



# The electrocatalytic performance of carbon ball supported RhCo alloy nanocrystals for the methanol oxidation reaction in alkaline media



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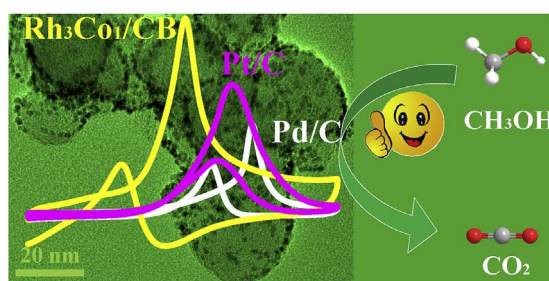
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## HIGHLIGHTS

- RhCo/CB nano hybrids are synthesized by a co-precipitation/co-reduction method.
- RhCo nanocrystals show the high alloying degree and good dispersion.
- RhCo/CB nano hybrids exhibit a composition-dependent catalytic activity for the MOR.
- Rh<sub>3</sub>Co<sub>1</sub>/CB nano hybrids reveal the higher MOR activity than Pt/C electrocatalyst.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

### Keywords:

RhCo alloy  
Electrocatalytic activity  
Methanol oxidation reaction  
Alkali medium  
Pt-alternative electrocatalyst

## ABSTRACT

Although both Pd and Rh fall into the Pd-group Pt-group elements (PPGEs), the electrocatalytic property of Rh nanocrystals for the methanol oxidation reaction (MOR) in alkaline media is rarely explored till now. In this work, we develop a surfactant-free co-precipitation/co-reduction method to synthesize the carbon ball supported RhCo alloy nanocrystals (RhCo/CB) nano hybrids with different Rh/Co atomic ratios and investigate their electrocatalytic activity for the MOR in alkaline media. Cyclic voltammetry and chronoamperometry measurements show Rh<sub>3</sub>Co<sub>1</sub>/CB nano hybrids have exceptional electrocatalytic activity and long-term stability for the MOR in alkaline media, much higher than commercial Pd/C and Pt/C electrocatalysts, demonstrating that Rh-based alloy nanocrystals may be highly promising Pt-alternative electrocatalyst for the MOR in alkaline media.

## 1. Introduction

Direct methanol fuel cells (DMFCs) are highly efficient and convenient energy conversion devices for transportation and portable applications [1–5]. At present, the state-of-the-art DMFCs use Pt nanocrystals as the anode electrocatalyst for the methanol oxidation reaction (MOR) [6–12]. Unfortunately, the high cost of Pt metal (\$ 1000 a troy ounce in 2016) and the limited supply are the great challenge for the

commercialization of DMFCs [13,14]. Recently, the alkaline DMFCs have attracted increasing interests due to the improved oxygen reduction reaction kinetics and enhanced MOR kinetics in alkaline media, the wide opportunity for application of non-Pt metal (such as Pd and Ag) anode electrocatalysts [15,16], and the potential use of non-noble metal cathode nanomaterials (such as various carbon nanostructures and transition metals-based oxides/sulfides/nitrides) in alkaline media [17–20].

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According to the behavior in geological systems, Pt, Pd and Rh elements are divided into the Pd-group Pt-group elements (PPGEs) and they have very similar physical/chemical properties [21]. Indeed, less expensive Pd (\$ 615 a troy ounce in 2016) and Pd-based multimetallic nanocrystals have been regarded as highly efficient Pt-alternative electrocatalyst for the MOR in alkaline media due to their high electrocatalytic activity and excellent carbonaceous intermediates tolerance [22–29]. Less expensive Rh (\$ 670 a troy ounce in 2016), as an important member of PPGEs family, has wide applications in heterogeneous catalysis [30–35]. Very recently, we investigate the electrocatalytic activity of monometallic Rh nanostructures for the MOR in alkaline media, which is superior than monometallic Pt and Pd nanocrystals without carbon support materials [36]. It is well known that electrocatalytic activity of PPGEs nanocrystals highly depends on their chemical composition and particle size. Generally, alloying PPGEs with a transition metal can improve electrocatalytic activity of PPGEs nanocrystals due to ensemble effect and electronic effect [37–39]. To further increase the utilization of PPGEs, bimetallic PPGEs alloy nanocrystals are generally supported on various carbon materials, which can effectively prevent the aggregation of particles, decrease the particle size, increase the electrochemical activity area, and accelerate the electronic communion [40–43]. Among carbon materials, commercial XC-72 carbon ball (CB) with big surface area and excellent electrical conductivity has been identified as an excellent support material [44–46].

During the synthesis of PPGEs/carbon nanohybrids, in order to stabilize nanocrystals and prevent aggregation, various surfactants (such as polyethylene glycol and polyvinylpyrrolidone) are generally used [47–50]. Unfortunately, such surfactants on the surface of PPGEs nanocrystals block adsorption of reactants, severely decreasing their electrocatalytic activity [51–53]. In this work, we successfully synthesize CB supported RhCo alloy nanocrystals (RhCo/CB nanohybrids) with different Rh/Co atomic ratios by a simple surfactant-free co-precipitation/co-reduction method and investigate the electrocatalytic performance of bimetallic Rh-based nanocrystals for the MOR in alkaline media. The as-prepared Rh<sub>3</sub>Co<sub>1</sub>/CB nanohybrids exhibit significantly enhanced reactivity and durability for the MOR in alkaline media compared to the state-of-the-art Pd/C and Pt/C electrocatalysts.

## 2. Experimental section

### 2.1. Reagents and chemicals

High-purity XC-72 carbon ball (CB) was supplied by USA Massachusetts. Prior to use, CB was pre-treated in concentrated HNO<sub>3</sub> solution for 2 h. The commercial 30 wt% Pd/C and 30 wt% Pt/C electrocatalysts were purchased from Johnson Matthey Corporation. Rhodium (III) chloride hydrate (RhCl<sub>3</sub>·3H<sub>2</sub>O), cobalt (II) chloride hexahydrate (CoCl<sub>2</sub>·6H<sub>2</sub>O), and sodium carbonate anhydrous (Na<sub>2</sub>CO<sub>3</sub>) were purchased from Sinopharm Chemical Reagent Co., Ltd. The sodium borohydride (NaBH<sub>4</sub>) and methanol were obtained from Shanghai Chemical Reagent Ltd. All other chemicals were of analytical grade and used as received without further purification.

### 2.2. Synthesis of Rh<sub>3</sub>Co<sub>1</sub>/CB nanohybrids

The Rh<sub>3</sub>Co<sub>1</sub>/CB nanohybrids were obtained by a facile co-precipitation/co-reduction method, which was schematically shown in Scheme 1. In a typical synthesis, 1.4 mL of 0.076 M RhCl<sub>3</sub> aqueous solution and 0.35 mL of 0.1 M CoCl<sub>2</sub> aqueous solution were added into 10 mL of CB suspension (3 mg mL<sup>-1</sup>) under vigorous stirring. After slowly adjusting the pH to 9.0 using 1 M Na<sub>2</sub>CO<sub>3</sub> aqueous solution, the suspension was heated at 50 °C for 6 h. Then, 4.2 mL of 5 M NaBH<sub>4</sub> aqueous solution was added into the reaction mixture. After stirring for 3 h, Rh<sub>3</sub>Co<sub>1</sub>/CB nanohybrids were obtained by centrifugation, washed and dried. For comparison, Rh/CB nanohybrids and Rh<sub>1</sub>Co<sub>1</sub>/CB

nanohybrids were also synthesized using the same procedure.

For comparison, Rh<sub>3</sub>Co<sub>1</sub>/CB-conventional nanohybrids were also synthesized by directly adding NaBH<sub>4</sub> solution in mixture of RhCl<sub>3</sub>, CoCl<sub>2</sub> and CB (i.e., the pH of reaction mixture doesn't be adjusted).

### 2.3. Electrochemical measurements

Cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and chronoamperometry measurements were carried out on a CHI 660E electrochemical analyzer with a conventional three-electrode cell at 30 °C, including a catalyst-modified glassy-carbon disk electrode (GCE, 3 mm in diameter) as working electrode, a saturated calomel electrode as reference electrode, and a Pt plate as the auxiliary electrode. All electrode potentials were reported with respect to the reversible hydrogen electrode (RHE). The catalyst-modified GCE was fabricated according to the procedure reported previously [54]. The working electrode was prepared by mixing 4 mg of electrocatalyst and 2 mL of water, and sonicating the mixture for 15 min. Then, 6 μL of the resulting suspension was laid on the clear glassy-carbon electrode surface. After drying at room temperature, 3 μL of Nafion solution (5 wt %) was covered on the electrocatalyst modified electrode, then drying again (The metal loadings on the GC electrode was 51.4 μg cm<sup>-2</sup>).

The electrochemical active surface area (ECSA) of RhCo/CB nanohybrids and Pd/C catalyst were obtained using the following equations, ECSA = Q/m<sub>Rh</sub> × 0.210 [36], ECSA = Q'/m<sub>Pd</sub> × 0.420 [54], respectively. In these equations, Q is the coulombic charge, which is calculated by integrating the charges associated with the peak of hydrogen desorption. Q' is the coulombic charge, which is calculated by integrating the charges associated with the peak reduction of Pd (II) oxide.

### 2.4. Instruments

Scanning electron microscopy (SEM) images and energy dispersive X-ray (EDX) spectra were obtained on a SU-8020 scanning electron microscope with the EDX accessory. Powder X-ray diffraction (XRD) was performed on a D/max-rC diffractometer with Cu Kα radiation. Transmission electron microscopy (TEM) images, high resolution TEM (HRTEM) images and selected area electron diffraction (SAED) pattern were taken on a JEM-2100F transmission electron microscope. X-ray photoelectron spectra (XPS) were recorded on an ESCALAB 250 XPS system. XPS binding energies were calibrated using the C 1s peak (284.6 eV). The inductively coupled plasma atomic emission spectrum (ICP-AES) was obtained on a Thermo Scientific X Series 2 instrument.

## 3. Results and discussion

### 3.1. Characterization of Rh<sub>3</sub>Co<sub>1</sub>/CB nanohybrids

Due to the slow hydrolysis of Na<sub>2</sub>CO<sub>3</sub>, RhCl<sub>3</sub> slowly transformed into the insoluble Rh<sub>2</sub>O<sub>3</sub> nanocrystals and CoCl<sub>2</sub> slowly transformed into the insoluble Co(OH)<sub>2</sub> nanocrystals, which uniformly anchored on the CB surface (Step 1 in Scheme 1). Then, Rh<sub>2</sub>O<sub>3</sub>-Co(OH)<sub>2</sub> nanocrystals are reduced to RhCo alloy nanocrystals by NaBH<sub>4</sub>, resulting in the generation of highly dispersed Rh<sub>3</sub>Co<sub>1</sub>/CB nanohybrids (Step 2 in Scheme 1).

TEM was performed to investigate the morphology of Rh<sub>3</sub>Co<sub>1</sub>/CB nanohybrids (Fig. 1A and B). Highly monodisperse nanocrystals are uniformly anchored on the CB surface. The particle size distribution histogram shows that the average size of nanocrystals is ca. 2.4 nm (inset in Fig. 1B). The chemical composition of Rh<sub>3</sub>Co<sub>1</sub>/CB nanohybrids was determined by EDX (Fig. 1C), which gave a molar ratio of Rh/Co of ca. 2.98:1. ICP-AES measurement shows the molar ratio of Rh/Co is ca. 3.03:1 and metal loading of Rh<sub>3</sub>Co<sub>1</sub>/CB nanohybrids is ca. 28.9 wt% metal. The distribution of Rh and Co elements on CB was investigated by EDX element mapping (Fig. 1D). The maps of Rh and Co are very similar to that of C, indicating the Rh and Co elements homogeneously

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