



# Preparation of cobalt silicide on graphene as Pt electrocatalyst supports for highly efficient and stable methanol oxidation in acidic media



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## ABSTRACT

Nanostructured CoSi with the diameter of 1–3 nm on graphene have been successfully synthesized by metal organic chemical vapor deposition (MOCVD) of  $\text{Co}(\text{SiCl}_3)(\text{CO})_4$  as a precursor supported on graphene. Pt electrocatalysts are then loaded on the CoSi/graphene composites (Pt/CoSi-graphene) using an intermittent microwave heating method. The above materials are characterized by XRD, Raman, TEM, EDS and cyclic voltammograms measurements. The results show that Pt/CoSi-graphene gives 3.2 times higher peak current density than that of commercial Pt/C(TKK) electrocatalyst at the same Pt loadings. In addition, Pt/CoSi-graphene shows superior activity and stability to commercial Pt/graphene for methanol oxidation in acidic media. The improved catalytic activity and stability is due to the synergistic effect (electron-donating) of CoSi to Pt. Since Pt/CoSi-graphene carries higher catalytic activity and stability comparing with Pt/graphene, less Pt will be required for the same performance and it will in turn reduce the cost of fuel cell electrocatalyst.

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## 1. Introduction

The electrochemical oxidation of methanol has been considered to be an attractive power source with potential applications over the past decades in the direct methanol fuel cells (DMFCs), which has high-energy conversion efficiency, system simplicity, environmental friendliness, low operating temperatures and the storage convenience of a liquid fuel cell [1–4]. The electrocatalyst is one of the critical parts, noble metals such as Pt and Pd have been remaining the main active ingredients of the electrocatalyst [5]. However, the high cost of the noble metals restricted the commercial application of the direct methanol fuel cells, therefore, reducing the use level of noble metals at the condition of keeping or increasing the catalytic activity and stability of the electrocatalyst is of great significance [6]. To realize this aim, various methods have been proposed and studied.

A great deal of effort has been devoted to reducing the use of Pt and enhancing the catalytic efficiency of Pt for methanol oxidation in their industrial applications [7–9]. It is believed that smaller noble metal particles could give more active sites and show higher catalytic activity. Yan et al. reported an intermittent microwave heating method to reduce the sizes of noble metal particles [10]. This method

could let the Pt nuclei grow intermittently and avoid big particles, which enhanced the catalytic activity to a large degree.

Another effort to increase the catalytic activity of the noble metal-based catalyst is using suitable catalyst promoter. Zhao et al. reported that the CO-like species as poisoning intermediate products could be easily oxidized by WC-noble metal electrocatalyst which reduced the overpotential of methanol electro-oxidation, displaying synergistic effect [11]. Since transition metal silicides could instead of some noble metal be widely used in catalyzing naphthalene hydrogenation and aromatic hydrogenation [12,13], they are more and more attractive and important in the field of aromatic hydrogenation. Unfortunately, metal silicides inherited from the microelectronic industry had low surface area and were nonporous, which restricted the application of metal silicides in catalysis. It is still an important challenge to synthesize well dispersed metal silicides for catalytic applications under controllable conditions. Metal-organic chemical vapor deposition (MOCVD) is an attractive and successful method for highly dispersed catalysts in a controlled and reproducible manner [14,15]. Liang et al. reported that highly dispersed CoSi nanoparticles supported on silica could be synthesized by MOCVD of  $\text{Co}(\text{SiCl}_3)(\text{CO})_4$  at atmospheric pressure and moderate temperature and could be used as high activity and selectivity catalysts in naphthalene hydrogenation [16]. However, to the best of our knowledge, no reports have been published on metal silicides as novel electrocatalytic promoter although they were found the

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noble metal-like catalytic property. According to the previous reports, we attempt to synthesize highly dispersed CoSi nanoparticles supported on graphene by MOCVD for the first time. Graphene, a two-dimensional carbon material with single or several atomic layers, have been regarded as a suitable supporting material for loading Pt nanoparticles in fuel cells due to the huge theoretical specific surface area, excellent electronic conductivity, thermal stability and durability [17]. Currently, most of graphene nanosheets used in DMFCs were produced by the over oxidation of graphite with strong oxidants. Abundant oxygen-containing functional groups were present in graphene oxide (GO) [18], which enable the solubilization of oxidized graphene sheets and thus allow for the intercalation of molecules such as metal silicides precursors into the interlayer space of GO [19,20].

Here, we have successfully synthesized highly dispersed CoSi nanoparticles with the diameter 1–3 nm supported on graphene by MOCVD and used as Pt electrocatalyst supports for methanol oxidation in acidic media. The novel Pt/CoSi-graphene electrocatalyst showed highly active and stable catalytic performance comparing with that of Pt/graphene and commercial Pt/C. The increased catalytic activity and stability were respectively ascribed to the synergistic effect and the strong interaction force between Pt and CoSi. The results make Pt/CoSi-graphene a promising candidate for fuel cell electrocatalyst.

## 2. Experimental

### 2.1. Materials

Natural flake graphite was obtained from Qingdao Guyu graphite Co., Ltd. with a particle size of 150 nm. Ethylene glycol (EG), trichlorosilane (SiHCl<sub>3</sub>), cobalt carbonyl (Co<sub>2</sub>(CO)<sub>8</sub>) and chloroplatinic acid (H<sub>2</sub>PtCl<sub>4</sub>) were purchased from Sinopharm Chemical Reagent Co., Ltd. China and used as received without any further purification. Distilled water was also used throughout the experiment.

### 2.2. Preparation of CoSi-graphene composites

Co(SiCl<sub>3</sub>)(CO)<sub>4</sub> was chosen as precursor because it allows precise control of stoichiometry, it has high vapor pressure, and it has stability in dry air at low temperature. Co(SiCl<sub>3</sub>)(CO)<sub>4</sub> precursor was synthesized under an atmosphere of dry argon using Schenkline techniques according to the literature [21,22]. Typically, about 20 mL of freshly distilled SiHCl<sub>3</sub> was added to 2.0 g of Co<sub>2</sub>(CO)<sub>8</sub> placed in a Carius tube and was cooled to -40 °C in an acetonitrile/dry ice slurry and was stirred for 2.5 h before warming to room temperature. Excess trichlorosilane was removed in vacuo. The residual, gray-brown powder was purified by repeated sublimation at 45 °C, 0.1 mbar. The final product of yellow crystal was obtained. GO was prepared from purified natural graphite using our previous work (a modified Hummers method) [18]. The Co(SiCl<sub>3</sub>)(CO)<sub>4</sub> precursor was sublimed and adsorbed on the GO support at 50 °C in vacuum. Then, the GO adsorbed precursor was put in a quartz-tube heater with a flow rate of 30 mL/min argon for 2 h at room temperature to remove oxygen in the reactor and keep the reaction under the inert atmosphere. The GO adsorbed precursor was treated in 200 mL/min of 10% H<sub>2</sub>/Ar at 300 °C for 120 min under atmospheric pressure, which led to a stable black CoSi/graphene.

### 2.3. Preparation of Pt/CoSi-graphene electrocatalyst

For the synthesis of Pt/CoSi-graphene nanoparticles, Typically, 10 mL of 0.107 mol/L H<sub>2</sub>PtCl<sub>4</sub> and 2.0 g CoSi-graphene were dispersed in 50 mL EG in beaker. The resulting solution was

uniformly dispersed by sonification for 10 min, vigorously stirred for 24 h at room temperature. The pH of the mixture was adjusted to 10 by 2.0 M NaOH/glycol solution. The sample was then put into a microwave oven (800 W) for heating at a 15 s on and 10 s off procedure for 10 times. After cooling to room temperature, the product was isolated by several washes with distilled water to remove the excess EG and subsequent separation by sintered discs. Afterwards, a successful Pt/CoSi/graphene was obtained. For comparison, Pt nanoparticles were prepared. The preparation procedure is similar to that of Pt/CoSi-graphene without loading CoSi. The theoretical Pt contents in Pt/CoSi/graphene was targeted at 60 wt.%. The inductively coupled plasma spectroscopy (ICP, Optima2000DV, USA) analysis gave the actual Pt contents as 57.5 wt.%.

### 2.4. Preparation of catalyst electrode

For electrode preparation, 28.7 mg Pt/CoSi/graphene were dispersed in 1 mL ethanol and 1 mL 0.5 wt.% Nafion suspension (DuPont, USA) under ultrasonic agitation to form the electrocatalyst ink. The electrocatalyst ink (10 μL) was then deposited on the surface of the glassy carbon rod and dried at room temperature overnight. The total Pt loadings were controlled at 0.05 mg cm<sup>-2</sup>. All chemicals were of analytical grade and used as received.

### 2.5. Characterization of the supports and the electrocatalysts

The morphology of the as-prepared samples was examined by a TEM (JEOL-JEM-2010, Japan) operating at 120 kV. The structures of the obtained samples were examined by XRD using D8 Advance X-ray powder diffraction (Bruker axs company, Germany) equipped with Cu-KR radiation (λ) 1.5406 (Å), employing a scanning rate of 0.02° s<sup>-1</sup> in the 2θ range from 10° to 80°. Raman scattering was AU10 performed on a Renishaw (In Via) spectrometer using a 532 nm laser source. Electrochemical measurements were performed by cyclic voltammetry (CV) using an IM6e potentiostat (Zahner-Elektrok, Germany) at 30 °C controlled by a water-bath thermostat. The three-electrode cell system consisted of a pre-treated glassy carbon working electrode (0.05 cm<sup>2</sup>), a platinum foil (1.0 cm<sup>2</sup>) and saturated calomel electrode were used as counter and reference electrodes. The CV was carried out in the potential range of -0.24 to 0.96 V at a scan rate of 50 mV/s in an ultra-high purity, N<sub>2</sub>-purged 0.5 M H<sub>2</sub>SO<sub>4</sub> electrolyte solution and in a 0.5 M H<sub>2</sub>SO<sub>4</sub> + 2.0 M CH<sub>3</sub>OH electrolyte solution. All chemicals were of analytical grade and used as received.

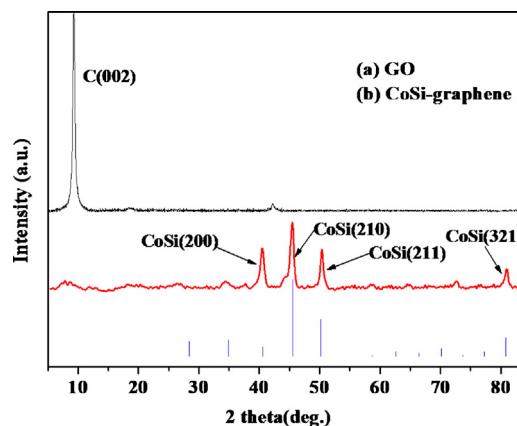


Fig. 1. shows the XRD patterns of (a) GO(b) CoSi-graphene.

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