

Electrooxidation of Methanol on PANI-CeO₂@Pt Catalysts

Qun Xiang, Ruiwen Yan,* Guiqi Gao, and Shuang Wang^[a]

Polyaniline (PANI) and Pt were synthesized in sequence by in situ electrochemical deposition on CeO₂ surface to prepare PANI/CeO₂/Pt ternary composites (PANI-CeO₂@Pt composites). The electrocatalytic activity of PANI-CeO₂@Pt composite was measured to 226 mA·mg⁻¹, which was 1.7-, 2.3-, 20-fold as that of CeO₂@Pt, Pt/C, and PANI@Pt catalyst, respectively. The PANI-CeO₂@Pt catalyst displayed noticeably the highest activity

toward methanol oxidation after the 4000 s among the tested CeO₂@Pt, Pt/C, and PANI@Pt catalyst. In a CO-stripping experiment, PANI-CeO₂@Pt composites exhibited better CO tolerance. These results meant that highly dispersed Pt nanoparticles and the oxygen storage capacity of PANI-CeO₂@Pt contributed to admirable catalytic activities for methanol oxidation reaction (MOR).

Introduction

The growing demand for energy with society progress is becoming more and more urgent. There are shortage and environmental pollution problems to use extensively fossil fuels. The evolution of environment-friendly energy with high efficiency is an important task. Fuel cells have the advantages of low cost, environmentally friendly, easy transportation and storage. Their applications are more and more extensive, especially in portable electronic equipment.^[1–3]

Fuel cells are diffusely applied own to their high usage efficiency and energy density. The Pt catalyst has been extensively researched as an anode material in direct methanol fuel cell (DMFC) and direct ethanol fuel cell (DEFC).^[4–11] But the high cost and low storage have severely limited the development of platinum-based catalysts. Recently, platinum alloys containing transition metals (nickel, copper, cobalt, etc.) have been attracted widespread attention. The alloy structure can significantly decrease Pt content and enhance catalytic performance.^[12,13] However, the transition metal is easily soluble in an acidic solution, and the stability of the alloy for MOR is poor. The platinum/rare earth element catalysts displayed effectively catalytic activity and stabilization.^[14–20] Among rare earth elements, cerium is the most studied in cryogenic fuel cells.^[21–23]

Studies of Pt/metal oxide (TiO₂, CeO₂, and SnO₂) composites have confirmed that the hybrid nanomaterials can exhibit higher catalytic activity and stability during methanol oxidation.^[24–27] Cerium dioxide and cerium dioxide-based nanomaterials can improve catalytic properties and stability by introduction of active metals on their surface.^[28] And the introduction of CeO₂ can efficiently oxidize CO_{ad}.^[29] The fluorite-structure of CeO₂ displayed abundant vacancies of oxygen and lower oxidation potentials of Ce³⁺ to Ce⁴⁺.^[30–32] Therefore, CeO₂ have oxygen storage capacity, defective structure, and a tendency to interact with various materials.^[33] Pt/CeO₂ composites are widely used in CO oxidation.^[34–36] The high dispersion

of platinum on cerium-based supporters is a key to directly affect the performance of catalyst. The interaction between Pt and CeO₂ can inhibit the growth of Pt.^[37,38] Polyaniline (PANI) has been commercially used for its characteristic of outstanding conductivity. The N atoms of polyaniline can effectively bind to metal atoms, allowing the catalyst to maintain high stability.^[39]

Pt/CeO₂ composites have been widely used in CO oxidation, but the high dispersion of platinum on cerium-based supporters is still a technical challenge. Moreover, the lower electrical conductivity of CeO₂ also affects the performance of the Pt/CeO₂ composites. PANI has been used as a single carrier material, but PANI would expand and shrink during oxidation-reduction process,^[40] which limits its applications. PANI-CeO₂@Pt composites can make full use of the excellent conductivity of PANI, high oxygen storage capacity of CeO₂, high dispersion of platinum, and overcome the shortcomings of PANI and CeO₂. In this paper, PANI-CeO₂@Pt composites were synthesized in sequence by in situ electrochemical deposition scheme. Ultrafine Pt nanoparticles were evenly dispersed on PANI-CeO₂ composites. PANI-CeO₂@Pt catalysts exhibited satisfactory stabilization and activity for MOR.

Experiments

Experimental materials

CeO₂ powder (Aladdin Holdings Group Co., Ltd. The size of CeO₂ was with 200~250 nm), sulfuric acid (AR), ultrapure water; aniline (AR), CH₃OH (anhydrous, AR), Nafion solution (5%) (Shanghai Hesen Electric Co., Ltd.), Pt/C (Sigma Aldrich, 20 wt.% Pt), and K₂PtCl₆ were equipped.

Experimental equipment

The glassy carbon working electrode was ground with alumina powder (size of 300 nm and 50 nm, respectively). The working electrode after active scanning in 0.5 M sulfuric acid solution was used. The reference electrode was saturated calomel electrode (SCE). The platinum wire was used as the counter electrode. All experiments were performed in an argon atmosphere.

[a] Q. Xiang, Dr. R. Yan, Dr. G. Gao, S. Wang
Institute of Physical Science and Information Technology,
Anhui University, Hefei, Anhui, 230601, China
E-mail: yrw@ahu.edu.cn

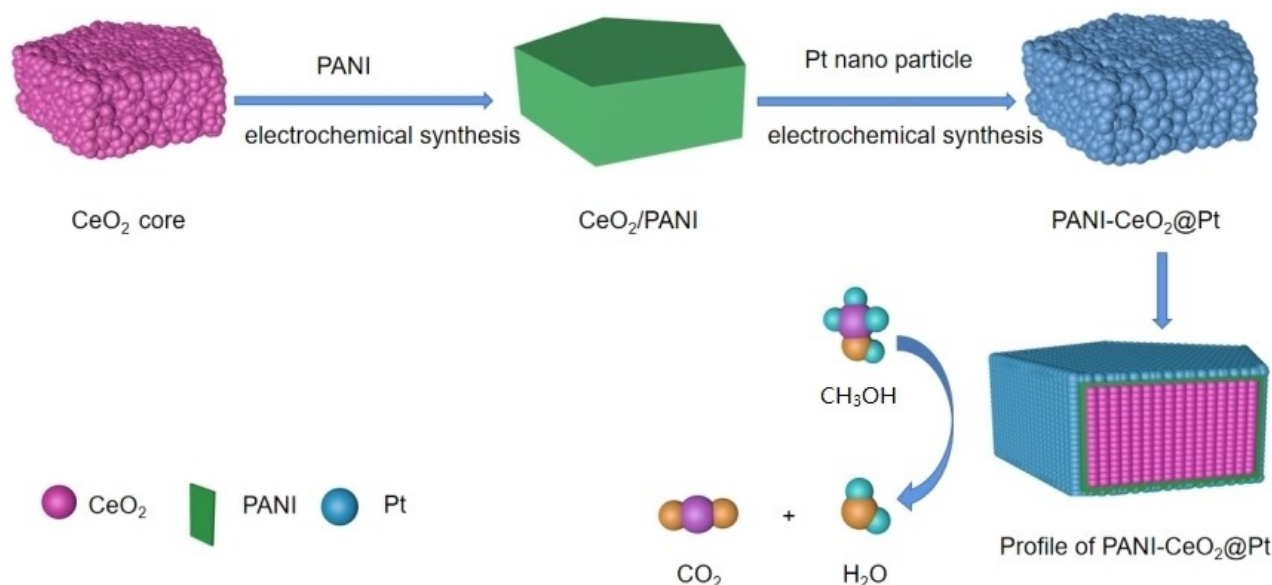


Figure 1. Synthesis schematic of PANI-CeO₂@Pt composites.

The morphology of PANI-CeO₂@Pt composites was characterized by Hitachi S8230 SEM, Bruker VERTEX80 spectrometer, JEOL 2100TEM. The atomic ratio of catalyst was mensurated by iCAPQ ICP-MS (Thermo Scientific). The PANI-CeO₂@Pt composites were digested by aqua regia. The content of platinum in the digested solution was detected by ICP-MS. The bond energy of elements was analyzed by 250Xi XPS (Thermo Scientific). Etching ion energy was 2000 eV. Etching area was 2 mm × 2 mm. Etching time was 100 s. The catalytic activity of PANI-CeO₂@Pt composites was explored by electrochemical workstation (660E, Chenhua Instrument Co., Ltd.).

Material preparation

10 mg CeO₂, 0.2 mL isopropanol, and 5 μL Nafion were thoroughly mixed to obtain a homogeneous solution for 1 h in an ultrasonic bath. 3 μL slurry was covered on the surface of glassy carbon electrode (GCE). The GCE was dried at 60 °C for two hours. PANI was electrodeposited on the CeO₂ electrode by CV in 0.5 M H₂SO₄ + 0.2 M aniline solution. The potential was −0.2–0.9 V. The sweep speed was 50 mV·s^{−1}. Then, Pt nanoparticles were synthesized on the CeO₂-PANI electrode to prepare the PANI-CeO₂@Pt catalyst by CV in K₂PtCl₆ (10 mm) and H₂SO₄ (0.005 M) solution. The potential was 0.4–0.7 V. The sweep speed was 50 mV·s^{−1}.

1 mg commercial Pt/C catalyst, 0.2 mL isopropanol, and 5 μL Nafion were thoroughly mixed in an ultrasonic bath for 1 h. 3 μL slurry was covered on the surface of GCE. The GCE was dried at 60 °C for two hours.

The CV curves for estimating the electrochemical active surface area (ECSA) were recorded in 0.5 M H₂SO₄ solution. The potential was −0.25–1.0 V. The sweep speed was 50 mV·s^{−1}.

Results and Discussions

The synthesis schematic of PANI-CeO₂@Pt composites was shown in Figure 1. Firstly, PANI was prepared on the surface of CeO₂. Ultrafine nanoparticles of Pt were evenly dispersed on CeO₂-PANI to prepare the PANI-CeO₂@Pt catalysts by CV. The CeO₂-PANI acted as core and the Pt nanoparticles acted as a shell was finally synthesized. The performance of PANI-CeO₂@Pt catalysts for MOR was investigated.

The morphology of CeO₂ was studied by TEM. The size of CeO₂ particles (in Figure 2) was about 220 nm.

Figure 3a showed the CV diagram of depositing 5 laps of PANI, and three groups of significant redox peaks can be seen.^[41] The first pair of redox peaks (−0.1–0.2 V) corresponded to oxidation the secondary amines of PANI. The second pair of redox peaks (0.3–0.5 V) corresponded to oxidation of terminal primary amines and terminal hydroxyl groups. The third pair of

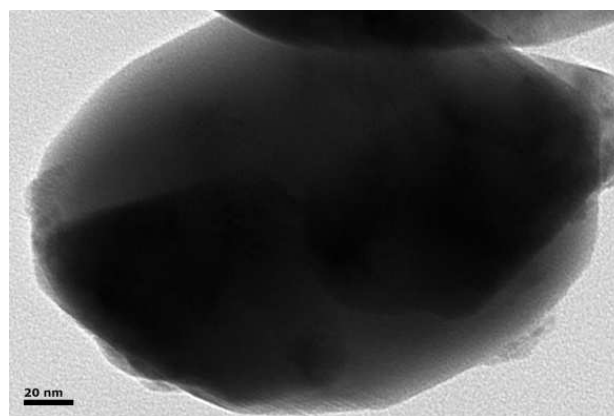


Figure 2. The TEM images of CeO₂.

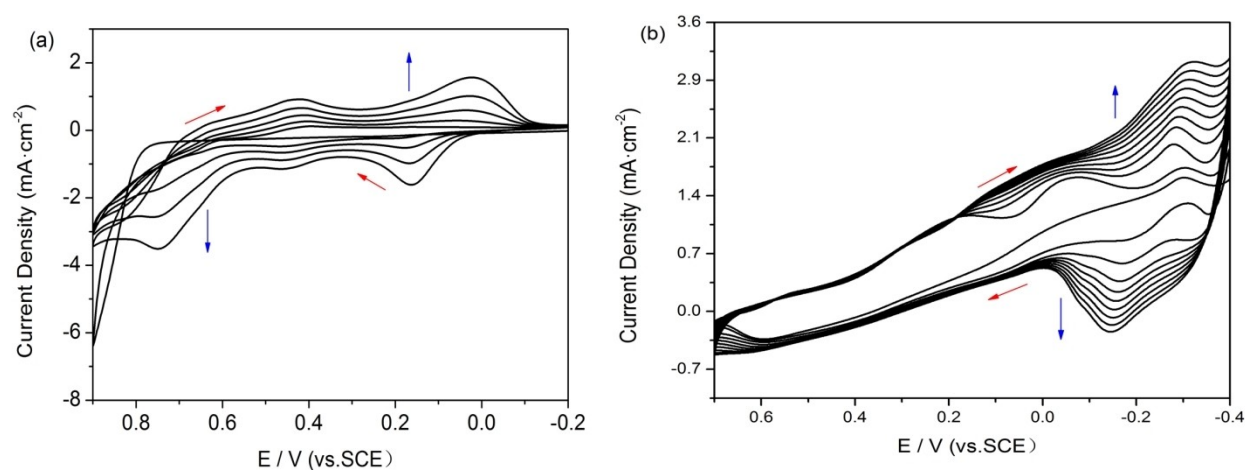


Figure 3. (a) CV curve of electrodeposition PANI, (b) CV curve of electrodeposition Pt nanoparticles.

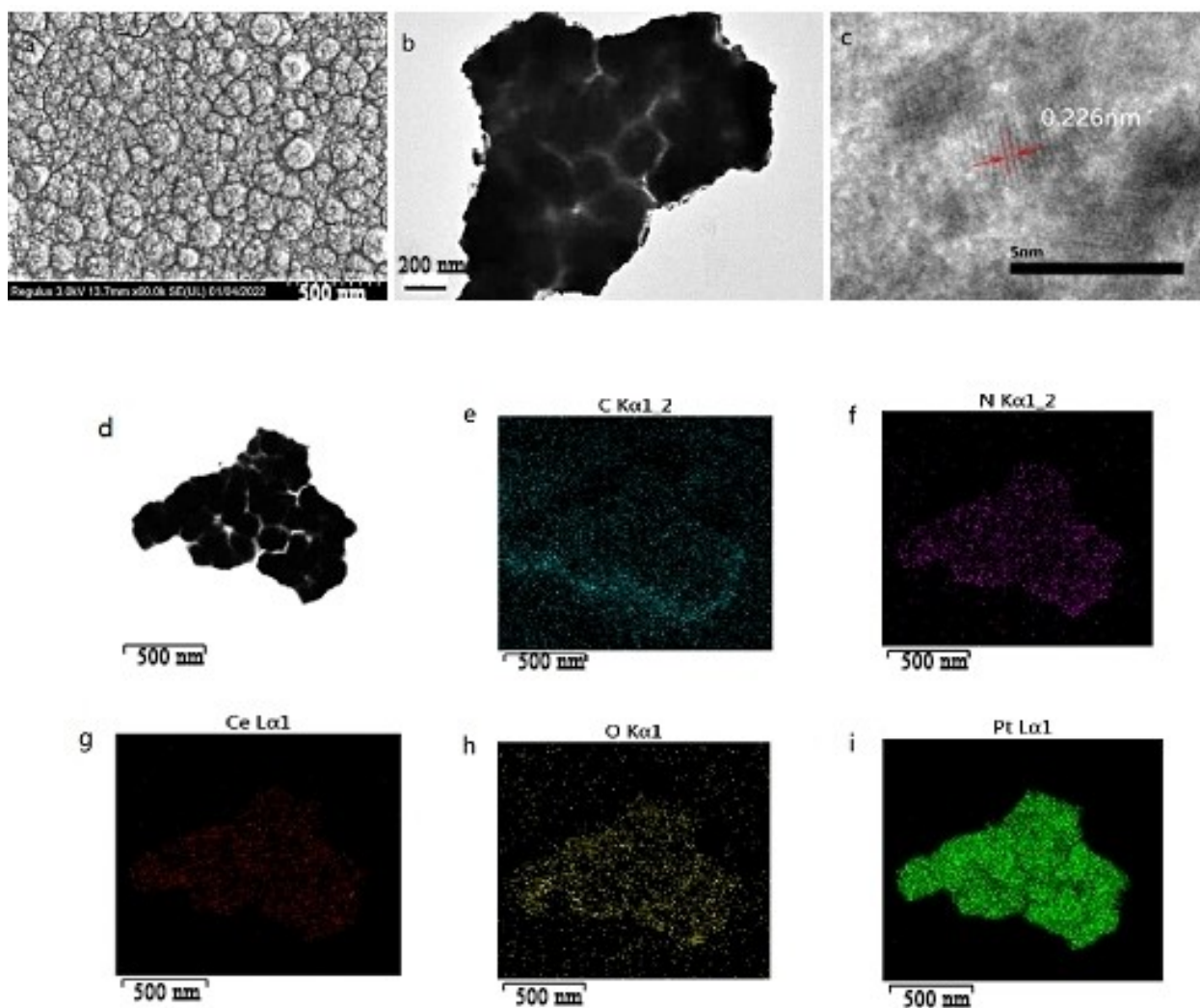


Figure 4. (a) SEM, (b, d) TEM, (c) HRTEM images, (e) C element, (f) N element, (g) Ce element, (h) O element, and (i) Pt element distribution of Pt–Ce/PANI composites.

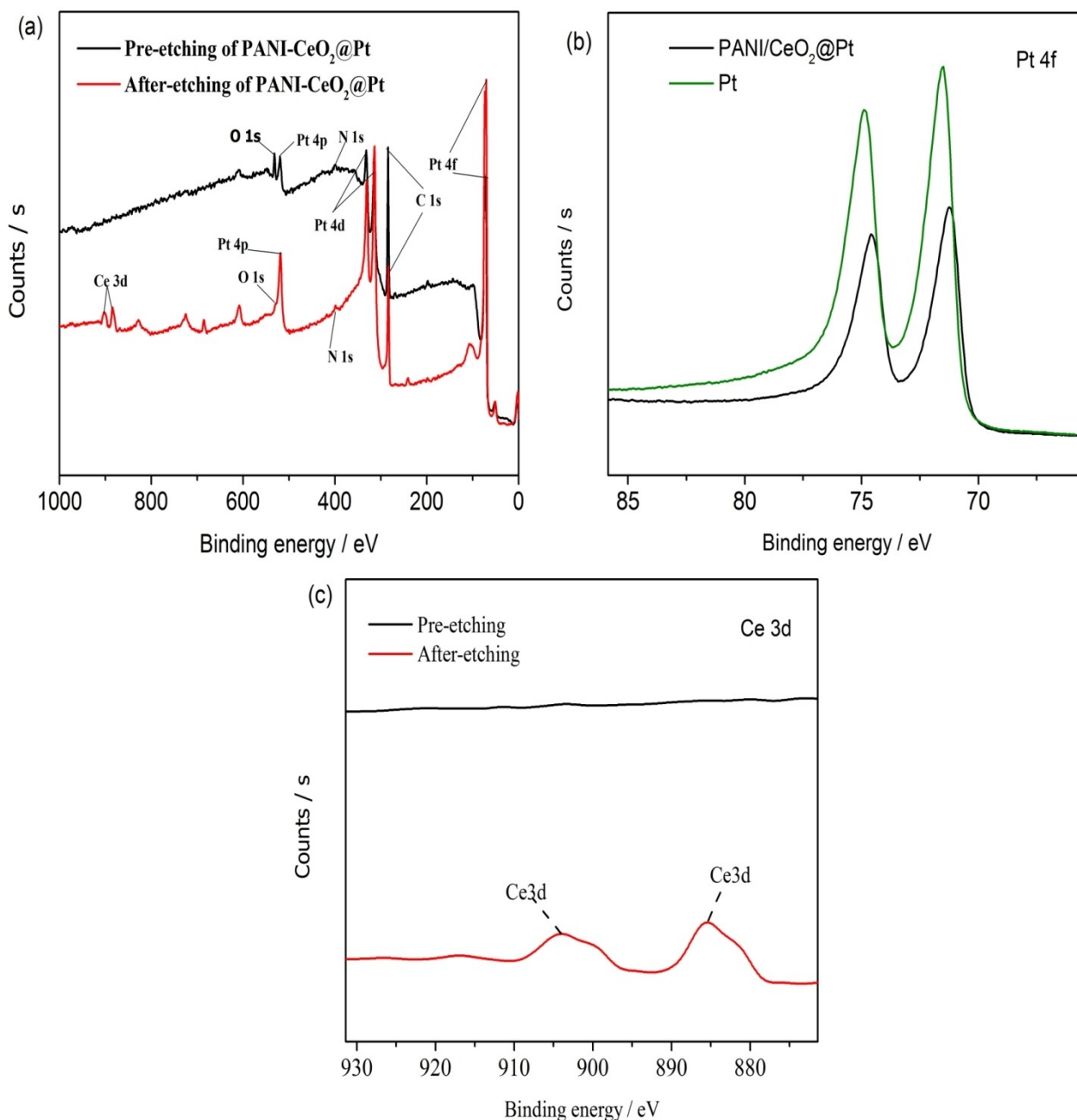


Figure 5. (a) Major elements, (b) Pt 4f, (c) Ce 3d XPS curve of PANI-CeO₂@Pt composites

redox peaks (0.55–0.85 V) corresponded to oxidation the polaronic PANI to the bipolaronic PANI. With the increased of the amount of PANI, the intensity of oxidation peak increased. As the number of cycle increased, the current of redox gradually enhanced, proving that PANI had been successfully polymerized on the surface of CeO₂. In Figure 3b, the deposition peak (about –0.3 V), the oxidation peak of hydrogen (about 0.15 V) on Pt as the number of cycles increased gradually, which was also confirmed Pt nanoparticles had been successfully electro-deposited on PANI-CeO₂ composites.

The morphology of PANI-CeO₂@Pt composites was studied by TEM and SEM. The size of PANI-CeO₂@Pt particles (in

Figure 4a) was about 200–300 nm. The TEM images (in Figure 4b and 4d) were consistent with the above results. Pt particles (size of 3 nm) were evenly coated on PANI-CeO₂ composites (in Figure 4c). The lattice stripe spacing of platinum was about 0.226 nm. This lattice stripe spacing is close to the (111) crystal face of cubic Pt (standard card of No. 4-802).

The distribution of Pt, C, Ce, N, O in PANI-CeO₂@Pt composites were determined by elemental mapping analysis. The selected representative area was shown in Figure 4d. The elemental distribution of C (in Figure 4e), N (in Figure 4f), Ce (in Figure 4g), O (in Figure 4h), and Pt (in Figure 4i) were fully indicated that the PANI was well coated on CeO₂. As shown in

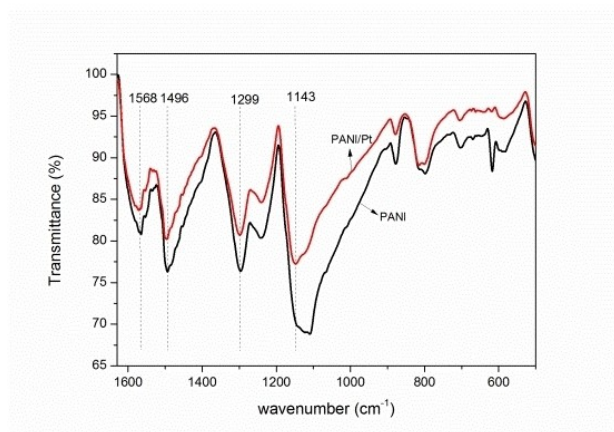


Figure 6. FTIR spectra of PANI and PANI/Pt.

Figure 4f, the N element of PANI was evenly distributed on the surface of cerium dioxide. The N atoms provided the abundant initial nucleation sites for the formation of Pt nanoparticles. Pt nanoparticles (in Figure 4i) were uniform deposited on PANI-CeO₂ composites. Overall, these results confirmed the successful preparation of PANI-CeO₂@Pt composites.

XPS curve was mainly employed to analyze the chemical properties and bond energy of elements on the surface of the material. The XPS spectra (in Figure 5a) indicated the existence of N, C, O, and Pt in the composite material, which confirmed

the existence of Pt and PANI in the composite. Because CeO₂ was at the core of the material, the Ce element was not detected. After etching for 100 s, XPS spectra of PANI-CeO₂@Pt composites indicated the existence of Pt, C, Ce, N, O. The Ce 3d XPS spectra (in Figure 5c) were further confirmed. The free electron pair of N atoms in PANI can interact with the space orbital of Pt atoms, which would lead to an increase in electron density of d orbital in Pt atoms. The increased electron density of the d orbital in Pt atoms would weaken the CO_{ad} binding energy.^[42] The Pt 4f peak of PANI-CeO₂@Pt composite had a negative shift of 0.3 eV compared with Pt in Figure 5b. The negative Pt 4f shift indicated that the CO_{ad} binding energy was weak, which was caused by the ligand effect between CeO₂, PANI, and Pt.

As shown in FTIR spectra of PANI and PANI/Pt (Figure 6), the main infrared absorption peak were 1568, 1498, 1299, 1143 cm⁻¹, which corresponded to the C=C stretching vibration of quinoid rings, C=C stretching vibration of benzenoid rings, C-N stretching vibration, and C-H stretching vibration, respectively. The ratio of the C=C stretching vibration peak area of quinoid rings to benzenoid rings were 0.889 in PANI and 0.948 in PANI/Pt. The free electron pair of N atoms in PANI interacted with the space orbital of Pt atoms, which would lead to an increase in the quinonoid unit structure of PANI/Pt.

Figure 7a showed that there was a significant redox peak of PANI-CeO₂@Pt composite for MOR. But there was no oxidation peak in the CV diagram of CeO₂, which indicated that pure CeO₂ materials had low catalytic activity for MOR. The electro-

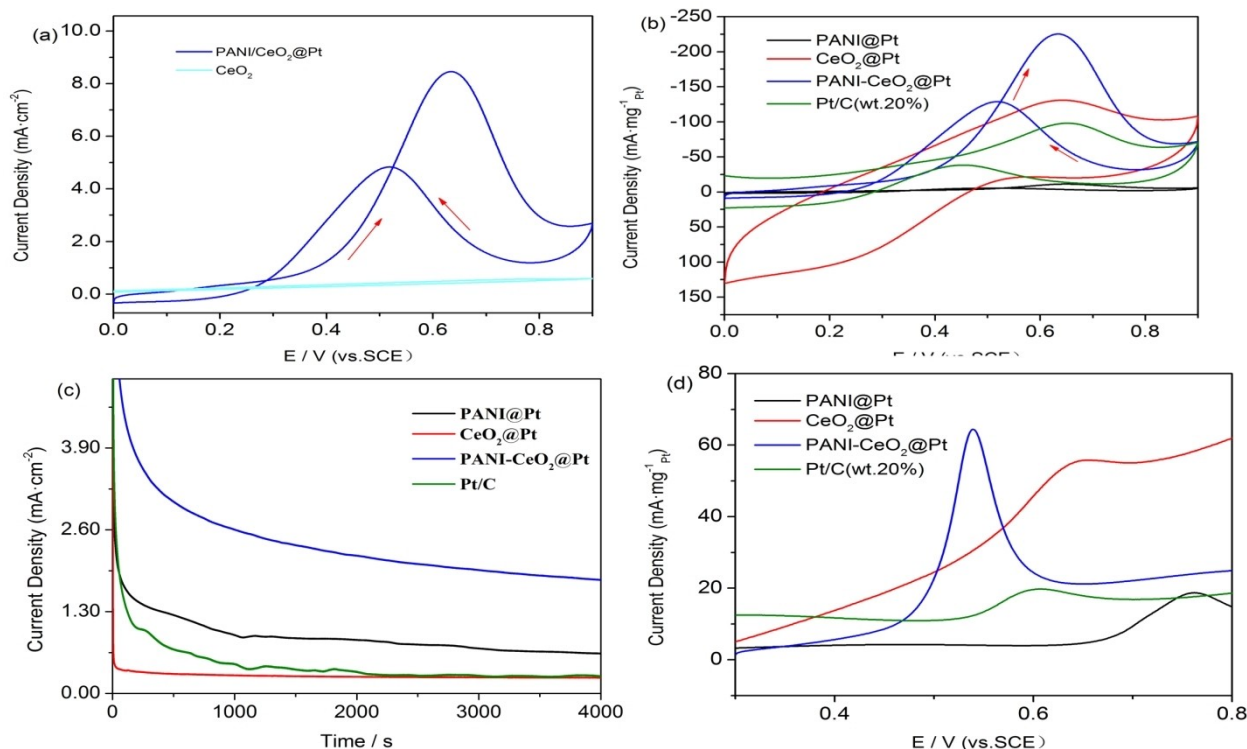


Figure 7. (a) CV curves of PANI-CeO₂@Pt composites and CeO₂, (b) CV curves and (c) CA curves of PANI@Pt, CeO₂@Pt, PANI-CeO₂@Pt, Pt/C in 1 M CH₃OH + 0.5 M H₂SO₄ solution, (d) LSV curve in 0.5 M H₂SO₄ saturated CO solution.

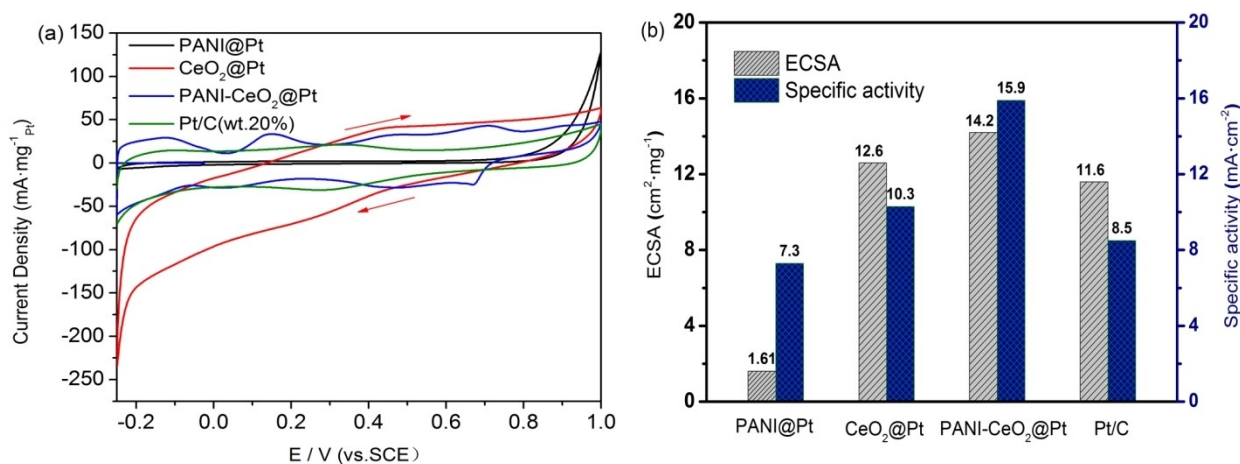


Figure 8. (a) CV curves, (b) ECSA and specific activity of PANI-CeO₂@Pt, Pt/C, PANI@Pt, CeO₂@Pt.

catalytic performance of PANI@Pt, CeO₂@Pt, Pt/C, and PANI-CeO₂@Pt composites for MOR were shown in Figure 7b. The onset potential and peak potential of PANI-CeO₂@Pt catalysts for MOR was 0.34 and 0.63 V, respectively, which was lower than those of the tested PANI@Pt, CeO₂@Pt, Pt/C, Pt₃-(CeO_x)₁/C,^[38] Pt-CeO₂-rods catalyst,^[39] The current density of the PANI-CeO₂@Pt composite (in Table 1) was 226 mA·mg⁻¹, which was 20-, 2.3-, 1.7- and 4.3-fold as that of the tested PANI@Pt, Pt/C, CeO₂@Pt and Pt-MOX/C (M=Ce₂Zr₁)^[41] respectively. The CA curve (in Figure 7c) was used to evaluate the durability of the catalyst over the 4000 s. The PANI-CeO₂@Pt catalyst displayed noticeably the highest activity toward methanol oxidation after the 4000 s among above tested catalysts. The CO_{ad} tolerance was investigated by LSV of CO-stripping (Figure 7d). The oxidation peak potential of CO_{ad} on PANI-CeO₂@Pt catalyst was lowest among the tested PANI@Pt, Pt/C, and CeO₂@Pt catalysts. The peak density in the CO-stripping experiment on PANI-CeO₂@Pt catalyst was highest among above tested catalysts. This result indicated that PANI-CeO₂@Pt catalyst displayed preferable tolerance to CO_{ad}.

The ECSA and specific activity were key indicators of MOR. The actual surface of Pt-based catalysts could be calculated from the hydrogen absorption charge of CV (Figure 8a).^[46] The specific activity was calculated by formula (1):

$$\text{Specific activity} = \text{Mass activity} \div \text{ECSA} \quad (1)$$

The ECSA were measured to 14.2, 1.61, 12.6, 11.6 cm²·mg⁻¹ of the tested PANI-CeO₂@Pt, PANI@Pt, CeO₂@Pt, and Pt/C catalysts, respectively. The specific activity (Figure 8b) were measured to 15.9, 7.3, 10.3, 8.5 mA·cm⁻² of the tested PANI-CeO₂@Pt, PANI@Pt, CeO₂@Pt, and Pt/C catalysts, respectively. The specific activity of PANI-CeO₂@Pt was 1.9-fold as that of the tested Pt/C catalysts, indicating that PANI-CeO₂@Pt had a higher activity. These results meant that the highly dispersed Pt nanoparticles and the oxygen storage capacity of CeO₂ in PANI-CeO₂@Pt contributed to the admirable catalytic activities for MOR.

Conclusions

The PANI-CeO₂@Pt composites with core-shell structure have been successfully synthesized. Platinum nanoparticles were anchored on the surface of the PANI-CeO₂ materials. The structure of the composite was explored by SEM, XPS, and HRTEM. The lower potential and higher current density for MOR among the tested PANI@Pt, Pt/C, and CeO₂@Pt catalysts showed that PANI-CeO₂@Pt catalyst displayed excellent catalytic performance. The current density of the PANI-CeO₂@Pt composite was 20-, 2.3-, and 1.7-fold as that of PANI@Pt, Pt/C, and CeO₂@Pt catalyst, respectively. The low peak potential and high current density in the CO-stripping experiment further verified that PANI-CeO₂@Pt composites had better CO tolerance.

Acknowledgements

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Conflict of Interest

The authors declare no conflict of interest.

Catalytic materials	Onset potential/ V	Peak potential/ V	Mass activity/ (mA·mg ⁻¹)
PANI@Pt	0.51	0.65	11.7
CeO ₂ @Pt	0.36	0.64	130
PANI-CeO ₂ @Pt	0.34	0.63	226
Pt/C	0.42	0.65	98.5
Pt ₃ -(CeO _x) ₁ /C ^[43]	0.40	0.70	/
Pt-CeO ₂ -rods ^[44]	0.38	0.65	/
Pt-MOX/C (M=Ce ₂ Zr ₁) ^[45]	/	0.655	52.2

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords: Methanol oxidation · PANI-CeO₂@Pt composites · Polyaniline

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