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Nanofiber enhanced stimulated Raman spectroscopy for ultra-fast, ultra-sensitive hydrogen detection with ultra-wide dynamic range

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The increasing importance of hydrogen as an energy carrier and industrial material calls for hydrogen sensors with higher sensitivity, better selectivity, faster response, and wider dynamic range. Here, we report a nanofiber (NF) sensor that satisfies these requirements with a single sensing element. The sensor is based on stimulated Raman scattering spectroscopy, but the tightly confined evanescent field associated with the NF enhances the Raman gain per unit length by a factor of 30 to 10^2 over the state-of-the-art hollow-core photonic crystal fibers and more than 10^4 over free-space beams. The NF has excellent mode quality, which ensures mode-noise-free measurement and maximizes the signal-to-noise ratio. An experiment with a 700-nm-diameter, 48-mm-long silica NF operating in the telecom wavelength band demonstrates hydrogen detection from a few parts per million to 100% with a response time less than 10 s. The sensor would be useful for a range of applications, including detection of hydrogen leakage as well as monitoring of battery charging, fuel cells, and electric power transformer health conditions. © 2019 Optical Society of America under the terms of the OSA Open Access Publishing Agreement

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1. INTRODUCTION

Hydrogen is an important source of energy and a widely used industrial material. It has unique properties such as low ignition energy, high combustion heat, fast flame velocity, and wide explosion range [1]. Detection of its presence and concentration level with high sensitivity and a fast response is critical for safe production, storage, transportation, and utilization of hydrogen [2]. A range of sensing techniques is available, including catalytic, thermal conductivity, electrochemical, work function, mechanical, and optical sensors [3]. However, there seems no single sensing element that can fulfill the performance requirements for hydrogen safety [4]. Currently, researches are directed towards new nanoscale materials and sensing technologies such as field effect-based and fiber-optic sensors [5].

Fiber-optic sensors have the advantages of remote interrogation, being free from electromagnetic interference, and the capability for multiplexing [6]. Most optical fiber-based hydrogen sensors rely on the reaction of hydrogen molecules with thin metallic or metaloxide films coated on the tip or surface of the fibers, and the reaction-induced change in reflectance, absorbance, or optical path length is measured [3]. However, these thin-film-based sensors have problems in achieving a fast response and large dynamic range as well as in temperature stability and cross-sensitivity to other gases such as H_2S , O_2 , and CO [3].

Spectroscopic techniques, utilizing the unique transition of a molecule between its energy levels when illuminated by light with

appropriate frequency, have the advantages of good selectivity and high sensitivity [7,8]. Although a hydrogen molecule has no strong absorption line from the visible to near infrared due to its zero permanent dipole momentum, its relatively large Raman scattering cross section can be used for spectroscopic detection of trace hydrogen [9,10]. With the newly developed hollow-core photonic crystal fibers (HC-PCFs), which simultaneously confine a propagating mode and gas molecules within the central hollow core, significantly enhanced spontaneous and stimulated Raman scattering (SRS) can be achieved, and trace hydrogen detections that are 3 orders of magnitude more sensitive than free-space systems have been demonstrated [11,12]. However, it is hard to fill gas into the long and thin hollow core from the fiber ends, even with the help of a pressure differential. Drilling side holes through the cross section of the fiber reduces gas filling time, but it also compromises the mechanical robustness of the fiber and introduces additional propagation loss [13].

Here we report a nanofiber (NF)-based evanescent-wave SRS spectroscopic technique for trace hydrogen detection. NFs are one of the best carriers for nonlinear light–matter interaction [14,15], and in virtue of the high light intensity in the evanescent field, the SRS efficiency of molecules around a NF could be orders of magnitude higher than in a HC-PCF. The technique has the merits of high selectivity, fast response, large dynamic range, and superior signal-to-noise ratio, enabling the best overall performance of fiber-optic hydrogen sensors to our knowledge.

2. EVANESCENT WAVE SRS WITH A NANOFIBER

Two beams of light, namely, pump and Stokes, are involved in the SRS process. When the frequency difference between them accords with the vibrational or rotational Raman transition of hydrogen molecules, pump photons are converted to Stokes photons, resulting in amplification of the Stokes beam, as illustrated in Fig. 1(a), where the $S_0(0)$ rotational transition of hydrogen with a frequency difference of 354.4 cm⁻¹ is taken as an example. For trace hydrogen detection, the pump beam may be assumed to be undiminished, and the gain of the Stokes beam may be expressed as [16]

$$\frac{\Delta I_s}{I_{s0}} \sim g I_p L \propto \alpha A_{\rm eff}^{-1} P_p N L, \tag{1}$$

where ΔI_s and I_{s0} are the incremental and initial intensities of the Stokes beam, respectively; I_p and P_p are the intensity and power of the pump beam, respectively; g is the Raman gain factor; L is interaction length; α is the fraction of light power (assuming the same for pump and Stokes) in air; $A_{\rm eff}$ is the mode field area; and N is number density of hydrogen molecules. For a fixed interaction length, e.g., 1 cm, the mode field diameter (MFD) at the waist of a free-space Gaussian beam is about 100 µm, obtained by assuming 1 cm Rayleigh length over which the beams propagate without suffering from significant divergence, as shown in Fig. 1(b). In the case of HC-PCF, the light beam is tightly confined in the central hollow core with a MFD of about 10 μ m, as shown in Fig. 1(c), and hence the SRS efficiency per unit length is about 2 orders of magnitude higher than that of the free-space beam. For NF-based SRS, as shown in Fig. 1(d), the pump and Stokes beams interact via evanescent fields mediated by the Raman transition of hydrogen molecules. Due to further reduction in the MFD (i.e., $\sim 1 \mu m$), an additional 2 orders of magnitude enhancement in SRS efficiency can be achieved with a proper diameter of NF.

For the NF-based SRS, there is a balance between the fraction of evanescent wave power α and the mode field area $A_{\rm eff}$. As the diameter of the NF reduces from the wavelength to sub-wavelength scale, the value of α increases monotonically, benefiting the SRS efficiency. However, the $A_{\rm eff}$ first drops then increases rapidly, which eventually reduces the SRS efficiency. The enhancement

of SRS with a NF over the state-of-the-art commercial HC-PCF designed to operate at a specific wavelength may be understood by evaluating the ratio of αA_{eff}^{-1} for the NF over that of the corresponding HC-PCF, and the results are shown in Fig. 2. For different operating wavelengths, there exist optimal diameters of NFs, at which the SRS efficiencies are over 30 to 100 times higher than that of the corresponding HC-PCF. In addition, a NF taper drawn from a standard single-mode fiber (SMF) guides a perfect fundamental mode and is intrinsically free from the mode noise that was identified as a major source of noise in the HC-PCF systems [17], which further improves the signal-to-noise ratio and hence enables higher-sensitivity gas detection. A more detailed analysis of the



Fig. 2. Enhancement of SRS with NFs over HC-PCFs. The wavelength of the pump beams is 1530, 1060, 800, 580, and 440 nm, which matches the transmission bands of NKT Photonics' HC-1550-02, HC-1060-02, HC-800-02, HC-580-02, and HC-440-02 HC-PCFs with MFDs of 9, 7.5, 5.5, 5.3, and 4 μ m, respectively. The MFD and the fractional evanescent wave power in air varies significantly with pump wavelength and the diameter of NF, resulting in a wavelength- and diameter-dependent enhancement factor.



Fig. 1. Spectroscopy with stimulated Raman scattering. (a) Energy diagram of stimulated Raman transition of a hydrogen molecule; the $S_0(0)$ rotational transition is used here as an example. The transition is excited by a pump (ν_P) and a Stokes (ν_S) beam. The pump and Stokes beams co-propagate in (b) free space, (c) a HC-PCF, and (d) a silica NF.

NF-based rotational SRS, considering the effect of polarization states of the pump and probe beams, is presented in the next section.

3. POLARIZATION DEPENDENCE OF SRS GAIN – A QUANTITATIVE ANALYSIS

Different from free-space and HC-PCF gas cells, in which the mode fields are basically transverse, there are significant longitudinal electromagnetic components in the mode field of a NF [18]. Combined with the intrinsic polarization-dependent gain of rotational Raman transition of hydrogen molecules, the SRS process in a NF gas cell is considerably more complicated [19]. A quantitative analysis of hydrogen sensing based on SRS with a NF of circular cross section is conducted, and the imaginary part of nonlinear polarization may be expressed as [20]

$$\vec{P}_{\omega_{S}}^{\rm Im} = -A_{c}E_{p}^{2}(E_{s}\vec{v}_{s} + E_{so}\vec{v}_{so}),$$
where,
$$\begin{cases}
A_{c} = \frac{2\pi^{2}\vec{e}_{o}^{2}\eta_{p}(J+1)(J+2)\gamma_{00}^{2}\Delta N}{15n_{i}(2J+1)(2J+3)\delta\Gamma} \\
\vec{v}_{i} = 3\vec{e}_{p}^{*}[\vec{e}_{p}\cdot\vec{e}_{i}] + 3\vec{e}_{p}[\vec{e}_{p}^{*}\cdot\vec{e}_{p}] - 2\vec{e}_{p}[\vec{e}_{p}^{*}\cdot\vec{e}_{i}],
\end{cases}$$
(2)

where ε_0 is the vacuum permittivity; n_p and n_s are the refractive indexes of the pump and Stokes beams in air, respectively; J is the quantum number of the lower rotational level; γ_{00} is the offdiagonal element of molecular anisotropic polarizability matrix; ΔN is the density difference of the hydrogen molecules between the lower and upper rotational levels of transition; h is Planck constant; Γ is the half-width-half-maximum linewidth of the Raman transition in hertz; E_p and E_s are the amplitudes of the input pump and Stokes beams, respectively; and \vec{e}_i represents $\vec{e_s}$ and $\vec{e_{so}}$, which are the normalized vector fields of the two orthogonal fundamental modes of the Stokes beam propagating along the NF. \vec{e}_s is the one excited by the input probe (Stokes) beam, while $\vec{e_{so}}$ is the orthogonal one generated due to Raman interaction. Putting $\vec{P}^{\rm Im}_{\omega_S}$ into the wave equation of the propagating Stokes beam and assuming a non-diminishing pump field, which is justified for trace hydrogen detection due to the low Raman gain, the coupled wave equations for the two orthogonal states of the Stokes beam are obtained as

$$\begin{cases} \frac{\partial E_s}{\partial z} = \frac{\omega_c^2}{2\beta_c \varepsilon_0 c_0^2} (c_{s,s} E_s + c_{so,s} E_{so}) E_p^2 A_c \\ \frac{\partial E_{so}}{\partial z} = \frac{\omega_c^2}{2\beta_c \varepsilon_0 c_0^2} (c_{s,so} E_s + c_{so,so} E_{so}) E_p^2 A_c \end{cases}, \quad \text{where } c_{i,j} = \frac{\int_{\rho}^{\infty} (\vec{v}_i \cdot \vec{e}_j^*) ds}{\int |\vec{e}_j|^2 ds}, \end{cases}$$

$$(3)$$

where ω_s and β_s are, respectively, the angular frequency and propagation constant of the Stokes beam, c_0 is the speed of light in a vacuum, and ρ is the radius of the NF. For a silica NF with pump and Stokes wavelengths of 1532 nm and 1620 nm, corresponding to the $S_0(0)$ rotational transition of a hydrogen molecule, the SRS gain coefficient for four different input polarization configurations, i.e., linearly parallel, linearly orthogonal, co-directional, and counter-directional circularly polarized, are calculated with varying diameter of the NF and shown in Fig. 3. The gain coefficient is defined as the increase in the total output power of the Stokes beam per parts per million (ppm) hydrogen per unit length per watt pump power over that of the input. It increases with decreasing diameter from 1000 to 700 nm, originating from the increased fraction of the evanescent field power in air and intensity near the surface of the NF.



Fig. 3. Theoretical SRS gain coefficient for different diameters of silica NFs with the pump at 1532 nm and Stokes at 1620 nm, corresponding to the $S_0(0)$ transition of hydrogen. The gain coefficient has a unit of cm⁻¹ · W⁻¹ · ppm⁻¹, representing the gain per centimeter-long NF, per watts of input pump power and per parts per million (ppm) of trace hydrogen. For any polarizations of the input pump and Stokes beams, the SRS gain coefficient should lie between those of the counter-directional (purple line) and co-directional (green line) circularly polarized configurations.

However, further reducing the diameter below 700 nm will decrease the gain, due to the much expanded evanescent field area and thus rapidly diminished pump intensity near the NF. The gain coefficient is the largest for the counter-directional circularly polarized configuration and smallest for the co-directional circularly polarized configuration and lies between these two extremes for other polarization combinations due to the intrinsic characteristics of rotational transition [19].

4. EXPERIMENT AND RESULT

A NF is taper-drawn from a standard silica SMF (Corning SMF-28) by the flame-brushing method [21]. The NF has a waist length of \sim 48 mm with a waist diameter of \sim 700 nm, as shown in Fig. 4(b), and the transmission loss is less than 0.3 dB. Immediately after fabrication, the NF is sealed into an aluminum gas cell (40 cm × 3 cm × 1.5 cm) with two SMF pigtails left outside for optical connection. Trace hydrogen of different concentrations is prepared by mixing pure hydrogen and nitrogen with their fluxes controlled by two mass-flow controllers. A dust filter is placed at the inlet of the gas cell to prevent dust particles from contaminating the NF. Such a packaged NF gas cell has worked well without performance degradation for a period of over six months. All the measurements are conducted at room temperature and atmospheric pressure.

A wavelength modulation spectroscopic technique [23], which, as shown in Fig. 4(c), can readily distinguish the sharp Raman transition line of hydrogen from the flat Raman spectrum of silica, is used to measure the forward-stimulated Raman gain signal. The experimental setup is shown in Fig. 4(a). The probe source is an external-cavity diode laser (ECDL) fixed at 1620.876 nm. The pump beam is from a distributed-feedback (DFB) laser and is amplified by an erbium-doped fiber amplifier (EDFA) before being combined with the probe beam by a wavelength-division

multiplexer (WDM). The DFB is wavelength modulated at 44 kHz through its inject current, while its center wavelength is ramped from 1532.826 to 1532.838 nm. A photodetector is used to detect the SRS signal, and the second harmonic is demodulated by use of a lock-in amplifier. For each set of experiments, the polarization controllers for both pump and Stokes beams are first



Fig. 4. Experimental details. (a) Experimental setup of NF-based SRS for trace hydrogen detection. DFB, distributed-feedback laser (Eudyna FLD5F15CX) with a linewidth of 5 MHz; EDFA, erbium-doped fiber amplifier (Amonics AEDFA-EX); F1, filter 1, for minimizing ASE noise from EDFA, with bandwidth of 0.8 nm; PC, polarization controller; WDM, 1530/1620 wavelength-division multiplexer; ECDL, externalcavity diode laser (Agilent 81600B), with linewidth of 300 kHz; F2, filter 2, for elimination of the pump beam, with bandwidth of 0.8 nm; PD, photodetector (Nirvana-2017); Lock-in, lock-in amplifier (Stanford Research Systems SR830); DAQ, data acquisition (National Instrument USB 6212); MFC, mass-flow controller (Sevenstar CS200); DF, dust filter (TAIYO SFF-08). (b) Scanning electron microscope image of the nanofiber. (c) Rationale of the wavelength modulation. The narrow Raman gain line of hydrogen can be distinguished from the broad and flat Raman gain spectrum of silica by method of wavelength modulation. Inset: Raman spectra of silica [22] and rotational Raman transition line positions of hydrogen [11] over a larger range of wavenumber.

adjusted to maximize the signal and then kept fixed throughout the experiments.

The second-harmonic outputs of the lock-in amplifier are shown in Fig. 5(a), with the pump laser detuned from -6 to +6 pm with respect to 1532.832 nm, at which the frequency difference between the pump and Stokes beams is 354.36 cm⁻¹ and corresponds to the line center of the $S_0(0)$ rotational transition. The pump level is kept at 305 mW, while the hydrogen concentration is varied from 0.20% to 0.4%. The noise level is evaluated by filling pure nitrogen into the gas cell and recording the secondharmonic output when the center wavelength of the pump beam is swept across the S(0) transition of hydrogen. The pink line in Fig. 5(a) shows the recorded noise, which has a standard deviation (i.e., 1σ value) of 0.248 μ V and is within 2 times of the theoretical shot noise for -4.2 dBm probe power into the photodetector. In comparison with the signal of 114.8 μ V for 0.4% hydrogen, a noise-equivalent detection limit of 8.6 ppm hydrogen is achieved. The dynamic range is also investigated by measuring SRS signal for different concentration levels from pure to 200 ppm hydrogen. As shown in Fig. 5(b), the SRS signal has a linear relationship for up to 50% hydrogen. For higher concentration, the slope of the SRS signal versus concentration increases due to the reduced linewidth of Raman gain for pure hydrogen. Considering the achieved sub-10-ppm detection limit, the dynamic range is determined to be over 5 orders of magnitude.

The SRS signal of 0.4% trace hydrogen for different pump power levels is shown in Fig. 6(a). As shown in the inset, with increasing pump power, the amplitude of the SRS signal increases linearly with it, while the noise level is approximately unchanged, indicating that a better detection limit could be achieved with a higher pump level. According to the slope of the SRS signal versus pump power, the Raman gain coefficient is determined to be 1.70×10^{-9} cm⁻¹ · W⁻¹ · ppm⁻¹, about 1.4 times lower than the optimal SRS gain calculated theoretically. This difference may originate from the non-uniform diameter of the NF and the nonoptimized polarization configuration between the pump and Stokes beams. We further recorded the second-harmonic output for pure nitrogen (noise) with the pump wavelength fixed at the center of the Raman line with a 100 ms lock-in time constant for 2 h and conducted Allan variance analysis; the results are shown in



Fig. 5. Results of hydrogen detection with SRS and a NF. (a) Second-harmonic output of lock-in amplifier when the pump is scanned across the Raman line; (b) second-harmonic output as function of hydrogen concentration. The pump level is 305 mW, and the time constant of the lock-in is set to 10 s with 18 dB/Oct roll-off.



Fig. 6. (a) Second-harmonic output of lock-in amplifier for different pump power levels with a fixed hydrogen concentration of 0.4%. (b) Evaluation of noise equivalent concentration (NEC) by Allan deviation. The lock-in time constants for (a) and (b) are 10 s and 100 ms, respectively, with the same roll-off speed of 18 dB/Oct.



Fig. 7. Response and recovery time of NF-based on SRS hydrogen sensor.

Fig. 6(b). The detection limit is about 3 ppm for the optimal integration time of 260 s.

A further advantage of the NF-based SRS hydrogen sensor is its fast response and recovery time. The exposed evanescent field of the NFs makes it easier to access than HC-PCFs and overcomes the issues of the long gas filling time associated with HC-PCF sensors. The Raman process is much faster than the chemical/ physical reaction between gas molecules and functional coatings, avoiding the problem of coated fiber sensors. The response time of our sensor is tested by fixing the pump wavelength to the center of the Raman line and recording the second-harmonic SRS signal when the hydrogen concentration is varied sequentially by adjusting the mass-flow controllers. Figure 7 shows the secondharmonic output of lock-in with a time constant of 1 s for three different hydrogen concentrations of 0%, 2%, and 4%. The response time is less than 10 s, and there is no residual signal in the recovery process. It should be mentioned that the measured response time is not limited by the NF sensor itself and could be further decreased by reducing the size of the gas cell and the

length of gas pipe between the gas cell and the mass-flow controllers.

5. DISCUSSION

To summarize, we have reported a trace hydrogen detection technique with NF-enhanced SRS. The technique employs the Raman signature of molecules and is intrinsically selective. The wavelengths of the pump and probe beams can be flexibly chosen, as long as their frequency difference still matches the selected Raman transition, to avoid overlap with the absorption lines of other common molecular species in air and hence to effectively alleviate the problem of cross sensitivity. The NF is taper-drawn from standard telecom SMF, and the pump and Stokes wavelengths are in the near-infrared telecommunication band, allowing the use of high-quality telecom-band lasers and other fiber-optic components to make cost-effective sensors. The large and tightly confined evanescent field around the NF enables significantly enhanced Raman gain over the conventional free-space systems and HC-PCFs for the same input pump power, while the excellent single-mode quality of adiabatically tapered NF ensures low noise detection of the Raman signal, resulting in significantly enhanced signal-to-noise ratio and hence unprecedented detection sensitivity. The intrinsically fast Raman process and linear dependence of the SRS signal on hydrogen concentration enable fast sensors with large dynamic range.

With a 700-nm-diameter, 48-mm-long NF, trace hydrogen detection with a noise equivalent concentration of 8.6 ppm (10 s lock-in time constant) and dynamic range of 5 orders is achieved with a pump power level of 305 mW. Allan variance analysis shows that the detection limit could go down 3 ppm for 260 s integration time. The response time is determined to be less than 10 s. The superior performance of the NF-based SRS hydrogen sensor, i.e., high sensitivity and selectivity, large dynamic range, fast response, non-residual recovery, and low cost, make it more advantageous for practical application than the previously reported techniques, as listed in Table 1.

The SRS signal and hence the performance of the hydrogen sensor may be further improved by operating at shorter wavelengths. With optimized diameter, the mode field is more tightly

Table	1.	Comparison	of O	ptical	Techniques	s for	Hydrogen	Sensing	ľ

Techniques	Functionalization	Sensing Elements	LLD (ppm)	ULD (ppm)	Response Time	
MZ [24]	Pd wire	6 cm coated single-mode fiber	2	10 ²	<8 min	
LPG [25]	Pd film	6 cm coated long-period grating	5×10^{2}	1.6×10^{5}	<7 min	
FBG [26]	Pd film	1.2 cm coated fiber Bragg grating	10 ³	4×10^4	<7 min	
FPI [27]	Pd film	1 cm coated Fabry-Perot interferometer	32	5×10^{4}	<70 s	
SPR [28]	Pd film	1.5 cm coated multi-mode fiber	8×10^{3}	10^{6}	<5 min	
EWA [29]	Pd film	1.5 cm coated multi-mode fiber	2×10^{3}	6×10^{3}	<60 s	
TLSRS [30]	None	40 cm thermal lens tube	9	5×10^{5}	N. A.	
PASRS [31]	None	14 cm acoustic tube with microphone	4.6	5.6×10^{4}	N. A.	
SR [11]	None	1 m HC-580-02 fiber	4.7	5×10^{4}	<3 min *	
SRGS [12]	None	15 m HC-1550-02 fiber	17	10^{6}	<4 h *	
This Work	None	4.8 cm silica nanofiber	3	10^{6}	<10 s	

"LLD, lower limit of detection; ULD, upper limit of detection; MZ, Mach–Zehnder; LPG, long-period grating; FBG, fiber Bragg grating; FP, Fabry–Perot interferometer; SPR, surface plasma resonance; EWA, evanescent wave absorption; TLSRS, thermal-lens stimulated Raman spectroscopy; PASRS, photo-acoustic stimulated Raman spectroscopy; SR, spontaneous Raman scattering; SRGS, stimulated Raman gain spectroscopy. * The response time is calculated based on the gas-filling dynamics with assumption of differential pressure of 1 bar [32].

confined around the NF at the visible, and thus the light intensity, reflected by the E_p^2 term in Eq. (3), of the evanescent field can be significantly higher than that in telecommunication band. Furthermore, as the SRS gain is proportional to optical frequency of the pump/Stokes beam, reflected by the $\omega_s^2 \beta_s^{-1}$ term in Eq. (3), there will be another proportional enhancement of the SRS signal due to increased optical frequency. As an example, with a 250-nm-diameter NF with a pump wavelength of 532 nm, another 20 times enhancement of SRS signal for the same $S_0(0)$ rotational transition is anticipated. The technique could also be used to detect other Raman-active gases such as nitrogen, oxygen, carbon dioxide, etc.

In real applications, temperature fluctuation and vibration would cause changes in the polarization states of the pump and Stokes beams and result in drift of the Raman signal. Polarization scramblers or highly birefringent NF combined with polarization-maintaining transmission fibers may be used to overcome this problem [33]. The ambient temperature and pressure, influencing the population density of the hydrogen as well as its Raman transition linewidth, may also cause drift in the amplitude of the Raman signal. Under moderate fluctuation of temperature and pressure, the change of signal amplitude is small and estimated to have drift coefficients of -4×10^{-3} K⁻¹ and 5×10^{-4} kPa⁻¹, respectively [20,34]. The stimulated Brillouin scattering (SBS) may cause power loss to the pump and set a limit to the pump power level as well as the length of the fiber link, which should be considered for applications that require remote detection [35].

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