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In situ electrochemical surface-enhanced Raman spectroscopy study of CO electrooxidation on PtFe nanocatalysts

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ABSTRACT

Combination of spectroscopic techniques with electrochemistry is a promising way to elucidate electrocatalytic mechanisms at a molecular level. Surface-enhanced Raman spectroscopy (SERS) is a non-destructive, ultrasensitive fingerprint technique that can detect metal–adsorbate and metal oxide vibrations. However, it is hard to study nanocatalysts because of the morphology limitation of SERS. In this paper, core-shell-satellite nanostructures have been fabricated by assembling PtFe nanocatalysts on shell-isolated nanoparticles (SHINs). CO electrooxidation on these nanostructures was studied by in situ electrochemical shell-isolated nanoparticle-enhanced Raman spectroscopy (EC-SHINERS). The in situ spectroscopic results correlate well with the results obtained using cyclic voltammetry, and show that PtFe bimetallic nanocatalysts have improved CO electrooxidation activity. The in situ SHINERS studies also show that this improvement is the result of weaker CO adsorption on PtFe compared to Pt, as revealed by the red shift of the Raman band of the Pt$-$C stretching vibration on PtFe. This work demonstrates that this method is a powerful tool for in situ investigation of the electrocatalytic processes occurring on nanocatalysts and provides a better understanding of the reaction mechanisms.

1. Introduction

Rational design of highly active and stable catalysts for proton exchange membrane fuel cells (PEMFCs) is crucially important for tackling the energy crisis. In PEMFCs, Pt-based nanomaterials are usually chosen as catalysts to accelerate the electrooxidation rate of small organic molecules [1,2]. However, they suffer serious deactivation when CO is present, which greatly hinders the commercialization of PEMFCs [3]. This is because CO bonds strongly to the catalyst surface and blocks the active sites for electrooxidation [4]. In recent years, great efforts have been made to solve the problem of CO poisoning by developing bimetallic nanoparticles, such as Pt$-$Sn, Pt$-$Mo, and Pt$-$Ru, with high activity toward CO electrooxidation [5–7]. Second transition series metals can modify the electronic and geometric structure of the catalysts, leading to familiar geometric and/or ligand effects which can greatly enhance catalytic activity. However, more fundamental information, especially data acquired under working conditions, is needed in order to better understand these effects and to guide the design of more efficient catalytic materials.

Surface-enhanced Raman spectroscopy (SERS) is a powerful surface analytical technique with high sensitivity. Furthermore, it can easily be used to detect molecules with Raman bands at low wavenumbers as well as species in aqueous solutions [8]. These characteristics make SERS a promising method for operando studies of electrocatalytic reactions. However, only few metals e.g. Au, Ag and Cu with special nanostructures provide a large SERS enhancement, so it is difficult to study the most widely used electrocatalysts (e.g. Pt, Pd, Rh, and Ru) using this technique [9]. To overcome this limitation, a “borrowing SERS activity” strategy has been developed by Tian et al. [9,10] and Weaver et al. [11]. In this strategy, electrocatalysts are deposited on Au (or Ag) substrates via electrochemical or wet-chemical methods, so that the Raman signal from the catalysts is greatly enhanced by the

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electromagnetic (EM) field generated on the Au/Ag substrates. For example, Tian's group used Au-core Pd-shell Pt-cluster nanostructures to study the process of formic acid electrooxidation (FAOR) in situ [12]; Kim et al. took advantage of the dendritic Au rod core to investigate the FAOR on Pt layers [13,14]; Zou's group deposited PtRu films on roughened Au electrodes to study CO adsorption and methanol oxidation [15].

Despite the great progress achieved via the borrowing strategy, it still has some limitations in the study of electrocatalytic reactions. Firstly, an electronic effect from the Au (or Ag) substrate cannot be avoided [16], which would then affect the catalytic behavior. The data acquired therefore does not reflect the intrinsic property of the catalysts. Secondly, the Au (or Ag) substrates used in the borrowing strategy usually have a large diameter (> 50 nm) in order to provide suitable Raman enhancement. The electrocatalysts deposited on them are therefore very different from practical catalysts, which are typically < 10 nm in diameter. Furthermore, highly active practical electrocatalysts usually have a very complex composition and structure, and consequently it is a great challenge to anchor them to the Au (or Ag) substrate.

We report the development of a satellite structure obtained by anchoring Pt-based nanocrystals on shell-isolated nanoparticles (SHINs) consisting of an Au core and an ultrathin, chemically inert SiO_2 shell. These satellite structures were used for in situ investigation of catalytic CO electrooxidation on Pt and PtFe bimetallic nanoparticles by electrochemical shell-isolated nanoparticle-enhanced Raman spectroscopy (EC-SHINERS). The in situ EC-SHINERS results showed unambiguously that the Fe species could change the electronic properties of the catalysts, weakening the CO adsorption and leading to improved performance of the PtFe bimetallic catalysts compared to the monometallic Pt catalyst. This work provides a deeper understanding of the mechanisms of catalytic CO electrooxidation and opens a new avenue for the study of electrocatalytic processes on nanocatalysts.

2. Experimental

The Pt and PtFe nanocatalysts were synthesized through a thermal decomposition method [17]. SHINs were prepared as described in previous reports [18–21]. Pt-based nanoparticles were deposited on the SHINs satellite structure by self-assembly through electrostatic interaction; details are given elsewhere [22]. These nanoparticles were analyzed by transmission electron microscope (TEM) (FEI Tecnai F30 microscope coupled with energy-dispersive X-ray spectrometry). All electrochemical experiments were carried out on a CHI-630E electrochemical workstation with Pt wire and saturated calomel electrode (SCE) as counter electrode and reference electrode, respectively. EC-SHINERS was performed in a home-made spectroelectrochemical cell with a confocal microscope Raman system Xplora (Jobin-Yvon France). The excitation wavelength was 638 nm in all Raman measurements.

3. Results and discussion

Fig. 1a is a schematic representation of our in situ EC-SHINERS study of CO electrooxidation on PtFe nanocatalysts. The nanocatalysts are on the surface of the SHINs, forming a nanostructure composed of Au core–silica shell–nanocatalyst satellites. With this hybrid nanostructure, the Raman signals from the catalysts can be enhanced by 8 orders of magnitude by the strong EM fields generated on the Au cores, based on a three-dimensional finite-difference time-domain (3D–FDTD) simulation (Fig. 1b). To obtain the described nanostructure, SHINs with 120 nm Au cores and ~2 nm SiO_2 shells are first prepared (Fig. 1c). Their surface charge is negative due to residual citrate on the surface. The as-prepared Pt_1Fe_1 nanocatalysts (Fig. 1d) are modified to create positively charged surfaces by ligand exchange [23]. The modified catalysts are then deposited on the SHINs by electrostatic interaction. It can be seen from Fig. 1e that the resulting nanocomposites show the core-shell-satellite structure, which is further confirmed by the element maps (Fig. 1f).

Prior to CO electrooxidation, the Pt_1Fe_1 nanoparticles on a glassy carbon (GC) electrode were electrochemically activated from -0.25 V to 1 V (vs. SCE in 0.1 M $HClO_4$). As shown in Fig. 2a, the H ad/desorption peaks in the cyclic voltammetric curves first increase then become stable as the number of cycles increases. This indicates that the protective agents are removed from the catalyst surface and that the Fe species are dissolved during the electrochemical activation, leading to the formation of Pt-skeleton surfaces [24,25]. This can be further illustrated by the results of high-sensitivity low-energy ion scattering (HS-LEIS), which gives the elemental composition of the outer surface layer. The HS-LEIS analysis shows that the amount of Pt is much higher on the activated dealloying Pt_1Fe_1 surfaces compared to the unactivated samples (Fig. 2b). With the Pt-skeleton structure, the performance of Pt_1Fe_1 for CO electrooxidation was examined by linear sweep voltammetry (LSV) in CO-saturated 0.1 M $HClO_4$. An early onset potential at about 0.2 V and a sharp oxidation peak at 0.48 V can be observed for the Pt_1Fe_1 catalyst (Fig. 2c), indicating its high catalytic activity for CO electrooxidation.

To understand the mechanism of CO electrooxidation on Pt_1Fe_1 nanocatalyst, an in situ EC-SHINERS study was carried out in CO-saturated 0.1 M $HClO_4$ solution at 0.1 V intervals from -0.2 V to 1 V vs. SCE. The SHINERS spectra of CO adsorbed on Pt_1Fe_1 nanoparticles can be clearly observed at -0.2 V (Fig. 2d). In the low wavenumber region, the Raman bands at 391 and 485 cm^{-1} are ascribed to Pt–CO stretching with bridge and on-top configurations, respectively. In the high wavenumber region, the band at around 2063 cm^{-1} is assigned to the corresponding C—O stretching of CO adsorbed at on-top sites. As the potential increases, the red shift of $\nu_{Pt\text{-}CO}$ and blue shift of ν_{CO} arise from the electrochemical Stark effect, which is in good agreement with the results of previous reports [12,15,26–28]. When the potential scans positively above 0.4 V, the intensities of both Pt–CO and C—O stretching bands dramatically decrease and completely disappear after 0.6 V. However, a new broad band at around 570 cm^{-1} ascribed to the Pt—O bending mode emerges after 0.7 V and can be related to the formation of a Pt oxide layer such as α-PtO_2 [29]. The in situ SHINERS spectra correlate well with the LSV results, and directly prove that the sharp increase in the current density at about 0.4 V in the LSV comes from CO electrooxidation.

The results outlined above demonstrate that the EC-SHINERS method can provide molecular insights into CO electrooxidation on Pt_1Fe_1 nanocatalysts. The structure–activity relationships of bimetallic nanocatalysts with different compositions (Pt, $Pt_1Fe_{0.5}$, and $Pt_1Fe_{1.5}$) but similar morphology and size were then studied by EC-SHINERS. All the bimetallic catalysts show a Pt skeleton structure after electrochemical activation, as demonstrated by the HS-LEIS analysis. The LSV of CO electrooxidation in Fig. 3a obviously shows that the onset and peak potentials for CO electrooxidation on PtFe catalysts shift to negative values compared to pure Pt. As the Fe content increases, the peak potential for CO electrooxidation decreases ($0.66\ V > 0.55\ V > 0.48\ V > 0.38\ V$ for Pt, $Pt_1Fe_{0.5}$, Pt_1Fe_1 and $Pt_1Fe_{1.5}$, respectively) (Fig. 3a and e). This indicates increasing CO oxidation activity on the Fe-alloyed Pt nanocatalysts, with the highest activity observed on $Pt_1Fe_{1.5}$. The in situ SHINERS studies of CO electrooxidation on these nanocatalysts show similar results (Figs. 3b–d). All of the Pt–CO stretching modes are present at low potentials, but they gradually disappear as the potential increases. At high potentials, all of the nanocatalysts are oxidized and show the Pt—O band at around 570 cm^{-1}. Fig. 3f shows the potential dependence of the band intensities of Pt–CO. The normalized Raman intensities of the Pt–CO bands decrease dramatically and disappear around the peak potential of CO electrooxidation. This is in good agreement with the results of the electrochemical measurements on these four nanocatalysts, though the intensity change slightly lags behind the LSV data. This further illustrates that the introduction of Fe species increases catalytic activity for