled carbon nanotubes (MWCNTs) and explored its use in aqueous reaction media. As described herein, the composite was able to function

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independently as electrolyte and also as the electrode, and to be applied to the electro-oxidative activation of C–H bonds. The composite showed excellent electro-oxidative activity and selectivity toward formation of carbonyl compounds and could easily be recovered and reused. In addition, adjustment of the pH value of the EmimAc/MWCNTs composite to the acid range, proved beneficial to the electro-oxidation to the carbonyl group, with yields for the conversion of *p*-methoxy toluene (*p*-MT) to *p*-methoxybenzaldehyde (*p*-MBA) improving from 55–63% to 87%.

2. Experimental section

2.1. Chemicals and measurements

EmimAc was purchased from Lanzhou Institute of Chemical Physics (Chinese Academy of Sciences), and used without further purification. MWCNTs, (97%, 40–60 nm in diameter) were purchased from Shenzhen Nanotech. Port. Co. Ltd. (China) and vigorously stirred in 65% HNO₃ solution for 4 h at 423 K. Following treatment of the MWCNTs with nitric acid, they were filtered and repeatedly washed with water until the aqueous filtrate tested neutral, then dried at 353 K for 12 h before use. *p*-MT and *p*-methoxybenzyl alcohol were purchased from Aladdin (China), 1-methoxy-4-propylbenzene was purchased from Sigma Aldrich (Iceland), *p*-xylene was purchased from Sinopharm Chemical Reagent Co. Ltd (China). All the reagents were analytical grade.

Scanning electron microscopy (SEM) images were obtained using a Hitachi S4700 (Japan) system with an accelerating voltage of 15 kV. Before observation, the surface of the sample material was coated with a thin layer of gold. Transmission electron microscopy (TEM) was obtained by using JEM-2010Ex (Japan) with an accelerating voltage of 200 kV.

Cyclic voltammetry (CV) was carried out using a CHI 660D electrochemical workstation. A platinum sheet (1 cm × 0.5 cm) was used as the working electrode, a 2 cm × 2 cm platinum sheet as the counter electrode, and a platinum wire (0.5 mm diameter) electrode as the quasi-reference electrode. Except when noted, the CV measurements were performed at room temperature.

Each controlled potential electrolysis was performed in a 10 mL undivided electrochemical cell. The concentration of the aromatic substrate was 0.04 M. The electrolysis potential used for experiments conducted using different electrolytes was based on the oxidation peak potential recorded using CV. All the electrolysis experiments were performed at 323 K for 6 h while the solution was stirred using a magnetic stirrer. When the composite was used as the electrolyte, the 1 cm × 0.5 cm platinum sheet was used as the working electrode. For each controlled potential electrolysis, comparison experiments involving the use of different electrolytes for the electro-oxidative electrolysis of *p*-MT, 0.16 g of EmimAc, 0.04 g of MWCNTs and 0.2 g of composite were independently

employed as the electrolyte. When the composite and the graphite electrode (5 mm diameter) were used as the working electrode, 0.02 M LiClO₄ was used as the supporting electrolyte in an aqueous solution. The major products were detected using GC–MS (Thermo Fisher). The yields (Y) were determined by GC (Agilent 7890A) analysis.

The pH of the different electrolysis systems was measured using a PHS-3C acidometer (Shanghai REX, China) at room temperature.

2.2. Preparation of EmimAc/MWCNTs

The MWCNTs were first mixed with EmimAc (the mass ratio of EmimAc to MWCNTs was 1:1, 2:1 and 4:1), using methylene chloride as a dispersant. The dispersion was stirred for 12 h at room temperature using a magnetic stirrer. Then, the resulting composite materials, referred to as EmimAc/MWCNTs, were dried at 353 K for 12 h.

Following electrolysis when the composite was used as the electrolyte, the composite was filtered, and the solid containing the EmimAc/MWCNTs composite was washed with ether. The filtrate containing the products and some desorbed EmimAc, was washed using distilled water. The product, contained in the organic phase, was detected by GC while the desorbed EmimAc was extracted using ether from the aqueous phase and combined with the solid, thereby constituting the recovered EmimAc/MWCNTs composite (marked as Re-EmimAc/MWCNTs).

2.3. Preparation of composite electrode

One hundred (100) mg of composite material, 1 mL of ethanol, 1 mL of distilled water and 100 μL of Nafion solution (5 wt%) were combined to form a slurry. Then, 150 μL of the slurry was added dropwise onto carbon paper (1 cm × 1 cm) and dried at room temperature for 12 h. After electrolysis, the resulting “composite electrode” was washed with distilled water, and dried at room temperature for reuse.

3. Results and discussion

The surface morphology of the nitrated MWCNTs and the EmimAc/MWCNTs composites were characterized by SEM (Fig. 1) and TEM (Fig. 2). After nitration, some of the ends of the MWCNTs were opened as evidenced by Fig. 1 a, but most of the tubes were tangled because of self-assembly and the nano-size effect [20]. After combining with the EmimAc, the MWCNTs became untangled (Fig. 1 b, d). The dispersion of the tubes was improved and the affinity of the ILs to the surface of the MWCNTs was ensured after they were combined due to the interaction between the electron deficient imidazolium cation and the π-electron-rich surface of the nitrated MWCNTs [21].

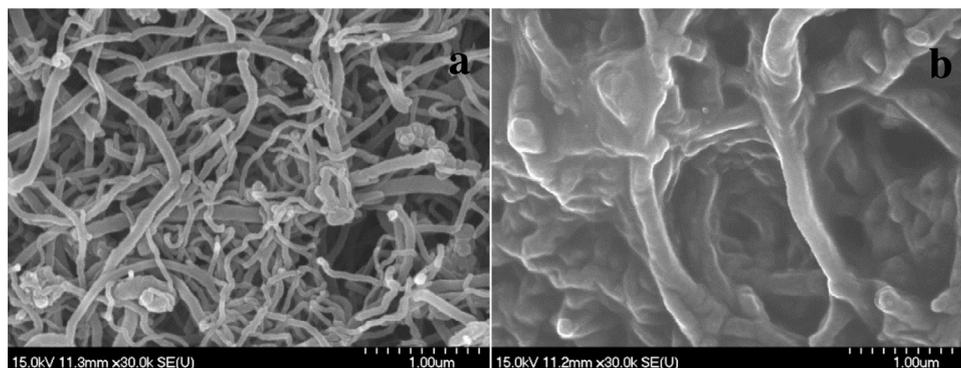


Fig. 1. SEM images of (a) the nitrated MWCNTs, and (b) EmimAc/MWCNTs (mass ratio = 4:1).

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