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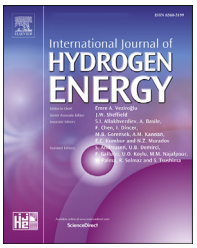

Designing of some platinum or palladium-based nanoalloys as effective electrocatalysts for methanol oxidation reaction

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ABSTRACT

Nano alloys contain noble metal nanostructures exhibit a wide theoretical and experimental interest in the field of fuel cells. Hard endeavors have been enhanced to improve the catalytic performance and minimize the usage of precious metals by alloying them with non-precious ones. Formation of bimetallic and trimetallic noble metal alloys with well-designed structures provide the opportunity to reach this goal. In this study, we first discuss the synthesis of noble metal alloy nanostructured thin films such as PtCu, PdCu, PtCu/reduced-graphene oxide (RGO), PdCu/RGO, PtCo, PtCo/RGO, PtPdCu and PtPdCu/RGO *via* a simple reduction of organometallic precursors including [$PtCl_2$ (cod)] and [$PdCl_2$(cod)], (cod = *cis*, *cis*-1,5-cyclooctadiene), in the presence of [$Cu(acac)_2$] and [$Co(acac)_3$] (acac = acetylacetonate) at oil/water interface and room temperature, including nanoparticles and nanosheets. Then the effects of the well-defined nanostructures on the improved electrochemical properties are outlined. Finally, we conclude that these non-precious bi and trimetallic alloy nanostructured thin films have better electrocatalytic performance than Pt monometallic thin films and other Pt nanostructures due to the geometric, electronic and stabilizer effect.

Introduction

Increasing the energy usage in spite of depletion of fossil fuel reserves and also rising environmental pollution, energy conversion devices such as fuel cells exhibit great interest [1–10]. Among various kinds of fuel cells, alcohol fuel cells are attractive power sources for different electric vehicle and mobile and immobile applications. Methanol fuel cells have a lot of advantages such as having low cost, easy storage and moving, being available and soluble in aqueous electrolytes [11–17]. Platinum-based catalysts are important for fuel cells

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to enhance the redox reactions due to their high catalytic activity and stability [18–23]. Extensive studies are simulated to decrease the Pt dosage in these catalysts due to their high cost and scarcity, and also increase and improve the catalytic activity [24,25]. Recently, there are some reports about decrease the loading amount of Pt in the catalysts with enhanced performance by alloying Pt with transition metals such as Co, Fe, Ni, Cu, Pb, etc [26–31]. Du et al. synthesized PtAu nanodendrites with interesting electrochemical properties than commercial Pt/C catalysts for methanol oxidation due to the dendritic structure, synergistic and electronic effects between Pt and Au [32]. Also, this group attempted for the synthesis of PtCu nanocrystal catalysts under ultrasonic condition that exhibit better electrocatalytic activity than commercial Pt/C toward ethylene glycol electrooxidation [33]. Furthermore, they reported the synthesis of PdNi hollow nanospheres with high active sites with the assistant of polyvinylpyrrolidone for ethylene glycol electrooxidation [34]. The main important facts that influence the catalytic activity are: (i) electronic and geometric effect (component, size and morphology of the catalysts) [35] and (ii) stabilizer effect (using carbon-based stabilizers such as graphene and carbon black) [36,37]. Previously, graphene-Pt composites have been attempted in the fuel cells for oxygen reduction reaction [38,39] and the methanol oxidation reaction (MOR) purposes [40,41]. Also, Pd–Ru alloy nanoparticles (NPs) dispersed on $CoWO_4$-doped graphene nanosheets was used for enhanced methanol electro-oxidation and obtained from the microwave-assisted polyol reduction method [42]. Pt NPs supported on titanium iron nitride nanotubes was synthesized at 120 °C and applied as electrocatalysts for MOR [43]. Microwave synthesis of the Pt NPs supported on undoped nanodiamond for MOR was also reported [44]. The role of Pb and MnOx in PtPb/MnOx-CNTs catalyst for MOR was also investigated [45]. Electrochemical deposition of hair shaped PtRu as methanol oxidation catalyst was investigated by Raoof et al. [46]. In all the reports, the synthesis of the electrocatalysts was done in the microwave or high temperature conditions. The "liquid–liquid interfacial assembly" is an interesting, simple, novel and low-cost bottom-up approach to provide a thin film applied in nanodevice fabrication due to their low cost [47–49]. Recently, there are some reports about various types of Pt and Pt-based NPs thin films that can be easily obtained at the liquid–liquid (organic–aqueous) interface by Hoseini et al. [50–57]. We have investigated the application of monometallic Pt thin films with different precursors in the MOR for the first time [51]. Also, we have reported the formation of monometallic Pd [53] and bimetallic PtPd [53], PtSn [52] and $PtFe/Fe_2O_3$ [54] NPs thin films at toluene-water interface and investigating their applications in methanol oxidation. Furthermore, Pd [58], PdZn [59], PdSn [59], PdCu [60] and PdCu/reduced-graphene oxide (RGO) [61] thin films were synthesized at liquid-liquid interface and applied as catalyst in the Suzuki-Miyaura C–C coupling reaction. Girault et al. have investigated the activities of a series of MoS_2-based hydrogen evolution catalysts studied by interfacial biphasic reactions. Carbon supported MoS_2 catalysts (supported with multi-walled carbon nanotube and RGO) performed best due to an abundance of catalytic edge sites and strong electronic coupling of catalyst to support [62]. Dryfe and coworkers have investigated the assembly of nanomaterials at liquid-liquid interface [47]. Toth and Dryfe used liquid-liquid interface strategy for the deposition of Pd and Au noble metal NPs on a free-standing chemical vapor deposited graphene monolayer that opens an alternative and useful way to prepare low dimensional carbon-based nanocomposites and electrode materials [63]. The present work reports the synthesis of several Pt-based and Pd-based bimetallic and trimetallic electrocatalysts for methanol electro-oxidation. Three interesting aspects of our study are notable. First, in this study, for the first time, we demonstrated a facile synthesis of PtCu, PtCu/RGO, PtCo, PtCo/RGO, PtPdCu and PtPdCu/RGO alloy electrocatalysts by reduction of organometallic precursors, [$PtCl_2$ (cod)] and [$PdCl_2$(cod)], (cod = *cis*, *cis*-1,5-cyclooctadiene), in the presence of [Cu(acac)$_2$] and [Co(acac)$_3$] (acac = acetylacetonate) at toluene/water interface. PtCo thin films exhibit a nanosheet morphology which is promising candidate for electrocatalytic reactions. This potential is due to its large surface area to volume ratio and high active sites, makes the nanosheets highly useful for a number of applications including catalysis and chemical sensing [64,65]. Second, organometallic precursors show excellent potential for the production of nano thin films. Third, the synthesized alloy nano films exhibit a high catalytic activity and CO tolerance among most other catalysts that were tested up to now toward methanol electrooxidation [66–68]. Furthermore, using the bimetallic and trimetallic alloys strategy can lead to a lower amount of Pt catalysts and in turn, can decrease the price of the electrocatalysts for MOR.

Experimental

Materials and methods

All of the chemical compounds were purchased from Merck and Aldrich companies. The [$PtCl_2$(cod)] [69] and [$PdCl_2$(cod)] [70] complexes were synthesized using reported procedures. The elemental composition of the treated samples was acquired by means of energy dispersive analysis of X-ray (EDAX) and elemental mapping. X-ray diffraction (XRD) patterns were recorded using a Bruker AXS (D8, Advance) instrument equipped with Cu Kα radiation. Transmission electron microscopy (TEM) images were recorded using a Philips CM-10 TEM microscope operated at 100 kV. By comparing the scale bar of the TEM images with the diameter of different obtained particles, the near mean diameter of the particles can be estimated. Scanning electron micrographs (SEM) were obtained using a Cambridge S-360 instrument with an accelerating voltage of 20 kV. These samples were sputter-coated with gold for this analysis. Inductively coupled plasma (ICP) was performed on Agilent 7500ce quadrupole ICP-AES. The surface atomic concentration and chemical composition of the samples were investigated by X-ray photoelectron spectroscopy (XPS) equipped with an Al KαX-ray source at energy of 1486.6 eV in an ultrahigh vacuum (UHV) system with a base pressure lower than $2 \times 10-9$ Torr.

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