

Monodisperse PtRu Nanoalloy on Carbon as a High-Performance DMFC Catalyst

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The direct methanol fuel cell (DMFC) is a promising future energy technology alternative to conventional energy-generating devices, because of its high energy-conversion efficiency, low pollutant emission, methanol fuel availability, easy distribution, and high energy density of the fuel.^{1,2} Although notable developments are being reported for the preparation of new carbon-based catalyst-support materials,^{3,4} the metal catalysts should be independently investigated to optimize DMFC performance, which calls for careful studies on size- and shape-related catalyst performance excluding the effect of catalyst supports. Bimetallic PtRu system seems to be the most promising material for the anode, where methanol is catalytically oxidized.^{1,5} It is well-known that the catalytic activity is strongly dependent on the shape, size, and size distribution of catalytic particles.⁶ Various synthetic strategies, such as the coimpregnation method,^{7,8} microemulsions,⁹ spray pyrolysis,¹⁰ and microwave irradiation,¹¹ have been employed in order to prepare bimetallic PtRu catalysts, but often have not provided adequate control of particle morphology. It is, therefore, prerequisite to develop reliable synthetic routes to monodisperse, stoichiometrically uniform PtRu nanoparticles to improve the catalyst performance.

In this paper, we report a simple, reliable preparation method for monodisperse, phase-pure PtRu colloidal nano-

alloy with a narrow size distribution in a surfactant–organic solvent system. The colloidal nanoparticles that are soluble in organic solvents are especially convenient for impregnation on support materials. Furthermore, we found that the carbon-supported PtRu colloidal nanoalloy can be activated by a simple acid treatment under mild conditions. The prepared carbon-supported PtRu catalyst exhibits a remarkable enhancement of catalytic activity for methanol oxidation as compared to that of the commercially available PtRu catalyst.

We prepared colloidal PtRu nanoalloy from the co-reduction of Pt(acac)₂ and Ru(acac)₃ (acac = acetylacetonate) by 1,2-hexadecanediol as a reducing agent in octyl ether in the presence of oleylamine and oleic acid as surfactants. Similar approaches have recently been applied for the preparation of FePt,¹² FePd,¹³ MnFe₂O₄,¹⁴ and MnPt¹⁵ systems. The size and composition of the alloy particles were analyzed by transmission electron microscopy (TEM) and point-resolved energy-dispersive X-ray spectrometry (EDX) measurements. Figure 1a shows a typical TEM image of the colloidal PtRu nanoalloy, which shows remarkably uniform and well-dispersed nanoparticles. The average diameter of 2.4 nm was accompanied by a relatively narrow particle size distribution (range = 1.9–2.9 nm, SD = 0.19 nm (~8%)). The particles are nearly spherical in shape. It is noted that most of the PtRu nanoparticles for DMFC catalyst reported thus far showed a wide size distribution up to 40% in a similar size (~2 nm).¹⁶ The high-resolution TEM (HRTEM) image (the inset in Figure 1a) demonstrates the highly crystalline nature of the nanoparticles. Figure 1b exhibits the selected area electron diffraction (SAED) pattern of the colloidal nanoparticles; diffractions of the (111), (200), (220), and (311) lattice planes are consistent with the face-centered cubic (fcc) structure of PtRu binary alloy. EDX analysis reveals that the atomic composition of Pt:Ru is 0.49:0.51, which is close to 1:1 stoichiometry. Prior to electrochemical measurements of the catalysts, colloidal nanoparticles are deposited on a high-surface-area Vulcan carbon (Vulcan XC-72R). As shown in the TEM micrograph in Figure 2a, the colloidal PtRu nanoparticles are uniformly dispersed on the Vulcan carbon, and all nanoparticles have a particle size and morphology identical to that of free colloidal particles.

We found that the protecting surfactants could be removed by acetic acid treatment at 80 °C for 10 h without altering the overall catalyst morphology and composition. The removal of surfactants is evidenced by the FTIR spectra

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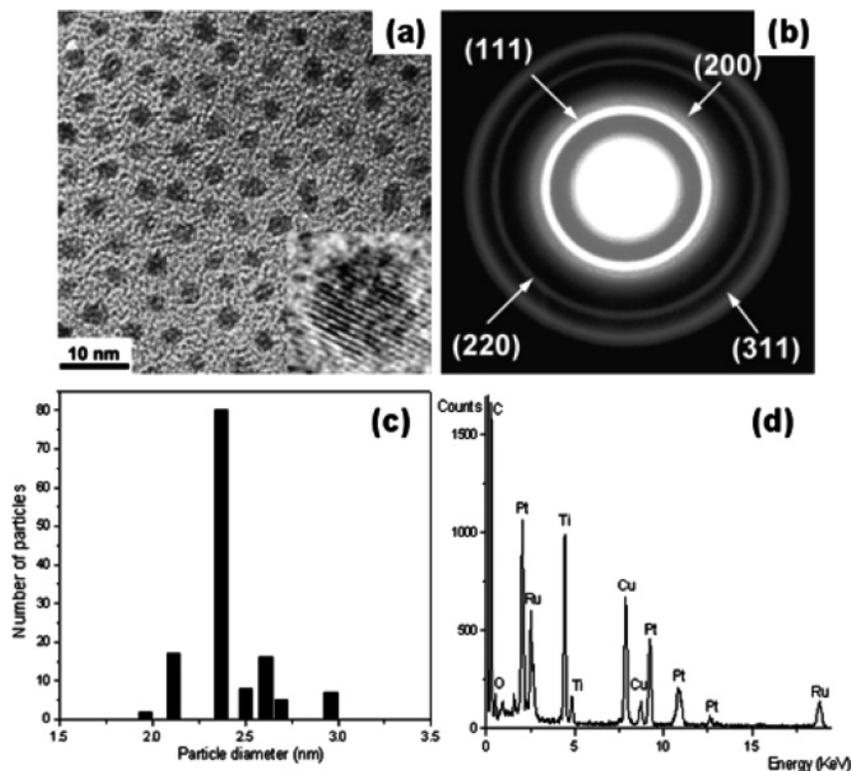


Figure 1. (a) TEM image of the colloidal PtRu nanoalloy (the inset represents the HRTEM image). (b) Selected area electron diffraction pattern. (c) Histograms of the particle distributions for colloidal PtRu nanoalloy as measured from 180 particles in TEM micrographs. (d) Typical EDX spectrum of colloidal PtRu nanoalloy.

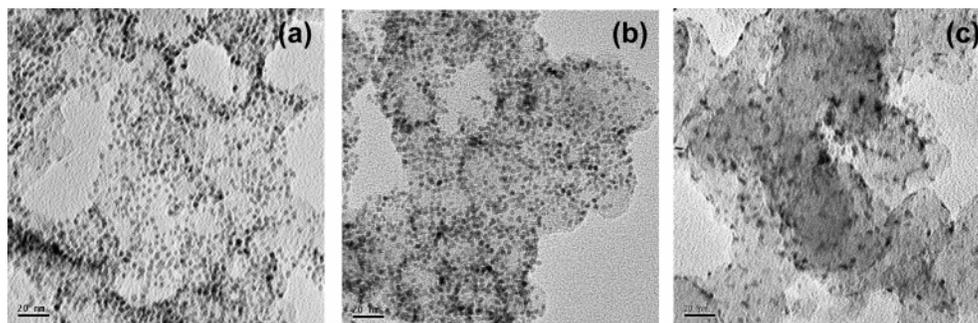


Figure 2. TEM images of (a) colloidal PtRu/Vc catalyst precursor, (b) PtRu/Vc catalyst, and (c) commercial E-TEK catalyst.

(Figure S2)¹⁷ before and after treatment of the colloidal PtRu nanoparticles with acetic acid. Figure 2b clearly reveals that the surfactant-free PtRu nanoparticles were still highly dispersed over the entire carbon surface and the size of the particles was unchanged by acid treatment. Figure 2b is sharply contrasted with Figure 2c of the commercial E-TEK (30 wt %) catalyst with poor dispersion and broad particle size distribution. The inductively coupled plasma (ICP) measurement showed a PtRu content of 26.9 wt % for PtRu/Vulcan carbon (abbreviated as PtRu/Vc). The EDX spectrum of PtRu/Vc revealed a Pt/Ru atomic ratio of 0.47/0.53, which agrees well with the original stoichiometric ratio of 0.49/0.51. X-ray diffraction (XRD) patterns for PtRu/Vc matched well but were slightly shifted to higher 2θ values compared to those of the pure Pt fcc structure, as shown in Figure S1.¹⁷ This observation is consistent with those by other groups.^{18,19} The particle size calculation using a Debye–Scherrer equa-

tion gave an average size of 2.4 ± 0.1 nm for PtRu/Vc, which is in a very good agreement with the TEM measurements.

To investigate the catalytic performance of the prepared PtRu nanoparticles for DMFC, we analyzed the electrochemical properties of the nanoparticles in an acidic solution using linear sweep voltammetry (LSV). The colloidal PtRu/Vc catalyst precursor showed no catalytic activity. Figure 3a exhibits cyclic voltammograms of methanol oxidation catalyzed by PtRu/Vc (26.9 wt % PtRu, solid line) and the commercial PtRu catalyst (30 wt %, E-TEK, dashed line) under acidic conditions. The methanol oxidation occurs at relatively lower potential and the current peak is significantly higher for the PtRu/Vc catalyst compared to that of the commercial one. The low onset potential of -0.01 V vs SCE of PtRu/Vc compares with 0.02 V of the E-TEK catalyst,²⁰ which indicates a superior electrocatalytic activity of our

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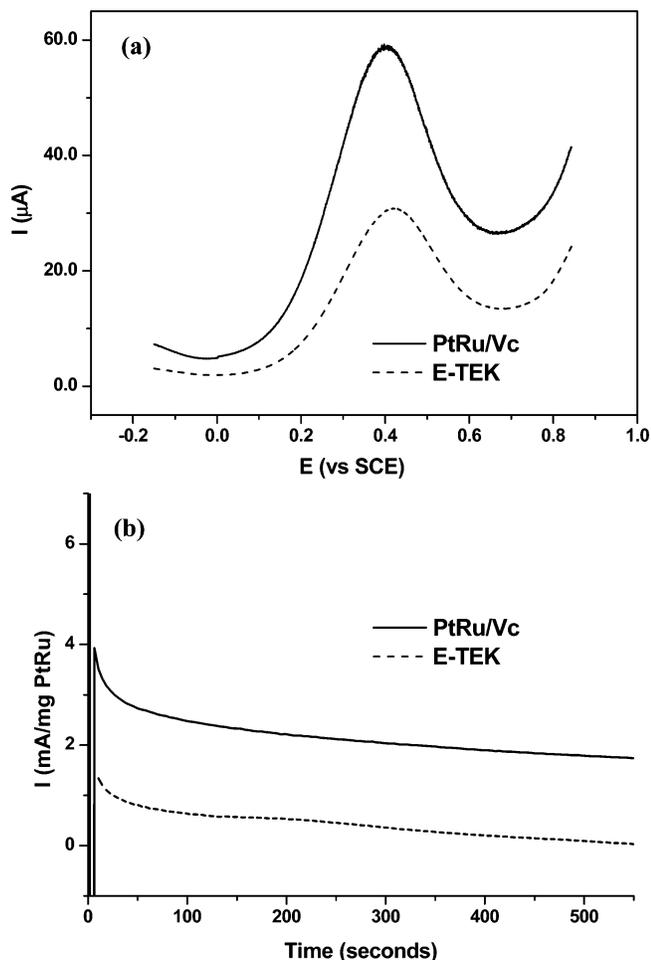


Figure 3. (a) Linear sweep voltammograms (scan rate = 0.010 V/s) and (b) chronoamperometry measurements of methanol oxidation in 1 M CH₃OH and 0.05 M H₂SO₄ solution for an electrode coated with PtRu/Vc catalyst (solid line) and with commercial E-TEK catalyst (dashed line).

catalyst due to the ideal surface structure for methanol adsorption on the catalyst surface. Mass activity calculated from the current at 0.21 V for PtRu/Vc is another indicator of the catalytic activity of catalysts under moderate polarization conditions.²¹ The current at this kinetically controlled potential exhibits true catalytic activity rather than mass transport limitation of the reactant. The value for PtRu/Vc of 32.9 mA (mg PtRu)⁻¹ is more than a 280% increase in mass activity compared to that for the E-TEK catalyst (11.7 mA (mg PtRu)⁻¹). Furthermore, our PtRu/Vc catalytic system shows an increase of at least 400% in methanol oxidation

current, on the basis of the previously reported mass activity at the same potential of electrocatalyst prepared from electrochemical deposition of Ru on commercial Pt nanoparticles supported on Vulcan carbon (E-TEK).²² The changes in the oxidation current density with time were recorded for both catalysts at the bias of 0.2 V, as shown in Figure 3b by the chronoamperometric method. The currents sharply decreased within 50 s and then decayed very slowly to approach the limiting currents for more than 500 s. The initial and limiting currents of PtRu/Vc are much higher than those of the E-TEK catalyst throughout all the ranges up to 500 s. It indicates satisfactory CO tolerance of both catalysts during methanol oxidation reaction. All of the results reveal a remarkable enhancement of catalytic activity for our PtRu/Vc catalyst in methanol oxidation compared to those of the E-TEK catalyst and earlier works.²²

In conclusion, monodisperse PtRu (1:1) nanoparticles have been synthesized by the coreduction of platinum and ruthenium precursors in the surfactant-organic solvent system. The PtRu/Vc catalyst was generated by impregnation on the Vulcan carbon support, and the surfactant was removed by acetic acid treatment. The electrochemical experiments exhibited that our PtRu/Vc catalyst had remarkably higher catalytic activity toward methanol oxidation reaction compared to that of commercially available PtRu catalysts and earlier works. The high activity of our catalyst is obviously due to nanosize and monodispersity of the catalyst particles and excellent dispersion of the catalysts on the carbon support by colloidal impregnation and mild activation of the catalyst. Details of controlled preparation and mechanistic studies on electrochemical properties of the PtRu catalyst are in progress.

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Supporting Information Available: Details of experimental procedures, XRD spectra of PtRu/Vc and E-TEK catalysts, and FTIR spectra of raw Vulcan carbon and before and after treatment of the colloidal PtRu/Vc with acetic acid. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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