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Room temperature synthesis of Pd–Cu nanoalloy catalyst with enhanced electrocatalytic activity for the methanol oxidation reaction

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ABSTRACT

Bimetallic Pd–Cu nanoparticles with controllable size, composition and superior electrocatalytic activity towards methanol oxidation reaction (MOR) in alkaline media were synthesized by a facile room temperature soft chemical method. Pd–Cu nanoalloy catalysts (17–25 nm) were prepared by templating Pd^{2+} and Cu^{2+} with ethylenediaminetetraacetic acid (EDTA) followed by controlled chemical reduction of metal–EDTA complex with hydrazine in highly basic medium at room temperature without any protection with an inert gas atmosphere. X-ray diffraction pattern indicates that the particles have an alloy structure. FESEM, EDX, HRTEM and SAED results further support the formation of Pd–Cu nanoalloy. Compliance of the lattice spacing corresponding to (1 1 1) and (2 0 0) planes obtained from HRTEM and SAED results with XRD data confirms the formation of Pd–Cu nanoalloy at room temperature. By varying the Pd^{2+}/Cu^{2+} molar ratio the compositions of these alloy NPs can be easily adjusted. The amount of Cu present in the Pd–Cu nanoalloy plays a key role on the catalytic activity for MOR in alkaline media. Upon increase in concentration of Cu in the Pd–Cu nanoalloy, the catalytic activity towards MOR increases, reaches a maximum in Pd–Cu(3:1) nanoalloy and then decreases. The maximum mass activity of 659.4 mA mg^{-1} of Pd obtained in the present work for the synthesized Pd–Cu(3:1) nanoalloy is much better than literature reported value. Multi-scan cyclic voltammetry and chronoamperometric studies confirm the electrocatalytic activity and stability of the synthesized electrode material. The present catalyst with low noble metal content promotes its practical use as anodes under alkaline conditions in direct methanol fuel cells (DMFC).

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1. Introduction

Surfaces of dispersed noble metal nanoparticles (NPs) with high specific catalytic activity are favourable for catalysis in modern synthetic organic chemistry [1–3]. The catalytic activities of noble metal NPs are highly dependent [4,5] on their sizes, active surface area and morphologies. Therefore lot of noble metal catalysts with various morphologies such as monodisperse NPs [6], nanowires [7], nanoporous [8], nanoplate arrays [9], nanotrees [10], nanoflowers [11] etc. have been synthesized to generate large active sites. For example Pt NPs of different morphologies are found to be effective catalyst for oxygen reduction reaction (ORR) and alcohol oxidation

reaction in DMFCs [12,13]. But limited resources of noble metals throw challenges to reduce the dosage of its use to material scientists. Mixing of non-precious metal with noble metal and subsequent alloying is the area of interest [14–18] to researchers in catalytic reactions viz. ORR and DMFC applications. Alloying of Cu, Co, Ni, Fe with noble metals shows enhancement in specific properties because of the synergistic effect of the composition [19]. When alloying is done between an electron donor atom like Cu and an electron acceptor such as Pd, then the d-band of the unit will be lowered and its local electronic properties are predicted to be more like Pt [20]. Another interesting property of Pd–Cu alloy is its high electrocatalytic activity for CO oxidation and weak metal-CO bond strength which promote the formation of a 'rescuer' intermediate, Pd–OH, at lower potential [21], showing its great potential for methanol oxidation for use in DMFCs. Pd–Cu alloying strategy [22] has been used to find non-Pt electrocatalysts that are effective and less expensive for the ORR. It is reported [23] that Cu reduces the Pd–O binding energy and Pd increases the Cu–O binding energy in

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Pd–Cu alloy and exhibit desirable catalytic properties for ORR and also improve [24] the Pd–H interaction. Hence there is a need to prepare such bimetallic NPs consisting of both electron donor and acceptor elements having good catalytic activity.

Considering the importance [25–28], it is always challenging to find out simple cost effective suitable methods to prepare such type of bimetallic nanomaterial. A few templates [8,20,29,30] have been used for the synthesis of Pd–Cu alloy NPs. The problems with the methods are requirement of higher temperature and lack of stoichiometry of high quality nanostructured Pd–Cu alloy. In this article, a single pot synthesis route has been developed to prepare Pd–Cu nanoalloy at room temperature by in situ reduction of metallo-templates with hydrazine in highly basic medium. Nanoalloy composition can also be tailored by this method. XRD, FESEM, EDX, TEM and HRTEM analyses are used for the structural investigations. The as synthesized Pd–Cu nanoalloys show great electrocatalytic potential towards MOR.

2. Experimental

2.1. Materials

All chemicals were purchased from Merck (India) and were used without further purification. Milli-Q water was used to make all solutions.

2.2. Synthesis of Pd–Cu bimetallic NPs

Pd–Cu(i) NPs (where i = 9:1, 3:1, 2:1, 1:1) were synthesized by co-reduction of Pd^{2+} and Cu^{2+} ethylenediaminetetraacetate complex at room temperature. To a 50 mL of NaOH (10 M) solution, 0.150–0.750 mL of aqueous $CuSO_4$ (0.5 M) solution was added drop wise with constant stirring. After the solution became clear, 0.0665–0.1198 g of anhydrous $PdCl_2$ and 2.20 g of solid Na_2EDTA was added and the resulting mixture was stirred for 4 h. Finally 1.5 mL 35% hydrazine hydrate solution was added to the resultant clear solution with constant stirring over a magnetic stirrer. The final products were separated, severally washed with deionised water and dried at room temperature. Pd and Cu nanopowders were synthesized by similar procedure for comparison (see ESI, Table S1 and Fig. S1 for details of synthesis). All experiments were carried out in air.

2.3. Structural characterization

The phases present in the powders synthesized were identified using X-ray diffractometer (XRD, Philips 1710, USA) with CuKα radiation ($α$ = 1.541 Å). The spatial, morphological, compositional and micro-structural investigations were carried out with field-emission scanning electron microscopy (FESEM: model Leo, S430i, UK), transmission electron microscopy (TEM, G2 30ST, FEI Company, USA operating at 300 kV), high-resolution TEM (HRTEM), energy-dispersive X-ray spectroscopy (EDX), TEM energy dispersion spectroscopy (TEM-EDS) and selected area electron diffraction (SAED) studies.

2.4. Fabrication of electrodes and electrocatalytic analysis

5 µL of the catalyst suspension (2 mg mL^{-1} of catalyst prepared in deionized water by ultrasonic mixing) was dropped over the surface of clean graphite rod electrodes (diameter: 3.02 mm). After the electrodes had been air dried for 1 h at ambient temperature, 2 µL Nafion solution (5 wt.%) was placed onto the surface of each of the electrodes. Finally the catalyst coating was dried at ambient temperature for overnight. The graphite rods were insulated from the sides using Teflon tape keeping both ends bare.

Cyclic voltammetric studies were performed using a computer aided Potentiostat/Galvanostat (AEW-2, Munistst, Sycopel Scientific Ltd., UK) at 30 ± 0.2 °C in a two compartment glass-cell fitted with a conventional three electrode assembly. Three-electrode electrochemical cells were fabricated using the modified graphite electrode as the working electrode, a Pt wire as the auxiliary electrode, and Hg/HgO/OH^{-} (1 M) (MMO having an equilibrium electrode potential of ~0.1 V with respect to the standard hydrogen electrode, SHE) as the reference electrode. All potential data recorded are presented with respect to MMO [31] electrode. Cyclic voltammetric measurements in 1.0 M NaOH with or without 0.5 M methanol were taken in the range between −0.9 V and +0.6 V at a scan rate of 50 mV s^{-1}. Cyclic voltammogram (CV) of each electrode was recorded for several consecutive cycles until a steady profile was obtained. The performance and stability of the electrodes are also tested by multi-scan CVs and chronoamperometric studies.

3. Results and discussion

3.1. Structural characterization

Fig. 1a–f shows the XRD patterns of Cu, Pd–Cu(1:1), Pd–Cu(2:1), Pd–Cu(3:1), Pd–Cu(9:1) and Pd NPs respectively synthesized under similar experimental conditions. The broadened peaks (Fig. 1a) at 43.20° (Cu(1 1 1)) and 50.32° (Cu(2 0 0)) of synthesized Cu NPs indicate the existence of nanosize metallic copper. The cubic lattice length for copper (3.626 Å) obtained from the XRD data is in good agreement with the reported (JCPDS, 1995, File No. 04-0836) value (3.615 Å). Absence of Cu(I)/Cu(II) oxide peaks in Fig. 1a confirms the formation of phase pure Cu NPs only. Similarly the synthesized Pd NPs show broadened peaks (Fig. 1f) at 40.17° (Pd(1 1 1)) and 46.67° (Pd(2 0 0)) and its cubic lattice length obtained (3.890 Å) from XRD data (reported 3.889 Å, JCPDS, 1995, File No. 05-0681) indicate the formation of phase pure Pd NPs only. Fig. 1b–e shows the XRD patterns of the synthesized Pd–Cu NPs having different compositions. The broad diffraction peaks suggest that the as-prepared NPs are small nanocrystals (crystallite size ~7 nm calculated from Debye–Scherrer's formula, Table 1, see ESI for detail calculation). The absence of characteristic peaks of pure Pd and Cu NPs indicate that the prepared Pd–Cu NPs are composed of a Pd–Cu bimetallic phase rather than a mixture of monometallic Pd and Cu NPs. For the bimetallic phase the XRD peaks appear at 41.26° and 48.44° for Pd–Cu(1:1), at 41.03° and 47.51° for Pd–Cu(2:1), at 40.80° and 47.44° for Pd–Cu(3:1), and at 40.48° and 47.30° for Pd–Cu(9:1) NPs.

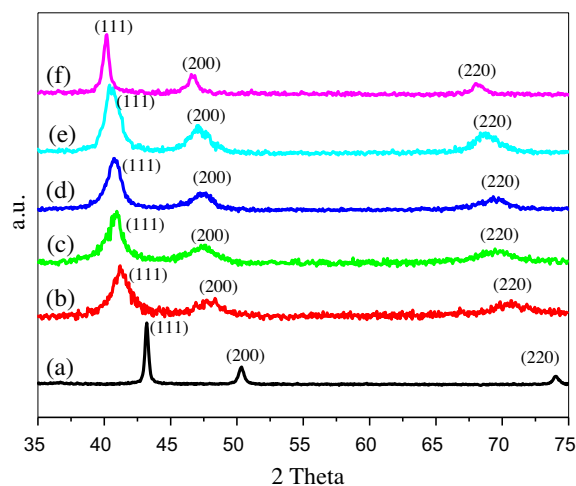**Fig. 1.** XRD patterns for the synthesized (a) Cu, (b) Pd–Cu(1:1), (c) Pd–Cu(2:1), (d) Pd–Cu(3:1), (e) Pd–Cu(9:1) and (f) Pd NPs.