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Electrochemical fabrication of dendritic silver–copper bimetallic nanomaterials in protic ionic liquid for electrocarboxylation

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ABSTRACT

Silver (Ag) and silver–copper (Ag–Cu) bimetallic composite electrodes were electrochemically prepared on a glassy carbon (GC) substrate in triethylammonium acetate (TEAA) by electrodeposition to investigate their suitability as cathodes for electrocarboxylation process. Cyclic voltammetric investigations reveal that with increase in Cu content, both the stripping as well as deposition current of Ag (I) ions decrease with a shift of cathodic and anodic peak potential in the positive side, where the onset deposition potential difference between Cu and Ag ions becomes less, favouring effective co-deposition of both ionic species. The morphologies of deposits change significantly from cubic structure to flower-shaped dendrites by the incorporation of more amount of Cu, as noted from scanning electron microscopy (SEM) images. Crystallographic (XRD) analysis confirms the formation of Ag–Cu co-deposits and the compositions of the different deposits were found out using atomic absorption spectroscopy (AAS). The Ag–Cu composite containing 23% of Cu (Ag_{77}–Cu_{23}) shows the highest cathodic potential window in N,N-dimethylformamide/tetrabutylammonium tetrafluoroborate (DMF/$TBABF_4$) medium. Further, Ag_{77}–Cu_{23} shows higher reductive current on the electroreduction of benzophenone in presence and absence of carbon dioxide than that of other Ag based composite electrodes resulting in an enhancement of the product yield.

1. Introduction

It is well known that the catalytic properties of NPs can be changed by the alloying or mixing of two metals with different dielectric constant. This mixing, in principle, would lead to the formation of bimetallic NPs. In many cases, compared to monometallic NPs, bimetallic NPs have shown better optical, electronic and catalytic properties, which can be attributed to ensemble and electronic effects [1,2]. When Ag is used as an alloy, its catalytic performance is enhanced and modified at lower cost [3,4]. In particular, silver–copper alloy material finds extensive uses in the fields of sensors [5,6], catalysis [7,8]. A recent study shows that Ag–Cu nanoalloy has been employed as an efficient catalyst for the selective electrochemical reduction of CO_2 to CO [9].

Different methods are adopted for the synthesis of Ag–Cu bimetallic nanoparticles which include polyol synthesis [10], chemical reduction [11,12] and electrodeposition [9,13]. Among these, electrodeposition is an effective technique to produce nanocrystalline deposits, where the size and shape of the electrodeposited material can be designed by controlling either electrode potential or current density. By controlling their shape and size, one can improve the performance of nanostructures and it has been well established that the properties of these alloy materials are much superior to their pure metals.

So far, the deposition of Cu–Ag nanomaterials has been carried out in aqueous cyanide bath [9] and in hydrazine medium [13]. These plating baths are highly corrosive and toxic in nature and the effluents generated at the end need additional costs for their disposal. On the other hand, room temperature ionic liquids (RTILs) are regarded as new class of materials for the electrodeposition, as they possess large cathodic window, negligible vapor pressure, high thermal stability, good conductivity and tunable physicochemical properties through strategic choice or appropriate modification of the cations and anions [14,15]. In particular, protic ionic liquids (PILs) become attractive in recent years, where they have been prepared at low cost and are environmentally benign in nature [16–18]. In this work, triethylammonium acetate (TEAA) has been chosen as the PIL medium for the electrodeposition of Cu–Ag alloy. The conductivity (20.40 mS/cm) and viscosity (24.18 mPa s) values are comparable with other protic ionic liquids [19].

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The development of an environmentally benign process utilising carbon dioxide (CO_2) into value added products has attracted considerable attention in recent years. The possible routes for the conversion of CO_2 include electrochemical, thermal, photocatalytic and photo electrocatalytic reduction under solar radiation. Among this, electrosynthesis has been considered as a convenient, low cost and eco-friendly method for CO_2 reduction [20]. In particular, electrocarboxylation of aromatic ketone in non-aqueous solvents leading to the formation of hydroxy carboxylic acid, an intermediate in the production of non-steroidal anti-inflammatory drug, is of paramount important process, where the chemical route for the preparation of acids involves the use of toxic cyanides [21,22]. Studies are available in the literature on the employment of different catalytic electrodes such as Cu [23], Ni [23,24] and Ag [25,26] for such electrochemical process and there is no report on the employment of Cu–Ag.

In this work, for the first time, nano Ag, Cu as well as Ag–Cu nanomaterials are fabricated on glassy carbon (GC) electrode in TEAA by electrodeposition. Electrochemical characteristics of Ag (I) and Cu (II) ionic species and their mixtures in TEAA are investigated using cyclic voltammetry (CV) and the electrodeposited Ag, Cu and Ag_x–Cu_y deposits are characterized by different surface analytical techniques. The effect of altering the compositions of the Ag_x–Cu_y materials on the reduction and carboxylation of benzophenone in N,N-dimethylformamide (DMF) containing tetrabutylammonium tetrafluoroborate ($TBABF_4$) electrolyte is also discussed in detail.

2. Experimental

Copper acetate $Cu(CH_3COO)_2$ and silver acetate, $Ag(CH_3COO)$ were obtained from SRL, India. Triethyl ammonium acetate (TEAA) was prepared based on literature method [18]. Coulometric Karl–Fischer titrator (Metrohm 756 KF) shows that the moisture content of the PIL is 50 ppm. N,N-dimethylformamide (DMF, SRL-India) was kept over anhydrous Na_2CO_3 for several days and stirred from time to time. Molecular sieves (4A) were used to remove residual water prior to use. Tetrabutylammonium tetrafluoroborate ($TBABF_4$, AG Fluka) was dried in a vacuum oven and benzophenone (AG Fluka) was used as such.

Voltammetric experiments were done with an Eco Chemie Autolab Potentiostat system under computer control in a glove box. For the potentiostatic deposition of the nanomaterials, a conventional three electrode setup was used with glassy carbon as a working electrode (Alfa Aesar with a purity of 99.99% with the exposed area of 0.07 cm^2), Pt as a counter electrode and a platinum wire immersed in a ferrocene/ferrocenium (mole ratio of Fc/Fc^+ is 1/1) BMP–TFSI solution stored in a glass tube with porous frit, as a reference electrode. For the electrocarboxylation studies, nanomaterials deposited on GC and Pt foil were used as working and counter electrodes respectively, where Ag/AgCl served as reference electrode.

Constant potential electrolysis of 0.1 M benzophenone in 0.1 M $TBABF_4$/DMF (10 ml) was done in presence of CO_2 in an undivided cell incorporated with nanomaterials deposited on GC along with bulk Ag and Cu foils as the cathodes, magnesium (Mg) rod as an sacrificial anode as well as a Ag/AgCl as the reference electrode with constant stirring. Potential corresponding to the reduction of benzophenone was taken as the applied voltage for the electrolysis with continuous passage of 2.1 F/mol. The electrolyte materials need usual work-up with distillation of the solvent followed by the treatment of the product with aqueous HCl (2.0 M). Extraction of the materials with diethyl ether (Et_2O) was carried out, where the ethereal solution was washed with saturated aqueous sodium chloride (NaCl) solution and dried in sodium sulfate (Na_2SO_4). Ether evaporation results in the formation of 2–hydroxy–2,2′-diphenyl acetic acid (benzilic acid) [26].

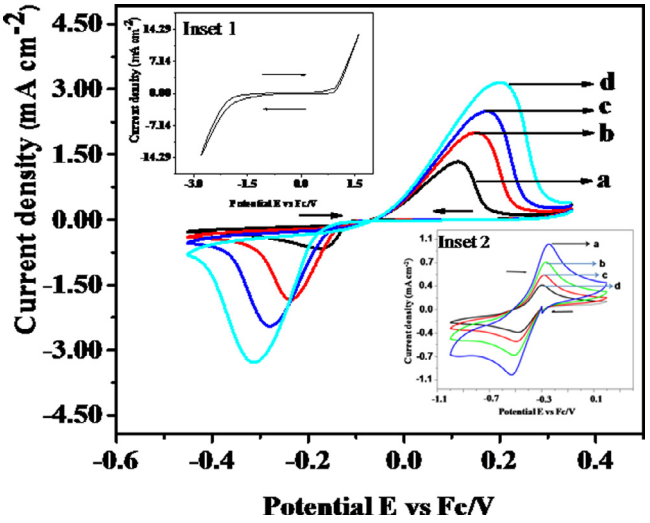

Fig. 1. CVs recorded in TEAA on GC for 50 mM of $Ag(CH_3COO)$ at different sweep rates (mV/s) (a) 10 (b) 20 (c) 40 and (d) 80. Inset 1 shows the background current recorded in TEAA medium at 40 mV/s and inset 2 shows the CVs recorded in the same medium on GC for 50 mM of $Cu(CH_3COO)_2$ at different sweep rates.

Surface morphologies of Ag, Cu and Ag–Cu alloy coatings were obtained using SEM with JEOL JSM6480LV system coupled with energy-dispersive X-ray spectrometer. The crystalline structure of the deposits was analyzed using XRD (Shimadzu XD-D1 X-ray diffractometer). The amount of Ag and Cu species present in the deposited materials was estimated using AAS (GBC 906 AA, Australia).

3. Results and discussion

Cyclic voltammograms recorded for GC electrode in presence of 50 mM of $Ag(CH_3COO)$ in TEAA at different sweep rates are shown in Fig. 1 and the inset 1 shows the background voltammogram. Potential limit is defined as a range of potential observed at a current density of 1.0 mA/cm^2 where, the GC electrode shows an excellent cathodic potential limit of 2.90 V at this current density (Fig. 1, inset 1). Voltammogram taken for GC in TEAA containing 50 mM of Ag (I) ions at 40 mV/s show a complete reversible redox peak at −0.31 V and 0.20 V *vs* Pt corresponding to deposition of Ag^+ to Ag and stripping of Ag respectively (Table 1). A similar voltammogram is obtained for 50 mM Cu (II) ionic species on GC in the same medium with a cathodic peak at −0.52 V followed by an anodic peak at −0.40 V associated with the reduction of Cu (II) to Cu (0) and oxidation of Cu respectively (inset 2 of Fig. 1)

Typical CVs of GC electrode in TEAA containing different concentrations of Ag (I) and Cu (II) ions at a same sweep rate of 40 mV/s are shown in Fig. 2. Voltammograms recorded in presence of Cu (II) and Ag (I) ions at a molar ratio of 5:45 show reduction peaks at −0.62 V and −0.29 V as well as oxidation peaks at −0.38 V and 0.15 V corresponding to reduction as well as oxidation of Cu/Ag nanomaterials respectively (Fig. 2(a) and Table 1). Both the deposition and stripping peak currents for Ag^+/Ag redox couple in the Ag–Cu material are found to be low considerably, when compared to the peak currents noted for Ag^+/Ag without copper. With further increase in the concentration of Cu (II) ions (from 5 to 10 mM) in TEAA containing Ag salt, the cathodic peak potential for Ag (I) ions shifts more towards anodic and the peak currents for deposition as well as stripping of Ag decrease further, as a result of decrease in the concentration of Ag (I) ions (Fig. 2(b)). On the other hand, the stripping current noted for copper increases considerably

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