High-temperature surface enhanced Raman spectroscopy for in situ study of solid oxide fuel cell materials†

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In situ probing of surface species and incipient phases is vital to unraveling the mechanisms of chemical and energy transformation processes. Here we report Ag nanoparticles coated with a thin-film SiO2 shell that demonstrate excellent thermal robustness and chemical stability for surface enhanced Raman spectroscopy (SERS) study of solid oxide fuel cell materials under in situ conditions (at ~400 °C).

The surging demand for energy and the ever-increasing concerns regarding greenhouse gas emissions have stimulated intense interest in the development of solid oxide fuel cell (SOFC) technologies, which offer a promising alternative to power generation with high energy efficiency, excellent fuel flexibility, and easy capture of CO2 emissions. To date, SOFC technology is too expensive for commercialization due largely to inadequate performance at low temperatures and insufficient robustness under realistic service conditions. Rational design of new electrode materials with high catalytic activity and resistance to contaminant poisoning depends critically on a fundamental understanding of the reaction mechanisms on electrode surfaces. In situ characterization of electrode surfaces under operation conditions is imperative to acquiring information vital to unraveling reaction mechanism(s).

Raman spectroscopy has unique advantages for in situ characterization of SOFC materials. Through "fingerprinting" the vibration modes of the materials, Raman scattering can be used to identify the phase evolution on the electrode surfaces.

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‡ Electronic supplementary information (ESI) available: Fig. S1–S12, fabrication and characterization of Ag@SiO2 nanoparticles, the preparation of the SERS samples, the details of the enhancement factor calculation and the apparatus for in situ SERS analysis of nickel coking and CeO2 redox. See DOI: 10.1039/c3ee42462f

Broader context
Minor alteration of surface composition and structure often dramatically affects the activity and stability of solid oxide fuel cell (SOFC) electrodes. For example, surface modification by a trace amount of catalysts or electrocatalysts can significantly enhance the rate of electrode reactions whereas deposition of a minuscule amount of an inactive phase (e.g., coking) may quickly degrade electrode performance. Probing such surface species or incipient phases is critical to understanding the mechanism(s) of electrode processes. Unfortunately, conventional Raman spectroscopy lacks the sensitivity to many surface species. In this contribution, we employ surface enhanced Raman spectroscopy (SERS) to boost the sensitivity to surface species on SOFC electrodes. This was achieved using SiO2-coated Ag nanoparticles as the SERS probe for in situ characterization at high temperatures. The thin SiO2 coating prevented silver oxidation and agglomeration, offering robust thermal stability and chemical inertness while allowing the surface species within the enhancement field of the silver nanoparticles. This SERS probe should find utility in characterizing a wide variety of electrodes and catalysts at high temperatures, including hydrocarbon reforming promoters, three-way catalysts, and gas separation membranes, where a trace amount of surface species plays a crucial role in functionality.

Unlike electron-based surface analysis techniques such as X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES) and energy-dispersive X-ray spectroscopy (EDS), Raman spectroscopy does not require vacuum, allowing in situ characterization of a functional electrode exposed to gases of interest at high temperatures. Raman spectroscopy has been utilized to study a wide variety of SOFC materials under in situ conditions, providing insight into electrochemical reactions on electrode surfaces such as sulfur poisoning of nickel-based anodes and adsorption of oxygen species on CeO2.

The low signal intensity of Raman spectroscopy, however, makes it difficult to detect the surface species present in trace amounts or to track the formation of surface species with short lifetimes. This problem is more severe when studying SOFC materials under realistic operating conditions because many ceramic phases possess weak Raman modes and all Raman peaks broaden at high temperatures.
Surface enhanced Raman scattering (SERS) is a promising solution to this problem. The surface plasmons of the nano-sized Au or Ag features resonate with the incident light, amplifying the Raman signal of the molecules in their vicinity. Our previous study demonstrated the utility of SERS for SOFC-related materials such as deposited carbon, CeO\textsubscript{2}, La\textsubscript{2}–xSr\textsubscript{x}MnO\textsubscript{3–δ} (LSM) and La\textsubscript{1–δ}Sr\textsubscript{δ}Co\textsubscript{1–δ}Fe\textsubscript{δ}O\textsubscript{3–δ} (LSCF) following deposition of Ag nanoparticles on the electrode. However, bare metal nanoparticles, the common SERS providers, tend to ripen and lose SERS activity at high temperatures. To make in situ SERS possible, robust nanofeatures of Au or Ag need to be created. Recently, the van Duyne group found that Ag nanofeatures with a thin layer of robust capping such as Al\textsubscript{2}O\textsubscript{3} have stable shapes and optical properties at high temperatures. In the shell-isolated nanoparticle enhanced Raman spectroscopy (SHINERS) technique developed by Tian et al., the Ag and Au nanoparticles with a few nanometers of Al\textsubscript{2}O\textsubscript{3} or SiO\textsubscript{2} coating provide an enhancement of the Raman signal of the underlying materials without interfering with the original surface properties.

In this work, we report the use of SiO\textsubscript{2} shell isolated Ag nanoparticles (Ag@SiO\textsubscript{2} NPs) for in situ SERS analysis of SOFC materials at high temperatures.

The diameters of the silver nanoparticles used in this study are ~60 nm, while the thicknesses of SiO\textsubscript{2} shells are ~10 nm, as seen from the TEM images in Fig. 1(A). The SiO\textsubscript{2} coating red-shifted the peak position of the localized surface plasmon resonance (LSPR) of the silver nanoparticles and reduced the extinction coefficient, as presented in the UV-vis extinction spectra (Fig. S1†). As the SiO\textsubscript{2} shell provides thermal robustness at the cost of the SERS enhancement effect, a 10 nm thick SiO\textsubscript{2} shell was chosen in this study to ensure adequate stability and a reasonable SERS enhancement.

The intrinsic enhancement factor of the Ag@SiO\textsubscript{2} nanoparticles was evaluated using Rhodamine 6G (R6G) loaded on a silicon wafer as shown in Fig. 1(B). The silicon wafer loaded with 0.1 M R6G shows a typical R6G spectrum, while the one loaded with 1 \times 10^{-3} M R6G has no observable spectral features. In contrast, the 1 \times 10^{-3} M R6G solution mixed with the Ag@SiO\textsubscript{2} nanoparticles generated significantly enhanced Raman signals. The enhancement factor is estimated to be 150, according to the calculation method provided in the ESI†.

The thermal and chemical stability of the microstructure and optical absorbance of the Ag@SiO\textsubscript{2} nanoparticles are key to the application of high temperature SERS. The localized surface plasmon resonance (LSPR) extinction spectra of the Ag@SiO\textsubscript{2} nanoparticles are shown in Fig. 1(C), before and after heat treatment at from 200 °C to 600 °C for 30 min in air. Despite the gradual decrease of intensity, the LSPR peaks of Ag@SiO\textsubscript{2} nanoparticles remain around 450 nm from room temperature to 500 °C, and a considerable portion of the resonance remained after heat treatments. The thermally-robust LSPR property results from the stable microstructure of the Ag cores protected by SiO\textsubscript{2} shells. As is evidenced by the SEM images presented in Fig. S2†, the Ag@SiO\textsubscript{2} nanoparticles largely retained the original size and structural integrity, although slight shape variation was observed after annealing at 450 °C for 1 h in different gases: air, argon with 10% H\textsubscript{2}, and argon with 15% C\textsubscript{2}H\textsubscript{2}. In addition, the LSPR peak remained stable after the initial drop (Fig. S5†), providing an advantageous time window for the SERS analysis. Clearly, the Ag@SiO\textsubscript{2} nanoparticles demonstrated better thermal robustness than the bare Ag nanoparticles. After annealing at 450 °C for 1 h, the bare Ag NPs (created by sputtering) lost all the LSPR resonance, as a result of catastrophic particle ripening (Fig. S6†). The highest temperature that the LSPR peak remains is 500 °C. As the targeted operation temperature of the low-temperature SOFCs is 400 to 600 °C, these Ag@SiO\textsubscript{2} nanoparticles may provide SERS enhancement for the SOFC electrode materials under near operating conditions.

While bare silver is susceptible to coking and oxidation of fuels, potentially introducing artefacts to the SERS study of the electrode processes, the SiO\textsubscript{2} shell isolated Ag nanoparticles are chemically inert and stable. Presented in Fig. S3† are some typical Raman spectra of Ag@SiO\textsubscript{2} nanoparticles after annealing in air, argon with 10% H\textsubscript{2}, and argon with 15% C\textsubscript{2}H\textsubscript{2}. All samples showed clean backgrounds after the heat treatments, suggesting that the Ag@SiO\textsubscript{2} nanoparticles are suited for SERS study of SOFC materials under in situ conditions.
SERS of carbon deposition on nickel. The calculation of the enhancement factor is provided in the ESI.†

These results demonstrate the feasibility of using Ag@SiO₂ NPs for SERS study of SOFC materials under in situ conditions. GDC is a typical electrolyte material of SOFCs, and is also widely used in both cathode and anode,15–17 while carbon deposition on nickel is a typical process that causes deactivation of Ni-based SOFC anodes. Ag@SiO₂ NPs enhanced the Raman signals of these phases of low concentration. More importantly, the signal enhancement remained stable after high temperature treatments, making possible in situ SERS analysis.

The process of carbon deposition was monitored in situ using Ag@SiO₂ nanoparticles as the SERS providers to enhance the sensitivity. Carbon deposition is a major source of degradation of nickel-based anodes when exposed to carbon-containing fuels, which could result in loss of active sites and damage of microstructure. Monitoring the coking kinetics at early stage helps to understand the mechanism and thus guide the design of effective anode modifiers to resist such degradation. Fig. 3(A and B) show the time-resolved normal Raman and SERS study of a polished nickel surface exposed to wet propane at 450 °C, respectively. In both occasions, the carbon D-band and G-band increased over time, but the SERS activated sample showed a much higher intensity and signal-to-noise ratio. The signal strength of both the carbon D-band and G-band is enhanced significantly. In Fig. 3(C), the integrated area under the carbon D-band for both samples was plotted over

The thermally robust SERS capability of Ag@SiO₂ nanoparticles was tested on both anode and cathode materials of SOFCs. Fig. 2(A) presents some typical SERS spectra of gadolinium-doped ceria (GDC) thin films. The normal Raman spectrum taken from the GDC thin film on a silicon wafer showed a weak peak at 460 cm⁻¹, corresponding to the F₂g mode of doped ceria.19–21 After the Ag@SiO₂ nanoparticles were applied to the surface, the F₂g mode was enhanced by a factor of ~15. For comparison, the Ag@SiO₂ nanoparticles loaded on a blank silicon wafer were also inspected and showed no significant peaks in that region, indicating that the enhancement of F₂g mode was due solely to the SERS effect of Ag@SiO₂ nanoparticles. The GDC thin film loaded with Ag@SiO₂ nanoparticles was then annealed in air at 400 °C for 30 min. The remaining enhancement of F₂g mode amounts to ~8 times. Fig. 2(B) presents the SERS study of carbon deposition on a nickel surface. A blank nickel foil, a Ag@SiO₂ loaded nickel foil, and a Ag@SiO₂ loaded silicon wafer control were exposed to a gas mixture containing 15% C₃H₄ and 85% of argon at 450 °C for 1 h. The Raman spectrum of the SERS-activated nickel foil showed a carbon signal that was ~10 times higher than that of the blank nickel foil. Again, the Raman spectrum of the Ag@SiO₂ loaded silicon wafer control did not show notable carbon peaks, implying that either the Ag@SiO₂ NPs or the silicon wafer did not develop coking and the carbon signal shown in the Ag@SiO₂–Ni sample must have come from the
The signal intensity from the SERS activated sample shows a better-resolved trend: carbon quickly deposited on the nickel surface initially and the deposition rate slowed down over time. The coked samples were then exposed to a gas mixture composed of 1% O₂, 3% water vapor and 96% Ar. The time-resolved Raman and SERS spectra of this carbon removal experiment, along with the integration of the carbon D-band, are shown in Fig. 3(D–F), respectively. In both cases, carbon peaks decrease with the introduction of oxygen. As evident from the SERS data (of higher sensitivity), most of the deposited carbon was removed within 1000 s.

To validate that the sensitivity towards carbon deposition and removal is a result of SERS of Ag@SiO₂ nanoparticles rather than the reaction of Ag@SiO₂ with wet propane, a controlled group consisting of Ag@SiO₂ NPs loaded on the GDC thin film was exposed to wet propane at 450 °C, as shown in Fig. S10.† Over the 5 h testing period, the enhanced F₂g mode of the GDC thin film remained constant while a small amount of carbon was detected. In addition, to validate that SiO₂ does not promote coking on the nickel surface, a controlled experiment was performed, as shown in Fig. S11.† When blank Ni, SiO₂[Ni], and Ag@SiO₂[Ni] samples were exposed to wet propane at 450 °C, only the Ag@SiO₂[Ni] showed a prominent signal of carbon deposition, suggesting that SERS is the key factor for such sensitivity.

The ability of performing in situ SERS at high temperatures allows us to probe the kinetics of coking at its incipient stage. Previous Raman monitoring of carbon deposition was possible only when a large amount of carbon had been accumulated after a long time of coking. Under realistic SOFC operation conditions, coking affects the performance of the anode slowly and does not always leave a detectable Raman signal. Ag@SiO₂ nanoparticles enhance the Raman cross-section, and the inspection of coking becomes possible at low temperatures and shorter durations. Furthermore, a higher signal intensity enables the use of shorter spectral collection times essential for time-resolved studies.

The in situ SERS technique was also applied to probe the oxygen species on CeO₂ surfaces in both reducing and oxidizing atmospheres, as illustrated in Fig. 4. CeO₂ powders were mixed with Ag@SiO₂ nanoparticles and drop-coated onto a silicon substrate which was subsequently heated to 450 °C in a Raman chamber for in situ study. The 465 cm⁻¹ peak is associated with the F₂g mode of CeO₂. On the SERS activated CeO₂ powders (Fig. 4(A)), a peak at around 540 cm⁻¹ appeared when exposed to argon with 4% H₂, and disappeared when exposed to air. This peak can be associated with the oxygen vacancies on the CeO₂ surface, which emerges under a reducing atmosphere and diminishes when exposed to an oxidizing gas. Another notable feature is the weak hump at 800-1000 cm⁻¹ which appears only when the sample is exposed to air. The Raman shift of this hump is consistent with the oxygen absorbed on CeO₂ and Au electrode surfaces. Control groups were tested with the same procedure, as displayed in Fig. 4(B and C). The pure Ag@SiO₂ nanoparticles showed no prominent features during the redox cycling; on the blank CeO₂ powders, only F₂g mode is observable while no oxygen vacancy or adsorbed oxygen peak can be detected.

Fig. 4. In situ SERS study of CeO₂ powders exposed to a reducing and an oxidizing atmosphere at 450 °C. (A–C) Typical Raman spectra taken at 450 °C under air, 4% H₂, and back to air on the sample of (A) CeO₂ powders mixed with Ag@SiO₂ NPs, (B) pure Ag@SiO₂ NPs, and (C) blank CeO₂ powders. All spectra were taken with a 633 nm laser at 10 mW with an acquisition time of 10 s. (D) SEM image of the CeO₂ powders mixed with Ag@SiO₂ after the redox test. (E) TEM images of the Ag@SiO₂ NPs loaded on CeO₂ powders after annealing at 450 °C for 1 h in air and (F) in 4% H₂.

Observation of the accumulation and depletion of oxygen vacancies on the CeO₂ surface at high temperatures revealed the role of CeO₂ in the SOFC electrodes. As a catalyst, CeO₂ is often used as an electrode modifier to help resist carbon deposition on the nickel-based anode and promote oxygen reduction on the cathode. It is believed that CeO₂ stores and releases oxygen under oxidizing and reducing conditions, respectively, leading to the unique catalytic activity. The cycling of the oxygen vacancy band in response to the change of gas atmosphere supports this mechanism. More importantly, this suggests that the surface species, which were undetectable previously under in situ conditions using ordinary Raman spectroscopy, can now be identified using SERS – a powerful tool for in situ study of materials for fuel cells and catalysis. Currently, we are applying this technique to SOFC materials under well-controlled chemical/electrochemical conditions in order to unravel the mechanisms of electrode processes vital to efficiency and stability of the materials under or near operating conditions.

**Conclusions**

In summary, we fabricated Ag@SiO₂ nanoparticles to provide surface enhanced Raman scattering for the study of SOFC electrode materials under conditions approaching those found...
in operation. The SiO₂ shell helps to maintain the structural stability of Ag cores at high temperatures. The in situ SERS of carbon deposition on and removal from the nickel surface demonstrated a sensitive method to study the kinetics of surface species evolution. The revealing of surface oxygen vacancies and adsorbed oxygen molecules on the CeO₂ powders under reducing and oxidizing atmospheres provided a promising route to probe the reaction intermediates that influence the performance and stability of electrodes. The application of SERS techniques in probing SOFC electrode materials exposed to reacting gas mixtures at 400–450 °C represents an important step towards in situ or in operando SERS study of SOFC electrode surfaces. Furthermore, we are optimizing the geometry of Ag@SiO₂ nanoparticles to improve the SERS stability and efficiency at even higher temperatures (e.g., 600 °C). Other coating materials such as TiO₂ and ZrO₂ (ref. 37–40) are also being explored for better thermal stability, although their chemical and photo-catalytic properties under SOFC operating conditions and laser excitation need to be carefully evaluated before implementation.

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Notes and references