



# Copper phthalocyanine functionalization of graphene nanosheets as support for platinum nanoparticles and their enhanced performance toward methanol oxidation



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## HIGHLIGHTS

- A new Pt nanoparticles electrocatalyst using copper phthalocyanine (TSCuPc) functionalized graphene as support is reported.
- Pt nanoparticles with high electrochemical active surface area are uniformly deposited on the functionalized graphene surface.
- The Pt/TSCuPc–graphene catalyst exhibits much higher electrocatalytic activity and stability for methanol oxidation.

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## ABSTRACT

We herein report a facile and effective ultrasonication method to non-covalently functionalize graphene with copper phthalocyanine-3,4',4''',4''''-tetrasulfonic acid tetrasodium salt (TSCuPc) as a promising catalyst support for Pt nanoparticles. With the assistance of TSCuPc, Pt nanoparticles are homogeneously deposited on the surface of graphene, and their dispersivity and electrochemical active surface area (ECSA) are obviously enhanced. Studies of cyclic voltammetry and chronoamperometry demonstrate that the as-prepared Pt/TSCuPc–graphene catalyst exhibits much higher electrocatalytic activity and stability than the Pt/graphene and commercial Pt/C catalysts for methanol oxidation. It is concluded that the strategy of TSCuPc-functionalized graphene with Pt catalysts will be potential in design and synthesis of the highly efficient electrocatalysts for DMFCs applications.

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## 1. Introduction

Direct methanol fuel cells (DMFCs) have received much attention because of its advantages of low operating temperature, easy transportation and storage of fuel, high energy conversion efficiency and low pollution emission [1–4]. Nevertheless, the commercialization of DMFCs still faces serious problems such as poor kinetics of methanol oxidation, methanol crossover through the membrane and CO poisoning of the catalysts [5,6]. One of the keys to overcoming these barriers is to develop the anodic electrocatalysts with high performance. At present, the most

commonly used electrocatalysts in DMFCs are Pt-based nanoparticles supported on carbon black (e.g., Vulcan XC72) [7,8]. In spite of their high surface area and good electrochemical performance, low Pt utilization and significantly high cost of the catalysts remain unresolved. In recent years, extensive efforts have been devoted to finding various new carbon supports such as carbon nanotubes [9,10], carbon nanofibers [11], ordered mesoporous carbon [6,12], carbon nanospheres [13] and graphene [14–20] to obtain the high dispersion and electrochemical active surface area (ECSA) of Pt nanoparticles. It is worth noting that, among those carbon materials, graphene with an atom-thick two-dimensional plane structure has attracted particular attention due to its theoretically large surface area, excellent electrical conductivity, good chemical, thermal, optical and electrochemical stabilities and low cost [21]. For instance, Dong et al. loaded Pt and PtRu nanoparticles

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on graphene sheets, which exhibited enhanced efficiency for both methanol and ethanol oxidation compared to the catalysts supported on Vulcan XC-72R carbon black [15]. Xin et al. prepared Pt/graphene catalyst with higher electrocatalytic activity and stability for methanol oxidation by the  $\text{NaBH}_4$  reduction route [17]. More recently, Yu et al. fabricated a novel  $\text{CeO}_2/\text{rGO}/\text{Pt}$  sandwich nanostructure through a facile hydrothermal approach, the electrochemical tests indicated that this structure exhibited higher methanol oxidation activity and stability than the Pt/rGO,  $\text{CeO}_2/\text{Pt}$  and Pt/C catalysts [20]. Unfortunately, pristine graphene is insoluble in organic solvents and susceptible to aggregation in aqueous solutions, which greatly hinders its practical applications in the preparation of graphene-based catalysts [21,22]. Therefore, it is necessary to further functionalize graphene sheets in order to improve their surface properties and dispersions in solvents.

The functionalization of graphene can be performed by covalent or non-covalent methods [23–26]. Covalent functionalization is commonly carried out by reacting acid-treated graphene containing hydroxyl ( $-\text{OH}$ ) and carboxyl ( $-\text{COOH}$ ) groups with functional molecules, which will have a significant effect on the electronic properties of graphene. Non-covalent functionalization is preferable for catalyst support applications, since it enables attachment of molecules through supermolecular interactions such as  $\pi$ – $\pi$  stacking, electrostatic interaction and hydrogen bonding, and thus preserves the intrinsic electronic and structural properties of graphene. Metal phthalocyanines (MPcs), the two-dimensional 18  $\pi$ -electron aromatic macrocycles with a metal atom located at the central cavity, are of great interest due to their excellent electronic properties and potential applications in some fields such as electrical devices, solar cells and biosensors [27–30]. Very recently, several research groups have explored MPcs functionalized graphene composites for the achievement of dispersed graphene and the cathode electrode materials of fuel cells [30–34]. Mensing et al. reported the electrochemical production of a stable aqueous dispersion of graphene–copper phthalocyanine hybrid material [32]. Zhang et al. prepared iron tetrasulfophthalocyanine functionalized graphene composites with enhanced activity for the oxygen reduction reaction (ORR) in a dual-chamber microbial fuel cell [33]. Zhang et al. also reported the synthesis of iron phthalocyanine and nitrogen-doped graphene composite, which exhibited superior ORR catalytic activity and excellent tolerance to methanol crossover [34]. However, to the best of our knowledge, MPcs functionalized graphene composites used as the anodic catalyst support of fuel cells have not yet been reported.

Herein, for the first time, we report a facile and effective ultrasonication approach to non-covalently functionalize graphene with copper phthalocyanine-3,4',4'',4'''-tetrasulfonic acid tetrasodium salt (TSCuPc) as a promising catalyst support for Pt nanoparticles. The prepared nanocomposites were characterized by UV–vis absorption spectroscopy, Raman spectroscopy, X-ray diffraction (XRD), thermogravimetric analysis (TGA), transmission electron microscopy (TEM) and energy dispersive X-ray (EDX) spectroscopy. The electrocatalytic activity and durability of the Pt/TSCuPc–

graphene catalyst were evaluated by cyclic voltammetry (CV) and chronoamperometry methods. Results demonstrate that the Pt/TSCuPc–graphene exhibits much higher electrocatalytic activity and stability than the Pt/graphene and commercial Pt/C catalysts for methanol oxidation. The present work provides a promising strategy to design and fabricate the highly efficient graphene-based electrocatalysts for DMFCs applications.

## 2. Experimental

### 2.1. Materials

Graphene sheets (99.95%) used there was prepared by direct current arc-discharge method as reported in our previous work [35]. 5 wt% Nafion solution and copper (II) phthalocyanine-3,4',4'',4'''-tetrasulfonic acid tetrasodium salt (TSCuPc) were purchased from Sigma–Aldrich. Hydrogen hexachloroplatinate (IV) hexahydrate ( $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ ), methanol and sulfuric acid were obtained from Sinopharm Chemical Reagent Co. Ltd (Shanghai, China), and commercial Pt/C catalyst (20% Pt loading) was supplied from Alfa Aesar. All the chemicals are of analytical grade and used as received without further purification. All aqueous solutions were prepared using triple-distilled water.

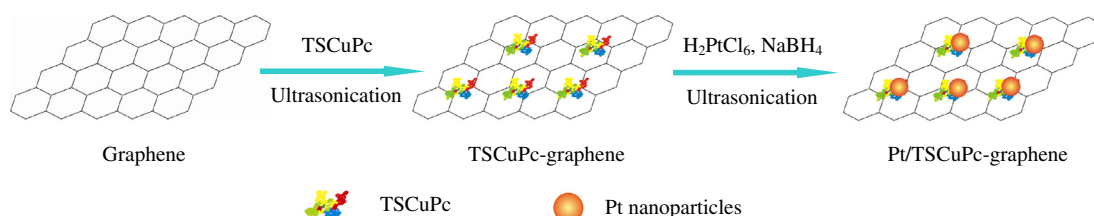
### 2.2. Preparation of Pt/TSCuPc–graphene catalyst

Scheme 1 briefly illustrates the preparation process of Pt/TSCuPc–graphene catalyst. 10 mg graphene and 25 mg TSCuPc were dispersed in 8 mL triple-distilled water by ultrasonic treatment for 6 h, and then the as-obtained suspension was allowed to stand overnight. Subsequently, 665  $\mu\text{L}$   $\text{H}_2\text{PtCl}_6$  solution (19 mM) was added into the suspension in 30 min with ultrasonication, and the pH value of system was adjusted to 10.5 by NaOH solution. An excess quantity of  $\text{NaBH}_4$  solution (10 mg  $\text{mL}^{-1}$ ) was then slowly added dropwise into the above solution under ultrasonication. After reaction for 6 h under ultrasonication, the resulting black solid product were collected by centrifugation, washed repeatedly with triple-distilled water and absolute ethanol several times to remove the ions possibly remaining in the final product, and then dried in vacuum at 40 °C for 24 h. For comparison, Pt nanoparticles supported on graphene (Pt/graphene) was prepared with the similar procedure as described above.

### 2.3. Physical characterization

#### 2.3.1. UV–vis absorption spectroscopy, Raman spectroscopy and thermogravimetric analysis (TGA)

UV–vis absorption spectra were recorded by a UV–vis spectrophotometer (Varian–Cary 100, USA). The samples were dissolved in triple-distilled water prior to the UV–vis spectroscopy measurements. Raman spectra were obtained by a confocal microscopic Raman spectrometer (Renishaw–InVia, UK), using an argon ion laser with a wavelength of 514.5 nm. Thermogravimetric analysis



**Scheme 1.** Schematic illustration of the preparation process of Pt/TSCuPc–graphene catalyst.

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