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Multi-component optical sensing of high temperature gas streams using functional oxide integrated silica based optical fiber sensors

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ABSTRACT

In-situ monitoring of the multi-component gas streams in high temperature energy conversion devices offer the promises to higher efficiency via improved understanding of the chemical environments during device operation. While conventional resistive based metal oxide semiconductor gas sensors suffer from strong cross-sensitivity, optical sensing approaches offer intrinsic advantages to achieve gas selectivity based on wavelength specific interactions. This manuscript describes a novel method to achieve multicomponent gas sensing during gas exposure of H_2, CO_2, CH_4 and CO in humid high temperature environments. A single sensor element comprised of a perovskite $La_{0.3}Sr_{0.7}TiO_3$ (LSTO) oxide thin film layer coated on silica optical fiber was used. The sensing responses consisted of two wavelength-specific near infrared (NIR) mechanisms, namely broadband absorption associated with the metal oxide layer, and wavelength localized thermal emission responses associated with the hydroxyl defects within the silica fiber. Principal component analysis (PCA) was applied to couple the two mechanisms to achieve selective gas identification. Successful discrimination of H_2 and CO_2 on a single fiber sensor was achieved, where the results are both stable and reversible. This design demonstrates that by coupling multiple optical mechanisms on a single oxide coated fiber sensor, simple platforms can also achieve multi-component sensing functionality without the added complexity of a sensor array. Thus, it suggests a new approach to construct simple, robust and functional sensor designs capable of gas discrimination and quantification in multi-component gas streams.

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1. Introduction

The efficient operation of energy generation devices such as solid oxide fuel cells rely on the continuous consumption of fuel gases at high temperature (600 – 1000 °C) to generate power [1]. Typical gas stream compositions include a mixture of reducing gas species such as H_2, CO, CH_4, and their reaction products CO_2 and H_2O. In-situ monitoring of the gas concentration and discrimination of gas species offers a promising approach to improve fuel utilization rate, optimize the process control, and enhance the device efficiency [2].

While resistive based semiconductor metal oxide gas sensors have been extensively studied [3–5], they generally suffer from strong cross-sensitivity and poor gas selectivity. Multi-element gas sensor arrays containing different sensing materials coupled with machine learning algorithms offer promises to improve selectivity. [6,7] Although such devices have increased platform complexity and require a large number of electrical connections and contacts, which pose stability risks for high temperature applications [8]. Alternatively, optical approaches based on the characteristic free-space infrared absorption exhibits excellent sensitivity and gas selectivity [9]. However, their implementations inside energy conversion/generation devices remain a major challenge, since the required free-space optical access with a long effective path length is generally not practical, and the instrumentation is not high temperature compatible.

Functionalized oxide based optical sensors have been demonstrated as a promising gas sensing platform in high temperature and harsh environments. They utilize the evanescent wave tunneling effect and waveguiding properties of optical fibers to couple the optical responses (such as absorption or emission) from the metal oxide sensing layer to the detector, without the need for

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electrical wiring or contacts. High conductivity metal oxides which exhibit modulated near infrared (NIR) intensities due to free carrier absorption, such as Al-doped ZnO [10], Nb-doped TiO_2, perovskite $La_{0.3}Sr_{0.7}TiO_3$ (LSTO) [11], and gold nanoparticle embedded binary oxides, which exhibit localized surface plasmon resonance (LSPR) effects [12–16], have all been used for gas sensing applications. In addition, the use of an active light source can be eliminated via collection of either ambient thermal emission from the environment [14,15], or changes in the thermal emissivity of the sensing layer, which can also include near-field effects due to the evanescent overlap between near-field and the guiding modes of the fiber [17]. Distributed temperature and gas sensing can be achieved on a single Bragg reflection based fiber sensor [18], or by leveraging advanced optical interrogation methods such as optical backscattering reflectometry [19]. These advances make optical fiber platforms particularly promising for in-situ mapping of the thermal and chemical profiles inside high temperature energy generation devices.

This manuscript describes a novel approach to achieve successful multi-component gas sensing at 800 °C based on a single metal oxide coated optical fiber sensor. It incorporates two independent near infrared (NIR) sensing mechanisms, namely broadband absorption associated with the applied metal oxide sensing layer, and wavelength localized thermal emission peaks associated with hydroxyl defects within the silica fiber. Wavelength specific optical responses were analyzed for gas discrimination by principal component analysis (PCA), a multivariate data analysis procedure based on singular value decomposition [14,16]. The results showed successful discrimination of H_2 and CO_2 with a monotonic concentration based response on a single LSTO coated silica fiber sensor. This work demonstrates that by coupling multiple optical mechanisms on a single oxide coated optical fiber sensor, simple platforms can also achieve multi-component sensing functionality without the added complexity of a sensor array. It suggests a new approach to construct simple, robust and functional sensor designs capable of gas discrimination and quantification in multi-component gas streams.

2. Materials and methods

As shown in Fig. 1, three sensors with different structures were prepared to evaluate design impacts on their high temperature stability, sensitivity and selectivity. All sensors were based on commercial multimode silica fibers (Thorlabs FGA105-LCA), which consist of a 105 μm core, a 20 μm fluorine doped cladding. First, the plastic protective layer was stripped and the cladding layer was etched by buffered hydrofluoric acid (BHF) [10,17]. This exposed a silica core region of about 5 cm long for oxide coating. One sensor was prepared this way (Fig. 1a) and tested without further treatment. The second sensor was dip coated with a $La_{0.3}Sr_{0.7}TiO_3$ (LSTO) layer onto its etched region (Fig. 1b). The LSTO stock solution was prepared by sol-gel synthesis [18] and deposited via dip coating. A LSTO layer of approximately 60 nm thick was produced after 950 °C annealing in air, consistent with films previously reported [20]. A third sensor was dip coated with an additional SiO_2 capping layer, on top of another LSTO coated fiber (Fig. 1c). The SiO_2 stock solution was prepared via sol gel synthesis by mixing tetraethoxysilane (TEOS): ethanol: D.I. H_2O and dilute HCl at molar ratios of 1: 45: 45: 0.004. The SiO_2 film had an estimated thickness of 60 nm after the same annealing treatment at 950 °C in air when deposited without an underlayer of LSTO sol-gel. However, the multi-layer coating of TEOS-based sol-gel and the LSTO sol-gel was observed to exhibit a nanocomposite microstructure of predominantly LSTO-based nanoparticles embedded within an amorphous silica matrix and having an average thickness of ~80–100 nm, as illustrated in the cross-sectional TEM image of Fig. 2. TEM imaging was conducted on a 200 kV FEI Tecnai F20 TEM and the Focused Ion Beam (FIB) lift-out process was conducted on an FEI Nova Nanolab 600 dual beam FIB using standard lift-out procedures.

3. Results and discussions

3.1. Aging treatment and sensor stability

Details of the gas sensing characterization setup were included in the SI. Prior to sensing experiments, an "aging" treatment at 800 °C was applied to all sensors to investigate their high temperature stability. The treatment consisted of alternating gas flows of 100 sccm N_2 and 100 sccm H_2, each lasting 1 h, for 49 total hours, while a constant 4 sccm humid flow was maintained in the background. For the LSTO coated sensor, initial and final thermal emission spectra, and the time series relative emission intensities were shown in Fig. 3.

For the LSTO coated sensor, the thermal emission spectra in Fig. 3(a) consisted of a broadband region (1400–2000 nm), which is theoretically centered around 2.7 μm according to Wien's displacement law, and two local absorption regions (near 2220 nm and above 2500 nm), which corresponded to the vibration and stretching modes of silica hydroxyl (-OH) defects [17,21,28]. Here, attenuation near the hydroxyl peaks in the regions outside the high temperature zone can strongly reduce and in some wavelength ranges completely obscure the thermal emission intensities from the high temperature portion.

Stability of the fiber sensor can be monitored by the time series plots of baseline intensities in Fig. 3(b). The broadband intensities showed small decreases by less than 10% over 49 h. This region also exhibited reversible gas responses that increased in H_2 and decreased in N_2. This is consistent with the strong reducing ability of H_2 gas, which can increase the free carrier densities in the LSTO thin film, producing a higher absorptivity and hence higher emissivity, based upon Kirchoff's law [17]. Meanwhile, the hydroxyl peak around 2220 nm showed a much stronger intensity reduction of nearly 40%, which did not saturate over 49 h. This is presumably associated with increased formation of silica hydroxyl (-OH)

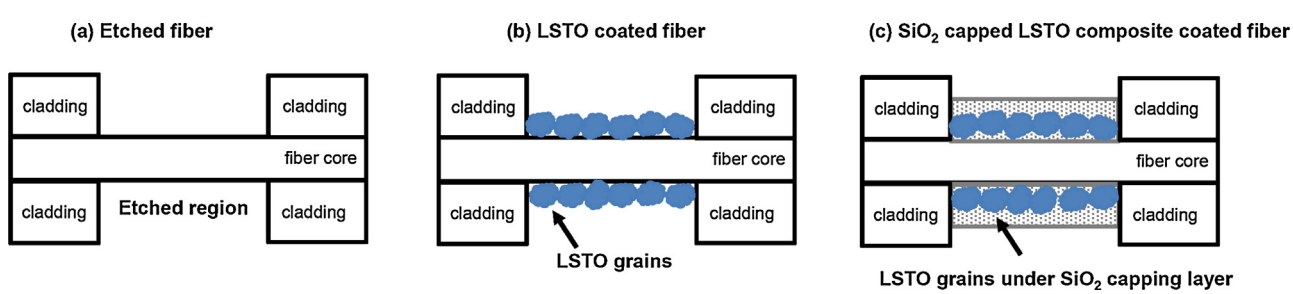

Fig. 1. Schematics of three silica fiber based optical sensors, including: (a) an etched, uncoated fiber, (b) an etched fiber coated with LSTO oxide layer; (c) an etched fiber coated with LSTO and capped with a thin SiO_2 layer.

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