Electrochemical-Method-Induced Strong Metal-Support Interaction in Pt-CNT@SnO₂ for CO-Tolerant Hydrogen Oxidation Reaction

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The classical strong metal-support interaction (SMSI), which has been extensively studied in supported metal catalysts, refers to the encapsulation effect of the support material on metal particles under specific conditions. In 1978, Tauster et al. discovered that the adsorption behavior of CO on the TiO₂ supported Pt nanoparticles (NPs) catalyst was significantly changed after annealing in H₂, and named this phenomenon as the “strong metal-support interaction”. In recent years, with the advancement of characterization techniques, it has been gradually recognized that these changes in catalytic properties should be attributed to the evolution of catalyst structure.  

During the reductive thermal treatment conditions, the support materials would migrate and form a thin amorphous encapsulation layer on the metal NPs. This encapsulation structure modifies the catalytic site of the metal NPs, and could impart unique catalytic properties of the catalysts, especially in the adsorption of reactants and reaction intermediates, which are related to the electronic effect of synergistic effect. The most commonly used method to induce SMSI is thermal reduction. However, the harsh conditions of thermal reduction method (usually above 773 K) usually induce additional structural evolution of the supported catalysts, such as metal NPs growth/ripening and alloying with the elements of supports. Some efforts have been devoted to induce SMSI under mild conditions. Inducing SMSI typically requires two processes: creating defects of supports and facilitating atomic migration. Dai et al. utilized ultraviolet (UV) radiation to stimulate the photocarrier in TiO₂ and lead to the formation of Ti²⁺ species and oxygen vacancies, thereby achieving encapsulation of Pt NPs. Moreover, high-speed particle collisions and shock waves during ultrasound treatment could cause surface damage and oxygen vacancies in TiO₂, also resulting in SMSI. Electrochemical method is also a gentle and controllable way to induce SMSI. Strasser et al. proposed the electrochemical-method-induced SMSI in Pt-RuTiO₃ system and the encapsulation of Pt by oxides was demonstrated. The encapsulation structure suppressed the catalytic activity towards oxygen reduction reaction (ORR) as it impeded the O₂ transport to the Pt surface. Although the electrochemical-method-induced SMSI exhibits unique electrochemical behavior, the mechanism still needs further in-depth exploration. Additionally, since the thin encapsulation layer on the metal NPs does not have a blocking effect on small molecules such as H₂, the SMSI-derived catalysts hold promise for hydrogen electrocatalysis, which has not been studied yet. Herein, we demonstrate an electrochemical method to induce the SMSI on core@shell structured CNT@SnO₂ supported Pt NPs (Pt-CNT@SnO₂) and the encapsulated Pt NPs (E-Pt-...
CNT@SnO\textsubscript{2} exhibits excellent hydrogen oxidation reaction (HOR) activity and CO-tolerance. After a certain CV scanning treatment (0.05-1.2 V vs. RHE, 200 cycles), amorphous SnO\textsubscript{2} encapsulation was observed on the surface of Pt NPs while the adsorption of CO on Pt surface was reduced, which proved the occurrence of SMSI. The obtained E-Pt-CNT@SnO\textsubscript{2} catalyst exhibits an excellent exchange current density of 1.55 A·mg\textsubscript{Pt}\textsuperscript{-1} for HOR, higher than that of the commercial Pt/C (1.24 A·mg\textsubscript{Pt}\textsuperscript{-1}) and Pt-CNT@SnO\textsubscript{2} (1.22 A·mg\textsubscript{Pt}\textsuperscript{-1}). Impressively, the elective permeability (penetrating H\textsubscript{2} but blocking CO and O\textsubscript{2}) of SnO\textsubscript{2} encapsulation layer make E-Pt-CNT@SnO\textsubscript{2} has great CO tolerance and can still maintain an 85% of current density in the presence of 10000 ppm CO after 2000 s. Theoretical calculations and in-situ Raman spectra results reveal that the supported Pt NPs could extract electrons from SnO\textsubscript{2} supports and reduce the bond order of Sn-O bonds, thereby weakening the Sn-O bond strength and promoting the migration of SnO\textsubscript{2} to form encapsulation.

**Experimental Section**

**Preparation of catalysts**

19 Synthesis of CNT@SnO\textsubscript{2}: 10 mg CNTs were dissolved in 40 mL hydrochloric acid with pH = 1 under ultrasonic dispersion for half an hour. Then 1 g of anhydrous SnCl\textsubscript{4} was added and sealed with polyethylene film. The reaction was performed at 60 °C for 3 h, and then centrifuged with deionized water and ethanol. The CNT@SnO\textsubscript{2} was obtained after freeze-drying.

20 Synthesis of E-Pt-CNT@SnO\textsubscript{2}: 16 mg as-prepared CNT@SnO\textsubscript{2}-T was dispersed in a mixture of ethylene glycol and water, and 1 mL of 10 mg·mL\textsuperscript{-1} chloroplatinic acid solution was added to the mixture. Finally, the ratio of ethylene glycol to water was controlled to 3:1. The mixture was stirred and reflux at 130 °C for 1 h. The final catalyst Pt-CNT@SnO\textsubscript{2} was obtained by centrifugation and freeze drying and the loading of Pt is 9.78 wt.%. Then the catalyst was loaded on carbon glass electrode following by cycling the potential between 0.05 and 1.05 V\textsubscript{RHE} at a scan rate of 200 mV·s\textsuperscript{-1} in N\textsubscript{2}-saturated 0.1 M HClO\textsubscript{4} to finally obtain E-Pt-CNT@SnO\textsubscript{2}.

**Electrochemical Measurements**

38 Electrochemical measurements were performed with 3-electrode system on CHI760e electrochemical workstation (Shanghai Chenhua Instrument Corporation, China). Glassy carbon rotating disk electrode was used as a working electrode (5 mm in diameter), Ag/AgCl (saturated KCl) as a reference electrode and graphite rod as a counter electrode. All potentials were experimentally converted to values with reference to a reversible hydrogen electrode (vs. RHE).

39 Pt-C, Pt-CNT@SnO\textsubscript{2} were dispersed in a mixture containing water, isopropanol and Naflon (5%) (v/v/v = 1:1:0.1) to form a 1 mg·mL\textsuperscript{-1} ink. Ink was cast on the glassy carbon and dried under ambient condition. The final loading of the Pt was kept at about 10 μgPt·cm\textsuperscript{-2} (determined by ICP-MS).

The CV measurements were performed in N\textsubscript{2}-saturated 0.1 M HClO\textsubscript{4} solutions at a scan rate of 50 mV·s\textsuperscript{-1}. The HOR polarization curves were measured in H\textsubscript{2}-saturated 0.1 M HClO\textsubscript{4} using a rotating disk electrode (RDE) at a rotation rate of 400 - 2500 rpm and a sweep rate of 1 mV·s\textsuperscript{-1}.

For CO stripping measurements, pure CO gas at an ambient pressure was bubbled into 0.1 M HClO\textsubscript{4} for 30 min while holding the potential at 0.1 V\textsubscript{RHE}. After the electrolyte was purged with Ar gas for 30 min to completely remove residual CO molecules in the electrolyte, CO-stripping curves were obtained in Ar-saturated electrolyte with a scan rate of 20 mV·s\textsuperscript{-1} at room temperature and in the potential range of 0.05 - 1.2 V\textsubscript{RHE}. The electrochemical surface areas (ECSA) was calculated by integrating the currents in the underpotential deposition region of hydrogen and CO oxidation peak region, assuming a monolayer H\textsubscript{2} charge of 210 μC·cm\textsuperscript{-2} and a monolayer CO charge of 420 μC·cm\textsuperscript{-2}.

Kinetic current density (j\textsubscript{k}) could be deduced from the Koutecky-Levich equation:

\[ \frac{1}{j_k} = \frac{1}{j_l} + \frac{1}{j} = \frac{1}{j_l} + \frac{1}{B \omega^{1/2} \Gamma} \]  \hspace{1cm} (1)

where \( j, B, \omega \) are the measured current density, the Levich constant, the solubility of H\textsubscript{2} (7.33×10\textsuperscript{-4} mol·L\textsuperscript{-1}), and the speed of the rotating, respectively. Exchange current density (j\textsubscript{0}) could be extracted from the Butler-Volmer equation:

\[ j_k = j_0 \left[ e^{\frac{B \omega^{1/2} \Gamma}{RT}} - e^{-\frac{B \omega^{1/2} \Gamma}{RT}} \right] \]  \hspace{1cm} (2)

j\textsubscript{0} could also be obtained from the approximate Butler-Volmer equation:

\[ j = j_0 \frac{\eta F}{R T} \]  \hspace{1cm} (3)

where \( \alpha, \eta, R, T, F \) represent the transfer coefficient, the overpotential, the universal gas constant (8.314 J·mol\textsuperscript{-1}·K\textsuperscript{-1}), the temperature in Kelvin (298 K) and the Faraday constant, respectively.

**Physicochemical Characterizations**

TEM images were taken from a FEI Tecnai G2 20 with an operation voltage of 200 kV. HRTEM images were taken from a FEI Tecnai G2 F30 with an operation voltage of 300 kV. The HAADF-STEM characterization was conducted on a JEOL JEMARM200F STEM/TEM with a guaranteed resolution of 0.08 nm. XRD were collected from Rigaku MiniFlex 600 diffractometer with a Cu radiation source (\( \lambda = 0.15406 \) nm). XPS spectra were collected from AXIS-ULTRA DLD-600W. ICP-MS result was carried out from ELAN DRC-e. EPR spectra were acquired on a Bruker EMXplus spectrometer. In situ Raman measurements were performed on Renishaw invia with 532 nm excitation wavelength and a 50× microscope objective. Raman frequency was calibrated by a Si wafer during each experiment. In situ electrochemical Raman experiments were employed in a Raman cell (Gaoss Union) and potentiostat (CHI 760e) was used to control the potential.

**First Principles Calculations**

All the first principles calculations are performed with density-functional theory (DFT) implemented in Vienna ab initio
simulation package (VASP)\cite{26} using the projector augmented-wave method\cite{27}. The valence electron wave functions are expanded on the plane-wave basis sets with a kinetic energy cutoff of 400 eV. The electronic exchange-correlation functional is in the Perdew-Burke-Ernzerhof (PBE) form\cite{28} with generalized gradient approximations. Based on the convergence test, the K-points sampling in first Brillouin zone employ Monkhorst-Pack scheme\cite{29} with a $1 \times 1 \times 1$ mesh. The SnO$_2$ slab model was constructed based on the SnO$_2$(101) surface model in a $4 \times 2$ plane supercell. The adjacent slabs were separated by a 15 Å vacuum in the normal direction. The COHP analysis was performed by using the LOBSTER software.\cite{30}

**Results and Discussion**

**Structural analysis**

The schematic illustration of catalyst preparation process is shown in Figure 1a. The SnO$_2$ coated CNTs were prepared by a precipitation method that the Sn$^{2+}$ precursor nucleated and oxidized into SnO$_2$ at the carbonyl group of CNTs. The obtained CNT@SnO$_2$ presents a cable structure, and the CNT is effectively sealed by an external SnO$_2$ layer (Figure 1b and Supporting Information Figure S1). Then, Pt NPs were supported on the CNT@SnO$_2$ by a glycol reduction method and named as Pt-CNT@SnO$_2$. The average size of Pt NPs in Figure 1c and Supporting Information Figure S2 is $3.18 \pm 0.62$ nm. Finally, CV scanning on the Pt-CNT@SnO$_2$ with the potential range of 0.05-1.2 V vs. RHE was executed to induce the SMSI, and the final catalyst was obtained after 200 cycles (denoted as E-Pt-CNT@SnO$_2$). As shown in Figure 1d and Supporting Information Figure S3, the overall structure and the average particle size of Pt NPs of E-Pt-CNT@SnO$_2$ have no obvious change after the electrochemical treatment. In addition, X-ray diffraction (XRD) patterns of the catalysts are shown in Figure 1e and the peaks located at 26.6°, 33.9°, and 51.8° corresponds to the rutile SnO$_2$ (space group P42/mnm, JCPDS PDF 41-1445), while the peaks located at 39.8°, and 46.2° corresponds to the fcc Pt (space group Fm-3m, JCPDS PDF 04-0802). The particles size can be calculated by Scherrer formula and the grain sizes of SnO$_2$ and Pt are ~4.2 nm and ~3.6 nm, respectively, which is consistent with the result of TEM.
Figure 1. (a) Schematic illustration of the synthetic route to E-Pt-CNT@SnO₂. HRTEM image of the (b) CNT@SnO₂, (c) Pt-CNT@SnO₂, and (d) E-Pt-CNT@SnO₂. Inset: statistical distribution of Pt particle size. (e) XRD patterns of the CNT@SnO₂, Pt-CNT@SnO₂, and E-Pt-CNT@SnO₂. (f) CV curves of the process of the electrochemical-induced SMI.

The curves of CV scanning for Pt-CNT@SnO₂ is shown in Figure 1f, and it should be noted that the electrochemical behavior of the catalyst changes significantly as the electrochemical cycling proceeds. The region of underpotential deposition of hydrogen (H₂UPD) has a little change, but the region of OH adsorption (OHad) is significantly reduced. At the beginning of CV scanning proceeds, an obvious shrinking of the OHad region could be observed in each cycle, and then the shrinking rate gradually slowed down. After 128 cycles, the CV curve tended to be stable, indicating the stabilization of the structure and the preparation of E-Pt-CNT@SnO₂. This unusual electrochemical behavior could be attributed to encapsulation of Pt NPs by the amorphous SnO₂ layers during electrochemical cycling, that is, the electrochemical-induced SMI. It has been studied that the thin oxide encapsulation layer acts as shielding layer to hinder the oxygen intermediates to adsorption on the Pt surface,[22] but this thin oxide encapsulation layer doesn’t interfere with the transfer of H₂ or protons.

High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) is employed to characterize the nanostructures of E-Pt-CNT@SnO₂. As shown in Figure 2a-b, the Pt NPs of E-Pt-CNT@SnO₂ are in contact with the crystalline SnO₂ on the support, while some amorphous material exists around the Pt NPs. The spacings of lattice fringes are 0.262 nm and 0.223 nm, corresponding to (101) facets of SnO₂ and (111) facets of Pt, respectively, indicating that CNT@SnO₂ supports does not exert significant stress on Pt. In the energy dispersive spectroscopy (EDS) elemental mapping (Figure 2c-e), a faint signal of Sn around the Pt NPs proves that the amorphous material is SnO₂. Meanwhile, X-ray photoelectron spectroscopy (XPS) analysis indicates that there is no shift in the Pt 4f peak position of E-Pt-CNT@SnO₂ and Pt-CNT@SnO₂ (Figure 2f and Supporting Information Figure S4). However, the composition of Pt(0) increases from 46% to 59% after encapsulation in Figure 2g. This can be attributed to the fact that the encapsulation of Pt NPs increases the contact area between Pt and SnO₂, which enhances the electronic metal-support interaction (EMSI). Consequently, more electrons are transferred from SnO₂ to Pt NPs, leading to a reduction in the oxidation state of Pt.

**Electrochemical process analysis**

To further explore the electrochemical properties of E-Pt-CNT@SnO₂, a series of electrochemical tests were conducted. Initially, CO-stripping tests were performed and CO could be utilized as a molecule probe to examine the surface state of Pt. The CO-stripping result for commercial Pt/C is illustrated in Figure 3a. During the first cycle (solid line) of the scanning process, there is no significant H₂UPD region observed and a
sharp CO oxidation peak appeared around 0.76 V due to the
surface of Pt being occupied by CO molecules. As CO is
oxidized to CO₂, the surface of Pt is re-exposed, resulting in the
appearance of normal signals of H₂UPD and OHad region during
the second cycle (dashed line) of scanning. The E-Pt-
CNT@SnO₂ exhibits a distinctive result for CO-stripping tests
(Figure 3a). During the first cycle, a certain area of H₂UPD region
is evident, while the CO oxidation peak is significantly
suppressed, suggesting restricted contact between Pt and CO.
In the second cycle of CV, the H₂UPD region of E-Pt-CNT@SnO₂
remains almost the same as in the first cycle, with a minimal
OHad region.

![Graph](image)

**Figure 3.** (a) CO-stripping curves of Pt/C, Pt-CNT@SnO₂ and E-Pt-CNT@SnO₂ in 0.1 M HClO₄ (scan rate: 20 mV s⁻¹). The solid line represents the data from the first cycle, dotted line is the data of second cycle. (b) ECSA calculated from different method for Pt/C, Pt-CNT@SnO₂ and E-Pt-CNT@SnO₂. (c) Schematic illustration of the selective permeability of encapsulation layer due to the electrochemical-induced SMSI.

Furthermore, the Pt surface of Pt-CNT@SnO₂ should be
exposed based on previous experimental results, but its
electrochemical behavior is closer to that of E-Pt-CNT@SnO₂.
This could be attributed to the low-potential treatment during the
CO-stripping process, which might lead to a partial structural
transformation towards E-Pt-CNT@SnO₂. The electrochemical
surface areas (ECSA) of catalysts were calculated from the
integrated areas of H₂UPD region and CO oxidation peak (Figure
3b). It was observed that the ECSA-H₂UPD and ECSA-CO, for
Pt/C are very similar (52.3 vs. 53.5 m²·g⁻¹). However, for E-Pt-
CNT@SnO₂, there is a significant disparity in ECSA between
two these methods (42.2 vs. 6.6 m²·g⁻¹). This phenomenon
further supports the validity of the hypothesis of
electrochemically induced SMSI, which form the thin oxide
capsulation layer to prevent the CO adsorption on the surface
of Pt NPs.

As depicted in schematic Figure 3c, due to the small size of
protons and H₂ molecules, they can penetrate through the thin
amorphous SnO₂ layer. Consequently, E-Pt-CNT@SnO₂ exhibits
a comparable ECSA-H₂UPD to Pt/C. However, CO molecule is
relatively larger than H₂ molecule and hard to penetrate the
encapsulation layer [33, 34] leading to a significantly smaller
ECSA-CO, for E-Pt-CNT@SnO₂. Similarly, *OH molecule also
struggles to permeate the oxide layer, which is the reason for
the quite smaller OHad region area in the CV curve of E-Pt-
CNT@SnO₂ than the H₂UPD region. Furthermore, as O₂ molecules
cannot effectively reach the Pt surface, E-Pt-CNT@SnO₂
exhibits a significantly inferior ORR activity to Pt-CNT@SnO₂
(Supporting Information Figure S5).

To further demonstrate the encapsulation of Pt NPs by SnO₂, E-
Pt-CNT@SnO₂ was subject to the CV scanning in 0.1 M KOH to
remove the SnO₂ layer. After the alkaline treatment, the OHad
region area of E-Pt-CNT@SnO₂ is observed (Supporting
Information Figure S6), and the ORR activity is noticeably
improved. This enhancement is attributed to the relatively poor
alkaline resistance of SnO₂, and a portion of the amorphous
SnO₂ encapsulation layer on the surface of Pt is removed. In
general, tradition thermal-induce SMSI is usually considered to
be reversible on metal-oxides systems: supports could
capsulate the metal NPs under reducing conditions and the
metal can be re-exposed under oxidizing conditions. Therefore,
we attempted an electrochemical oxidation treatment on E-Pt-
CNT@SnO$_2$ through CV scanning between 1.0 to 1.6 V. However, the electrochemical oxidation process does not lead to a greater exposure of Pt surface in E-Pt-CNT@SnO$_2$ (Supporting Information Figure S7), and the reason needs further investigations.

![Raman Spectra](image)

**Figure 4.** In-situ Raman spectra of (a) CNT@SnO$_2$ and (b) Pt-CNT@SnO$_2$. (c) Planar average charge density along the z-axis of Pt-SnO$_2$. Projected crystal orbital Hamilton population (pCOHP) for the Sn-O interaction in (d) defected SnO$_2$ and (e) Sn-Internal O in defected SnO$_2$ loaded with Pt.

### Mechanism analysis of SMSI

Typically, inducing SMSI requires two essentials: one is the introduction of defects in the supports (such as H$_2$ treatment, UV radiation, shockwaves, or using chemical reducing agents) and another is promoting atomic migration through thermal energy or mechanical force. In the Pt-CNT@SnO$_2$ system, the electrochemical process can readily satisfy the first condition by inducing defects in the SnO$_2$ support. Considering the standard redox potentials of Sn ($0.138$ V for Sn(0) → Sn(II) and $0.151$ V for Sn(II) → Sn(IV)), the electrochemical treatment of Pt-CNT@SnO$_2$ is in a potential window of 0.05-1.2 V would lead to continuous redox of SnO$_2$. In-situ Raman spectra measurements (Figure 4a-b) suggest that the continuous redox process will not change the structure of CNT@SnO$_2$, especially the defect concentration in SnO$_2$. However, during the same process for Pt-CNT@SnO$_2$, the $B_2$ mode located around 576 cm$^{-1}$ becomes more obvious, indicating the increment of defect concentration in SnO$_2$. The electron paramagnetic resonance (EPR) result is presented in Supporting Information Figure S8, indicating an increment of the concentration of oxygen vacancies within E-Pt-CNT@SnO$_2$. These results demonstrate the critical role of Pt in inducing defects in the SnO$_2$ support during the electrochemical treatment.

On the other hand, some studies suggest that the presence of noble metals could promote the migration of elements within the supports. As shown in Raman spectra, the location of $A_{1g}$ mode in E-Pt-CNT@SnO$_2$ (628 cm$^{-1}$) exhibits a negative shift compared to that in CNT@SnO$_2$ (632 cm$^{-1}$). Since the $A_{1g}$ and $E_g$ modes of rutile SnO$_2$ reflect the Sn-O bond vibrations perpendicular to the z-axis, the negative shift of wavenumbers indicates the weakening of the Sn-O bond strength and that SnO$_2$ are more susceptible to defect formation in the presence of Pt. This makes electrochemically induced SMSI feasible at a room temperature.

Density functional theory (DFT) calculations are also employed to unveil interaction between Pt NPs and supports, including the electrons transfer and the bond strength. Given that Pt in E-Pt-CNT@SnO$_2$ only interfaces with SnO$_2$, the computational model has been simplified with the ignoring of CNTs. When Pt NPs are loaded onto SnO$_2$, electrons transfer from SnO$_2$ to Pt, leading to the formation of a charge consumption layer on SnO$_2$, as illustrated in Figure 4c. The number of bonding electrons between Sn and O should decrease, resulting in a significant decrease in the Sn-O bond energy around Pt NPs. To quantify the Sn-O bond strength, the integrating of the projected crystal orbital Hamilton population (IpCOHP) within the occupied states for the SnO$_2$ under different conditions were analyzed. The more positive the IpCOHP value indicates the weaker Sn-O bond strength. As shown in Figure 4d and Supporting Information Figure S9, the Sn-O bond strength is slightly reduced when the SnO$_2$ is defective. Moreover, when Pt is loaded on the defective SnO$_2$, the Sn-O bond strength is significantly reduced (Figure 4e and Supporting Information Figure S10). It is worth mentioning...
that the bond strength between Sn atoms and the interior O atoms is weaker than that with surface O atoms. This facilitates the formation of small clusters of SnO$_2$ around the Pt NPs.

Subsequently, the small clusters migrate and realize the encapsulation of Pt NPs.

![Figure 5.](image) (a) HOR polarization curves of E-Pt-CNT@SnO$_2$, Pt-CNT@SnO$_2$ and commercial Pt/C in H$_2$-saturated 0.1 M HClO$_4$ (rotating speed, 1600 rpm; scan rate, 5 mV s$^{-1}$). (b) Micro region (-0.01 V - 0.01 V) of polarization curves. (c) Tafel plots of the kinetic current densities. (d) Comparison of mass and specific activities. (e) Chronoamperometry curves with 10,000 ppm CO.

**HOR performance**

Since the obtained E-Pt-CNT@SnO$_2$ exhibits excellent resistance to CO but does not impact the penetration of H$_2$, its performance as a catalyst for HOR is evaluated. The HOR performance of E-Pt-CNT@SnO$_2$, Pt-CNT@SnO$_2$ and commercial Pt/C were investigated in H$_2$-saturated 0.1 M HClO$_4$ at a scan rate of 5 mV s$^{-1}$. As shown in Figure 5a, the HOR polarization curve of E-Pt-CNT@SnO$_2$ exhibits the highest limit current density than that of Pt-CNT@SnO$_2$ and commercial Pt/C.

The increased limiting current density of E-Pt-CNT@SnO$_2$ can be attributed to the larger Pt-SnO$_2$ interface and stronger interfacial hydrogen spillover from SnO$_2$ to Pt surface. The micro region (-0.01-0.01 V) of polarization curves (Figure 5b) and the Tafel plots of kinetic current density ($j_0$) (Figure 5c) were plotted. The current density of E-Pt-CNT@SnO$_2$ increases faster with the potential, indicating the rapid reaction kinetics. The mass normalized $j_0$ of E-Pt-CNT@SnO$_2$ at the overpotential of 20 mV is 1.06 A mg$_{Pt}$$^{-1}$, which is higher than that of Pt-CNT@SnO$_2$ (0.81 A mg$_{Pt}$$^{-1}$) and Pt/C (0.76 A mg$_{Pt}$$^{-1}$). Moreover, the exchange current densities ($j_0$) based on the linear fitting of the polarization curves in the micro-polarized area by Butler-Volmer equation was calculated (Figure 5d and Supporting Information S11). The $j_0$ of E-Pt-CNT@SnO$_2$ (1.55 A mg$_{Pt}$$^{-1}$) is also higher than that of Pt-CNT@SnO$_2$ (1.22 A mg$_{Pt}$$^{-1}$) and Pt/C (1.24 A mg$_{Pt}$$^{-1}$), and it is the one of the best HOR catalyst in acidic media (Table S1). It has been studied that the electron transfer from SnO$_2$ to Pt will downshift the d-band center of Pt and then weakens its adsorption energy with the H intermediate.$^{37,38}$ which could account for the improved HOR activity of the catalyst.

Chronoamperometry tests were used to assess the tolerance of E-Pt-CNT@SnO$_2$ to CO (Figure 5e). Upon introducing 10,000 ppm of CO in H$_2$, the current density of Pt/C catalyst rapidly declined until complete deactivation within 300 s, as CO thoroughly poisoned the Pt sites. In contrast, E-Pt-CNT@SnO$_2$ exhibits a slower current density decay and maintains 85% of the current density preserved within 2000 seconds. This remarkable CO tolerance can be attributed to the effective protection of Pt sites from CO poisoning due to the electrochemical SMSI-induced SnO$_2$ encapsulation layer.

**Conclusion**

In summary, we reported an electrochemical method to induce SMSI in Pt-CNT@SnO$_2$ system for CO-tolerant HOR. It was found that the CV scanning process can induce the dynamic structural evolution of catalyst, and HRTEM images prove that amorphous SnO$_2$ layer covers Pt NPs. The E-Pt-CNT@SnO$_2$ encapsulated by amorphous SnO$_2$ exhibits unique electrochemical properties with confined adsorption of CO but normal adsorption of H$_2$, which determine the excellent CO-tolerance of E-Pt-CNT@SnO$_2$ that can retain 85% current density for 2000 s under 10,000 ppm CO conditions. The electrons transfer from SnO$_2$ to Pt NPs in E-Pt-CNT@SnO$_2$ improved the HOR activity, and the excellent exchange current density is 1.55 A mg$_{Pt}$$^{-1}$. In addition, theoretical calculations and in situ Raman spectra reveal that the electrochemical redox operation and the charge transfer at a heterogeneous interface resulted in the weakening the Sn-O bond, which is the key of the occurrence of SMSI. This mild electrochemical-method provides...
a new way for the design of supported catalysts, and also  
appeals attention to the evolution of structure during the  
electrochemical process of catalysts.

4 Supporting Information

The authors have cited additional references within the  
Supporting Information[13, 39-45]

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RESEARCH ARTICLE


Entry for the Table of Contents
电化学方法诱导强金属-载体相互作用提高氢氧化反应催化剂的 CO 耐受性

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摘要：诱导经典强金属-载体相互作用（SMSI）是一种提高负载型金属催化剂性能的有效途径，这指的是载体包覆金属纳米颗粒的结构重构效应。传统的 SMSI 诱导方式是热还原方法，但这过程中往往伴随着会损害催化活性的金属纳米颗粒的长大过程。为了解决这一问题，本研究开发了一种温和的电化学方法来诱导 SMSI，并在核壳结构 CNT@SnO₂载体上负载的 Pt 纳米颗粒催化剂中进行了验证。高分辨透射电镜（HRTEM）和电化学测试结果证实了电化学诱导方法成功在 Pt 纳米颗粒表面构建了 SnOₓ包覆层。这种 SnOₓ包覆层可以保护 Pt 纳米颗粒在氢氧化反应（HOR）中不受 CO 杂质的毒害。实验显示，当 H₂中混入 10000 ppm 浓度的 CO 时，E-Pt-CNT@SnO₂的 HOR 电流密度经过 2000 s 后仍能保持 85%，而商用 Pt/C 在相同条件下工作 300 s 则完全失活。此外，SnOₓ包覆层与 Pt 纳米颗粒之间存在电子相互作用，这导致电荷从载体迁移到 Pt 纳米颗粒上，并在远离界面处聚集。这种电荷转移降低了 Pt 对 H 中间体的吸附能，提高了 E-Pt-CNT@SnO₂的 HOR 活性，催化剂的交换电流密度为 1.55 A·mg⁻¹Pt⁻¹，是商业 Pt/C 的 1.3 倍。原位拉曼光谱和理论计算结果表明，电化学诱导 SMSI 的关键因素是 Pt 纳米颗粒对 Sn-O 键强度的减弱。此外，Pt 纳米颗粒对载体不同区域的 Sn-O 键强度的弱化存在差异，其中表面 Sn 原子与内部 O 原子之间的键强度弱于 Sn 原子与表面 O 原子之间的键强度，这促进了 SnOₓ团簇的形成和迁移。

关键词：强金属-载体相互作用；铂纳米颗粒；氢氧化反应；负载型催化剂；CO 耐受性