

# Surface-Enhanced Raman Spectroscopy Nanostructure in High-Temperature Processes

Subjects: Chemistry, Analytical

Contributor: Jingying Huang, Jiahao Wu, Jing Shao, Youkun Tao

Surface-enhanced Raman spectroscopy (SERS) is a highly sensitive analytical technique based on Raman scatter and utilizes the nanostructures of active metals, such as gold and silver, with roughened surfaces as a signal amplifier. With its enhancement effect and “fingerprint” ability, in situ SERS is able to capture the dynamics of microstructure evolution and trace surface species in real time, which provides direct information for the analysis of a reaction mechanism in various surface processes, including heterogeneous catalysis, electrochemical reactions, etc. SERS has been widely used in operando analysis of surface processes under ordinary temperatures. For application in high-temperature processes, the harsh environment puts forward additional requirements in addition to high sensitivity for the SERS nanostructures, especially concerning thermal stability, chemical inertness, and surface universality.

Keywords: in situ analysis ; SERS ; high temperature ; nanostructures ; thermal stability

---

## 1. Introduction

Surface-enhanced Raman spectroscopy (SERS) has drawn huge interest in trace analysis and chemical reaction mechanism analysis due to its high detection sensitivity, low demanding conditions, and abundant surface information, among others <sup>[1][2][3][4][5][6]</sup>. Despite unique advantages of SERS, materials exhibiting high SERS activity is only limited to a few nano-rough coinage metals, typically Au, Ag, and Cu, because of their unique plasmonic properties <sup>[7]</sup>. As a result, studies on SERS-active material substrates progressed easily early on, but major challenges arose when scientists tried to extend SERS to other substrates. Therefore, numerous research efforts were devoted to improving enhancement capabilities of other substrates, generally by introducing SERS-active nanostructures, or Raman amplifiers, to the desired substrates, which is also referred to as the “borrowing strategy” <sup>[8][9]</sup>. In 1983, researchers had managed to deposit discrete Ag nanoparticles on the surface of n-GaAs, a SERS-inert material, and successfully observed Raman signals of probe molecules absorbing on the SERS-inert material <sup>[10][11][12]</sup>. However, the shortcoming of the method relates to the miscellaneous peaks that stem from the interaction of Ag and the probe molecules, since Ag is a highly chemically active material. Secondly, charge transfers between the electrode materials and Raman amplifiers would also bring interferences to the Raman spectra if the coinage metal is directly deposited on the surface of the materials to be characterized.

So far, SERS has been widely used in ordinary temperature conditions, such as trace molecular detection, electrochemical adsorption, catalysis, etc. SERS technology can detect molecules in ultralow concentration, and even a single molecule <sup>[13][14][15][16]</sup>. In the field of electrochemical reactions, SERS technology can be used to study the adsorption and desorption behavior of molecules and detect the chemical reaction on the electrode surface in real time <sup>[17][18]</sup>. In the field of catalysis, SERS can be used to obtain direct information on the evolution of catalyst surface species and local structure during the reaction processes <sup>[19][20]</sup>.

## 2. Design of Nanostructures for High-Temperature SERS

### 2.1. Substrate-Specific Nanostructures

#### 2.1.1. Layer Deposition

The layer deposition technique suggests that the thicker the protective layer (generally SiO<sub>2</sub> or Al<sub>2</sub>O<sub>3</sub>), the lower the SERS activity exhibited when compared to bare metal nanostructures, which means that thermal robustness is improved at the cost of SERS activity. On the other hand, the coating of protective layer on the SERS-active nanostructures and the substrate limits the studies to SiO<sub>2</sub>- and Al<sub>2</sub>O<sub>3</sub>-related systems <sup>[21][22]</sup>. Nevertheless, it is still a milestone improvement since more SERS activity is retained for the protected SERS-active nanostructures compared to their unprotected counterparts after the heating treatment.

### 2.1.2. Entrapped Nanorods

To stabilize Raman amplifiers without the presence of protective capping layer, Du et al. have managed to entrap Au nanorods (Au NRs) in anodized aluminum oxide (AAO) scaffolds, which make full use of the substrate to offer thermal protection and can be seen as a partial but ultrathick protective layer. The EF of the nanostructure is two to three orders of magnitude for Rhodamine 6G, which shows no significant change after 800 °C treatment for 1 h [23]. It is also worth noting that Au exhibits great chemical-inertness even at high temperature, while Ag exhibits very limited resistance to oxidation [24]. As a result, partial exposure of Au under high temperature could cause far less interference to the reaction system. The strength of the method is that it is capable of exhibiting relatively high SERS activity at ultrahigh temperature, compared to previously described layer deposition methods. However, for as-prepared samples that exhibit excellent performance, scaffold preparations cover or even deconstruct the interface of the samples so as to entrap Au NR, which unavoidably interferes with the analysis and limits the adoption of this approach to create the scaffold-related materials. Moreover, partial exposure of Au NR is likely to introduce a miscellaneous peak to the Raman spectra. Both of these could hinder the extension of the method to broad material systems.

## 2.2. Substrate-Universal Nanostructures

### 2.2.1. Core–Shell Nanostructures

To extend the substrate universality, researchers have managed to coat Raman amplifiers with a protective layer before it is deposited on the substrate. Weckhuysen et al. synthesized Au@SiO<sub>2</sub> and Au@TiO<sub>2</sub> shell-isolated nanoparticles, respectively, typically with the diameter of Au spheres being 76 nm and thickness of protective shell being 1–3 nm [25]. Both Au@SiO<sub>2</sub> and Au@TiO<sub>2</sub> nanoparticles with a 2.2–2.7 nm protective layer exhibited an enhancement factor of four orders of magnitude for Rhodamine 6G after 400 °C treatment for 3 h, which was less than one order lower compared to their unheated counterparts. The stability of Au@SiO<sub>2</sub> and Au@TiO<sub>2</sub> nanoparticles with a 1.2–1.3 nm protective layer were found insufficient above 300 °C. When the temperature was raised to 500 °C, all the structures collapsed.

To extend SERS to even higher temperature, Liu et al. [26] developed Ag@SiO<sub>2</sub> core–shell nanoparticles, with 60 nm Ag spheres being the core to offer SERS activity and SiO<sub>2</sub> shell being 10 nm thick to offer thermal stability, which maintained more than one third of its original enhanced capabilities after heating treatment at 500 °C for 30 min. However, the EF of the as-prepared Ag@SiO<sub>2</sub> nanoparticles was calculated to be around 150 for Rhodamine 6G due to the exponential decay of SERS activity with the increased contact distance from Ag core to probe molecules [26].

### 2.2.2. Embedded Core–Shell Nanostructure

Recently, a group developed a novel hybrid nanostructure of embedded Ag nanoparticles confined by core–shell silica nanospheres, denoted as ESCNs [27]. The approach is to plant ~30 nm Ag nanoparticles on the surface of the ~500 nm SiO<sub>2</sub> core first, and then deposit 3–5 nm SiO<sub>2</sub> shell afterward. The SiO<sub>2</sub> core–shell architecture functions as a thermally robust framework for embedded Ag nanoparticles due to the nanoconfinement effect. With introduction of SiO<sub>2</sub> as thermally robust core and decreased thickness of outermost SiO<sub>2</sub> shell, the EF of ESCNs for Rhodamine 6G reaches  $4.45 \times 10^4$ ,  $1 \times 10^4$ , 69 after 400 °C, 450 °C, 500 °C heat treatment for 2 h, respectively. In addition, it is revealed by 3D-FDTD (three-dimensional finite-difference time-domain) calculation that the self-assembled Ag nanoparticles that embedded in the SiO<sub>2</sub> core–shell consist of plasmonic “hot spots”, which contribute a strong enhancement on individual ECSNs. The theoretical calculation is found to be in good agreement with the experimental observation of ESCNs with different Ag embedding. Therefore, the SERS activity of the ECSNs does not depend on assembling dimers or trimers, as required in previously reported approaches.

## 3. Application of SERS Nanostructure in High-Temperature Processes

### 3.1. Structure Evolution

#### 3.1.1. Thermal Crystallization

The in situ analysis of lattice structure evolution could provide direct information for understanding thermal crystallization. The capability of high-temperature Raman spectra to monitor microstructural changes in melt makes it an effective tool to study the structure of melt at high temperature and provide information to expand the understanding of crystal growth. Sobol et al. studied the microstructure of Li<sub>2</sub>O–B<sub>2</sub>O<sub>3</sub>–MoO<sub>3</sub> using high-temperature in situ Raman spectroscopy [28].

In situ high-temperature SERS can monitor the phase development of crystals during heat treatment with enhanced sensitivity, which could provide abundant information for the study of the thermal crystallization. Tri (8-hydroxyquinoline) aluminum (Alq3) film is one of the most widely used electron transfer and emission materials for organic photodiodes

(OLEDs) [29]. However, the crystallization of Alq3 film and the increase in surface roughness leads to the degradation of OLED [30].

### 3.1.2. Interfacial Interaction

The ability for high-temperature SERS to observe interfacial interactions is of general significance for catalysis, as interfacial bonds play a key role in catalytic reactions. Dai et al. utilized robust SERS nanostructures to study in situ the effects of heating a solid acid, phosphotungstic acid (PTA), on an alumina surface while operating at elevated temperatures in various atmospheres [31]. The robust SERS nanostructures were generated by depositing an ultrathin protective coating (1.2 nm) of alumina on top of silver NWs via ALD. A thin layer of PTA was subsequently decorated on top of the nanostructures. The PTA powder on the silicon chip was tested to initialize the in situ Raman analysis. Raman bands at 1015 and 992  $\text{cm}^{-1}$  were observed, which were attributed to the  $\nu_s$  (W=O) and  $\nu_{as}$  (W=O), respectively, while bands at 935 and 890  $\text{cm}^{-1}$  were attributed to bridging  $\nu_{as}$  (W-O-W) modes. When PTA was loaded onto SERS substrates covered with an  $\text{Al}_2\text{O}_3$  protective layer, differences arose. Band intensities of  $\nu_s$  (W-O) and  $\nu_{as}$  (W-O) reversed, which corresponded to the analysis results of PTA adsorbed onto bare Ag colloids, which suggested that the orientation of PTA on the  $\text{Al}_2\text{O}_3$  surface was likely similar to that on the Ag surface. When the analysis was performed in  $\text{H}_2$  atmosphere at 400 °C, the intensity of the 890  $\text{cm}^{-1}$  band increased.

### 3.1.3. Lattice Dynamics

High-temperature SERS has been applied to monitor the lattice evolution of  $\text{CeO}_2$  in reducing and oxidizing atmospheres.  $\text{CeO}_2$  is an important functional material for various applications, such as heterogeneous catalysis, solid oxide fuel cells, and functional ceramics [32]. The functionality of  $\text{CeO}_2$  depends greatly on the oxygen storage and release capability, which is endowed by the generation and consumption of a key lattice defect, oxygen vacancies. The in situ observation of the lattice dynamics related with oxygen vacancies is critical to reveal the mechanism of  $\text{CeO}_2$  functionality as either a structure stabilizer or electronic promotor in wide applications.

## 3.2. Heterogeneous Catalytic Reaction

### 3.2.1. Ethylene Epoxidation

Raising temperatures can significantly improve reaction kinetics. Although the reaction energy barrier can be lowered by using catalysts, high temperature is still necessary for a large number of catalytic reactions to proceed effectively. SERS can be used to study the heterogeneous reaction in catalytic systems, which can provide valuable insights for understanding the active sites and reaction mechanisms. Kondarides et al. utilized in situ SERS to follow the changes in adsorption state of oxygen and ethylene epoxidation on Ag catalyst surfaces at 1 atmosphere and temperature between 25 and 400 °C [33]. Interactions and reaction mechanisms were carefully examined in three types of silver catalysts: (I) Ag supported on  $\alpha\text{-Al}_2\text{O}_3$ , (II) Ag films deposited on  $\text{SiO}_2$ , and (III) Ag films deposited on the oxygen ion conducting solid electrolyte material,  $\text{Y}_2\text{O}_3$ -stabilized  $\text{ZrO}_2$  (YSZ). For the Ag/YSZ catalyst, Raman spectra were obtained after the catalyst was heated to 300 °C and then cooled to room temperature in oxygen gas flow. Raman bands at 240, 345, 815, 870, and 980  $\text{cm}^{-1}$  were observed, for which 815, 870, and 980  $\text{cm}^{-1}$  were ascribed to the  $\nu$  (O-O) vibrations of adsorbed molecular oxygen, while 240 and 345  $\text{cm}^{-1}$  were ascribed to Ag-O vibrations of Ag- $\text{O}_2$  interactions.

### 3.2.2. NO Reduction

Williams et al. utilized in situ SERS to monitor the exact reactive nature of surface species during reduction of NO by CO on Pt and Pd [3]. The SERS architecture was prepared by electrodepositing ultrathin transition-metal films onto electrochemically roughened gold. When the Pt surface was exposed to an equivalent mixture of NO and CO at room temperature, SERS spectra showed bands at 240, 325, 470, 640, 2080, 2160, and 2230  $\text{cm}^{-1}$ , for which the 240 and 470  $\text{cm}^{-1}$  bands were attributed to Pt-NO stretching and Pt-N-O bending modes, respectively; the 325  $\text{cm}^{-1}$  band was attributed to the Pt-NO stretch of NO adsorbed on bridge sites; the 470 and 2080  $\text{cm}^{-1}$  bands were assigned to the Pt-CO and C-O stretches of terminally adsorbed CO, and the 2160 and 2230  $\text{cm}^{-1}$  bands were attributed to reaction products of CO and NO.

### 3.2.3. CO Oxidation

The oxygen storage capacity of  $\text{CeO}_2$ , which is the ability to accommodate a large number of oxygen vacancies in reducing atmospheres (becoming  $\text{CeO}_{2-x}$ ) without structural destruction of the fluorite ceria lattice and could be oxidized back to  $\text{CeO}_2$  in oxidizing atmospheres, is widely acknowledged as one of the reasons for improving metal/ $\text{CeO}_2$  catalyst activity. Catalytic tests showed that the reaction rate of CO oxidation on Pt/ $\text{CeO}_2$  was enhanced by about two orders of magnitude compared to Pt/ $\text{SiO}_2$ . Li et al. designed Au@Pt- $\text{CeO}_2$  satellite nanostructure to achieve in situ SERS

investigations of oxygen activation and reaction at Pt-CeO<sub>2</sub> interfaces [34]. The in situ SERS spectra of CO oxidation on Au@Pt-CeO<sub>2</sub> showed a Raman band at ~2090 and ~2110 cm<sup>-1</sup>, which were ascribed to CO adsorbed on Pt surfaces and Pt-CeO<sub>2</sub> interfaces, respectively.

### 3.3. High-Temperature Electrochemistry

#### 3.3.1. Molten Carbonate Electrolysis

Hu et al. employed Raman spectroscopy to investigate the solubility of CO<sub>2</sub> in the molten Li<sub>2</sub>O-LiCl system with 4–8 wt% Li<sub>2</sub>O at 873–973 K [35]. When CO<sub>2</sub> was dissolved in LiCl-Li<sub>2</sub>O melts, CO<sub>2</sub> interacted with O<sup>2-</sup> to produce CO<sub>3</sub><sup>2-</sup>, and the three species were at equilibrium when the temperature was held constant. For quantitative analysis of Raman spectroscopy, 13.33 wt% Li<sub>2</sub>SO<sub>4</sub> was used as the external standard. Characteristic bands of SO<sub>4</sub><sup>2-</sup> and CO<sub>3</sub><sup>2-</sup> were obtained at 988 and 1074 cm<sup>-1</sup>, respectively. After baseline subtraction and bandfitting to the Lorentzian equation, the area of the two bands for each spectrum could be attained, which was further utilized to study the relationship between the conversion rate of Li<sub>2</sub>O to Li<sub>2</sub>O<sub>3</sub> and the concentration of Li<sub>2</sub>O in the Li<sub>2</sub>O-LiCl system, along with the relationship of CO<sub>2</sub> solubility and temperature in the Li<sub>2</sub>O-LiCl system. Experimental results indicated that the solubility of CO<sub>2</sub> increases with Li<sub>2</sub>O concentration in the Li<sub>2</sub>O-LiCl system, and it reached a maximum when the Li<sub>2</sub>O concentration was 8 wt% at 923 K.

#### 3.3.2. Solid Oxide Fuel Cells

Solid oxide fuel cells (SOFCs) operating at around 600–1000 °C have the advantages of high energy conversion efficiency, low pollutant emission, and great fuel flexibility [36][37][38][39]. However, the practical application of SOFC has been limited by the degradation issue, in which the adoption of high-temperature SERS could provide important information by monitoring the evolution of the electrode surfaces related to the formation of undesirable phases and species. For example, nickel-based anodes are susceptible to carbon deposition when hydrocarbons are used as fuel. Liu et al. used Ag@SiO<sub>2</sub> as Raman amplifiers to study the deposition and removal of carbon on nickel-based anodes through in situ SERS [40]. Ag@SiO<sub>2</sub> nanoparticle effectively increased the sensitivity toward trace analysis of carbon species, therefore making the tracking of initial carbon deposition feasible. The initiation of coking was found at the exposure of the first 20 mL propane, and carbon deposition was accumulated gradually with continuous exposure. The in situ SERS analysis also revealed that the introduction of CeO<sub>2</sub> increased the resistance of coking on Ni due to surface modification. The in situ SERS study of the kinetics of the initial carbon deposition provided insights into the intrinsic coking tolerance of the material surface. Additionally, fast degradation of cathodes for SOFC due to poisoning by contaminants usually existing in air, such as CO<sub>2</sub>, is one of the major challenges for the development of high-performing cathodes for SOFC.

## 4. Summary

For structure design of high-temperature SERS, two types of strategies have been reported and categorized, which are substrate-specific and substrate-universal nanostructures. The substrate-specific nanostructures, prepared by layer deposition or entrapped metal NR, generally exhibit great thermal robustness with considerable SERS activity. However, this type of nanostructure could only apply to a minority of substrates due to the interference on the sample surfaces. The substrate-universal nanostructures, including core-shell nanostructures and embedded core-shell nanostructure, could apply to a wide range of substrates due to their “first assemble, then deposit” strategy. It is noted that when the thickness of protective layer is held constant, the substrate-universal nanostructures do not exhibit as great a thermal robustness as substrate-specific ones due to the higher surface energy of the former. This challenge is largely resolved by the introduction of a thermal-robust core in embedded core-shell nanostructure. For high-temperature applications, the thermal crystallization properties and local structural changes in the materials during heating treatment have been studied by employing specialized SERS nanostructures. For high-temperature catalytic reactions, the strength of in situ SERS analysis has also been demonstrated to a great extent. For example, with the assembling of “satellite” nanocatalysts around the SERS nanostructure, the reaction mechanism of CO oxidation is investigated by in situ monitoring the characteristic peak during the reaction process. In the field of high-temperature electrochemical reactions, thermally robust SERS nanostructures have been employed to identify the key intermediates in molten carbonate electrolysis and solid oxide fuel cells.

---

## References

1. Camden, J.P.; Dieringer, J.A.; Zhao, J.; Van Duyne, R.P. Controlled Plasmonic Nanostructures for Surface-Enhanced Spectroscopy and Sensing. *Acc. Chem. Res.* 2008, 41, 1653–1661.

2. Brus, L. Noble Metal Nanocrystals: Plasmon Electron Transfer Photochemistry and Single-Molecule Raman Spectroscopy. *Acc. Chem. Res.* 2008, 41, 1742–1749.
3. Williams, C.T.; Tolia, A.A.; Chan, H.Y.H.; Takoudis, C.G.; Weaver, M.J. Surface-enhanced Raman spectroscopy as an in situ real-time probe of catalytic mechanisms at high gas pressures: The CO-NO reaction on platinum and palladium. *J. Catal.* 1996, 163, 63–76.
4. Williams, C.T.; Takoudis, C.G.; Weaver, M.J. Raman spectral evidence of reactive oxide formation during methanol oxidation on polycrystalline rhodium at high gas pressures. *J. Catal.* 1997, 170, 207–210.
5. Ren, B.; Li, X.Q.; She, C.X.; Wu, D.Y.; Tian, Z.Q. Surface Raman spectroscopy as a versatile technique to study methanol oxidation on rough Pt electrodes. *Electrochim. Acta* 2000, 46, 193–205.
6. Kneipp, K.; Wang, Y.; Kneipp, H.; Perelman, L.T.; Itzkan, I.; Dasari, R.R.; Feld, M.S. Single molecule detection using surface-enhanced Raman scattering (SERS). *Phys. Rev. Lett.* 1997, 78, 1667.
7. Campion, A.; Kambhampati, P. Surface-enhanced Raman scattering. *Chem. Soc. Rev.* 1998, 27, 241–250.
8. Tian, Z.Q.; Ren, B.; Li, J.F.; Yang, Z.L. Expanding generality of surface-enhanced Raman spectroscopy with borrowing SERS activity strategy. *Chem. Commun.* 2007, 34, 3514–3534.
9. Wu, Q.; Luo, C.X.; Yu, H.M.; Kong, G.Z.; Hu, J.W. Surface sol-gel growth of ultrathin SiO<sub>2</sub> films on roughened Au electrodes: Extending borrowed SERS to a SERS inactive material. *Chem. Phys. Lett.* 2014, 608, 35–39.
10. Van Duyne, R.P.; Haushalter, J.P. Surface-enhanced Raman spectroscopy of adsorbates on semiconductor electrode surfaces: Tris (bipyridine) ruthenium (II) adsorbed on silver-modified n-gallium arsenide (100). *J. Phys. Chem.* 1983, 87, 2999–3003.
11. Van Duyne, R.P.; Haushalter, J.P.; Janik-Czachor, M.; Levinger, N. Surface-enhanced resonance Raman spectroscopy of adsorbates on semiconductor electrode surfaces. 2. In situ studies of transition metal (iron and ruthenium) complexes on silver/gallium arsenide and silver/silicon. *J. Phys. Chem.* 1985, 89, 4055–4061.
12. Rubim, J.C.; Kannen, G.; Schumacher, D.; Dunnwald, J.; Otto, A. Raman-spectra of silver coated graphite and glassy-carbon electrodes. *Appl. Surf. Sci.* 1989, 37, 233–243.
13. Nie, S.; Emory, S.R. Probing single molecules and single nanoparticles by surface-enhanced Raman scattering. *Science* 1997, 275, 1102–1106.
14. Wang, Y.Q.; Yan, B.; Chen, L.X. SERS Tags: Novel Optical Nanoprobes for Bioanalysis. *Chem. Rev.* 2013, 113, 1391–1428.
15. Hakonen, A.; Rindzevicius, T.; Schmidt, M.S.; Andersson, P.O.; Juhlin, L.; Svedendahl, M.; Boisen, A.; Kall, M. Detection of nerve gases using surface-enhanced Raman scattering substrates with high droplet adhesion. *Nanoscale* 2016, 8, 1305–1308.
16. Garg, P.; Dhara, S. Single molecule detection using SERS study in PVP functionalized Ag nanoparticles. In *Proceedings of the 57th DAE Solid State Physics Symposium, Indian Institute of Technology, Bombay, India*, 3–7 December 2012; pp. 206–207.
17. Li, J.F.; Zhang, Y.J.; Rudnev, A.V.; Anema, J.R.; Li, S.B.; Hong, W.J.; Rajapandiyam, P.; Lipkowski, J.; Wandlowski, T.; Tian, Z.Q. Electrochemical Shell-Isolated Nanoparticle-Enhanced Raman Spectroscopy: Correlating Structural Information and Adsorption Processes of Pyridine at the Au(hkl) Single Crystal/Solution Interface. *J. Am. Chem. Soc.* 2015, 137, 2400–2408.
18. Wu, D.Y.; Ren, B.; Jiang, Y.X.; Xu, X.; Tian, Z.Q. Density functional study and normal-mode analysis of the bindings and vibrational frequency shifts of the pyridine-M (M = Cu, Ag, Au, Cu<sup>+</sup>, Ag<sup>+</sup>, Au<sup>+</sup>, and Pt) complexes. *J. Phys. Chem. A* 2002, 106, 9042–9052.
19. Song, C.Y.; Sun, Y.Z.; Li, J.X.; Dong, C.; Zhang, J.J.; Jiang, X.Y.; Wang, L.H. Silver-mediated temperature-controlled selective deposition of Pt on hexoctahedral Au nanoparticles and the high performance of NPs in catalysis and SERS. *Nanoscale* 2019, 11, 18881–18893.
20. Liu, J.B.; Long, L.; Zhang, Y.S.; Wang, Y.P.; Liu, F.S.; Xu, W.Y.; Zong, M.J.; Ma, L.; Liu, W.Q.; Zhang, H.; et al. Optical properties of Au-core Pt-shell nanorods studied using FDTD simulations. *Front. Phys.* 2016, 11, 118501.
21. Mahurin, S.M.; John, J.; Sepaniak, M.J.; Dai, S. A Reusable Surface-Enhanced Raman Scattering (SERS) Substrate Prepared by Atomic Layer Deposition of Alumina on a Multi-Layer Gold and Silver Film. *Appl. Spectrosc.* 2011, 65, 417–422.
22. Formo, E.V.; Mahurin, S.M.; Dai, S. Robust SERS Substrates Generated by Coupling a Bottom-Up Approach and Atomic Layer Deposition. *Acs Appl. Mater. Interfaces* 2010, 2, 1987–1991.

23. Liu, K.; Ohodnicki, P.R.; Kong, X.Q.; Lee, S.S.; Du, H. Plasmonic Au nanorods stabilized within anodic aluminum oxide pore channels against high-temperature treatment. *Nanotechnology* 2019, 30, 405704.
24. Petrova, H.; Juste, J.P.; Pastoriza-Santos, I.; Hartland, G.V.; Liz-Marzan, L.M.; Mulvaney, P. On the temperature stability of gold nanorods: Comparison between thermal and ultrafast laser-induced heating. *Phys. Chem. Chem. Phys.* 2006, 8, 814–821.
25. Hartman, T.; Weckhuysen, B.M. Thermally Stable TiO<sub>2</sub>- and SiO<sub>2</sub>-Shell-Isolated Au Nanoparticles for In Situ Plasmon-Enhanced Raman Spectroscopy of Hydrogenation Catalysts. *Chem. -A Eur. J.* 2018, 24, 3733–3741.
26. Li, X.X.; Lee, J.P.; Blinn, K.S.; Chen, D.C.; Yoo, S.; Kang, B.; Bottomley, L.A.; El-Sayed, M.A.; Park, S.; Liu, M.L. High-temperature surface enhanced Raman spectroscopy for in situ study of solid oxide fuel cell materials. *Energy Environ. Sci.* 2014, 7, 306–310.
27. Liu, Y.; Lu, J.M.; Tao, Y.K.; Li, N.; Yang, M.T.; Shao, J. Ag-Embedded Silica Core-Shell Nanospheres for Operando Surface Enhanced Raman Spectroscopy of High-Temperature Processes. *Anal. Chem.* 2020, 92, 9566–9573.
28. Sobol, A.; Shukshin, V.; Lukanin, V.; Moiseeva, L. High-temperature Raman scattering study of the Li<sub>2</sub>O–B<sub>2</sub>O<sub>3</sub>–MoO<sub>3</sub> system: I. Detailed comparison of the structures of molten lithium and potassium molybdates. *Inorg. Mater.* 2018, 54, 984–989.
29. Wang, L.-Y.; Chen, L.-L.; Huang, X.-L.; Wang, M.; Zhu, X.-H.; Zou, J.-H. 24.4: A Linear High-Tg Arylphosphine Oxide-Triazine Conjugate as a Doped Electron-Transport Material for Stable Phosphorescent OLEDs. *Proc. SID Symp. Dig. Tech. Pap.* 2021, 52, 321–324.
30. Tang, C.W.; VanSlyke, S.A. Organic electroluminescent diodes. *Appl. Phys. Lett.* 1987, 51, 913–915.
31. Formo, E.V.; Wu, Z.L.; Mahurin, S.M.; Dai, S. In Situ High Temperature Surface Enhanced Raman Spectroscopy for the Study of Interface Phenomena: Probing a Solid Acid on Alumina. *J. Phys. Chem. C* 2011, 115, 9068–9073.
32. Schilling, C.; Hofmann, A.; Hess, C.; Ganduglia-Pirovano, M.V. Raman Spectra of Polycrystalline CeO<sub>2</sub>: A Density Functional Theory Study. *J. Phys. Chem. C* 2017, 121, 20834–20849.
33. Kondarides, D.I.; Papatheodorou, G.N.; Vayenas, C.G.; Verykios, X.E. In-situ high-temperature study of oxygen adsorbed on AG-support and electrochemical promotion effects. *Ber. Der Bunsen-Ges. -Phys. Chem. Chem. Phys.* 1993, 97, 709–720.
34. Wei, D.-Y.; Yue, M.-F.; Qin, S.-N.; Zhang, S.; Wu, Y.-F.; Xu, G.-Y.; Zhang, H.; Tian, Z.-Q.; Li, J.-F. In situ Raman observation of oxygen activation and reaction at platinum–ceria interfaces during CO oxidation. *J. Am. Chem. Soc.* 2021, 143, 15635–15643.
35. Hu, X.W.; Deng, W.T.; Shi, Z.N.; Wang, Z.X.; Gao, B.L.; Wang, Z.W. Solubility of CO<sub>2</sub> in Molten Li<sub>2</sub>O–LiCl System: A Raman Spectroscopy Study. *J. Chem. Eng. Data* 2019, 64, 202–210.
36. Abdalla, A.M.; Hossain, S.; Azad, A.T.; Petra, P.M.I.; Begum, F.; Eriksson, S.G.; Azad, A.K. Nanomaterials for solid oxide fuel cells: A review. *Renew. Sustain. Energy Rev.* 2018, 82, 353–368.
37. Fan, L.D.; Zhu, B.; Su, P.C.; He, C.X. Nanomaterials and technologies for low temperature solid oxide fuel cells: Recent advances, challenges and opportunities. *Nano Energy* 2018, 45, 148–176.
38. Hossain, S.; Abdalla, A.M.; Jamain, S.N.B.; Zaini, J.H.; Azad, A.K. A review on proton conducting electrolytes for clean energy and intermediate temperature-solid oxide fuel cells. *Renew. Sustain. Energy Rev.* 2017, 79, 750–764.
39. Bao, C.; Wang, Y.; Feng, D.L.; Jiang, Z.Y.; Zhang, X.X. Macroscopic modeling of solid oxide fuel cell (SOFC) and model-based control of SOFC and gas turbine hybrid system. *Prog. Energy Combust. Sci.* 2018, 66, 83–140.
40. Li, X.X.; Liu, M.F.; Lee, J.P.; Ding, D.; Bottomley, L.A.; Park, S.; Liu, M.L. An operando surface enhanced Raman spectroscopy (SERS) study of carbon deposition on SOFC anodes. *Phys. Chem. Chem. Phys.* 2015, 17, 21112–21119.