Hydrogen has gained a substantial amount of interest in recent years, and it is considered to be an important future carrier of energy. Hydrogen has been well-known since the 18th century and was used as the first lifting gas for balloons and airships in history. The current use of hydrogen is quite diverse.

In the chemical industry hydrogen is used as hydrogenating agent, e.g., to increase the saturation level of unsaturated fats and oils or as reducing agent of metallic ores. The petroleum industry makes use of hydrogen for the production and processing of petrochemical fuels. There are some side-show branches where hydrogen is used for example as a shielding gas for welding methods or as a power fuel in submarines. The underlying idea of the future use of hydrogen is to use a renewable or nuclear energy source to dissolve water – via electrolysis – into hydrogen and oxygen. The hydrogen would then be stored in one way or another and function as an energy carrier that can be turned back into energy either by burning it with oxygen or by using it in a fuel cell to directly generate electrical power. In particular fuel cells have received a lot of attention in the past ten years because of their very high efficiencies.

Why is Sensing of Hydrogen so Important?

Hydrogen will, upon ignition, detonate in air at mixing levels between 4% (vol.) to 72% (vol.), a very wide range.
by the human eye. To make things worse, it is tasteless, odourless, and colourless, making detection for a human without aids almost impossible. Wherever hydrogen is used, and wherever it can mix with air and ignite, monitoring for leaks is necessary to avoid catastrophes. For industrial, research and military applications, the sensors are part of the inevitable initial investment and the costs are not a major issue. However, if consumer products are to be powered with hydrogen, there can be no doubt that the most stringent measures will be required to prevent a hydrogen leak and to detect it once it has occurred. Currently, sensors capable of registering a hydrogen leak at explosive levels and reporting it quickly cost on the order of a thousand US dollars. Research is urgently required into hydrogen sensors that are small, light, reliable, fast, reusable and above all — cost effective.

**Applications for Photonic Crystals**

Here, we are going to present a metallic photonic crystal sensor for gas applications. In general, plasmonics has the potential to touch many different fields as diverse as physics, nanooptics, spectroscopy, biology and sensing. Micro- and nanostructuring of the material allows us to tailor the optical properties in a wide spectral range. Many revolutionary concepts seem to be feasible with this kind of tailored materials in the future, e.g., cloaking or the “perfect lens”. However, up to today there are few real-world applications for photonic crystals even though the optical plasmon resonance has been a promising candidate for sensing applications for a number of years. In the structure we present here, the optical properties of our device are sensitive to hydrogen, providing a distinct effect that can be measured optically. The structure in this work is a multilayer sample, consisting of a WO$_3$ waveguide and an additional nanostructure of gold on top. The structure is depicted in Figure 1a, Figure 1b shows a height profile of the sample. The cross-section in Figure 2 gives detailed information about the dimensions.

In order to obtain some more information about the whole sample, the different layers can be resolved with scanning electron microscopy (Fig. 3a). In higher magnification, the gold wires are nicely visible (Fig. 3b).

The effect that we aim to measure is shown qualitatively here. It is called the gasochromic effect. Hydrogen incorporation into the WO$_3$ causes a colour change to this layer. Hydrogen diffuses into the porous WO$_3$ crystal, which causes a change of the optical properties of the photonic crystal (Fig. 4). This effect has been well known for several years and has been established in the construction industry as part of so-called “smart windows”.

**Nanostructured Surface**

Why use a nanostructured surface? Figure 4 demonstrates that the response of bare WO$_3$ to hydrogen is rather qualitative, making it difficult to predict the exact amount of hydrogen. In our configuration, the WO$_3$ acts as a waveguide, and in combination with the gold wire array on top, its resonance frequency depends on the amount of hydrogen around. Choosing the right dimensions, coupling of the waveguide mode and the plasmonic mode of Au to a new quasiparticle called waveguide-plasmon-polariton takes place. Its spectral behaviour is strongly depending on the hydrogen concentration due to the hydrogen sensitivity of WO$_3$. Figure 5 shows a typical simulated extinction spectrum and the shift of the resonance due to H$_2$ incorporation. The presence of the waveguide resonance and its steepness increase the sensitivity substantially.
The change of the extinction spectra in presence of 5 % Vol. H₂-gas is shown in Figure 6. The spectra show the extinction of the metallic photonic crystal as a function of time, demonstrating the increased diffusion of hydrogen into the structure. We plot the extinction (negative logarithm of transmission) over wavelength. A typical increase in extinction of 0.5 corresponds to a transmission change of 500 %. The advantage stems from the combination the sensitivity of WO₃ and the accuracy of photonic resonances which are combined in this new sensor design.

Most conventional hydrogen sensors available on the market are based on electrochemical changes of certain properties of a semiconductor in presence of hydrogen, e.g., the ohmic resistance. They are longlife stable and very precise but expensive and dangerous in explosive environments such as refineries or in the process industry. An optical sensing does not require electric contacts in the potentially explosive environment. In mass-production fabrication, this could be a very sensitive, secure, small, and cost effective option in comparison to the conventional ones.
In Figure 7, we show a hand-held prototype of our sensor, suitable for threshold surveillance of the lower-explosion-limit of hydrogen at 4 % (Vol.). The laser diode operates at 640 nm and a photodiode measures in reflection the change in the signal due to hydrogen incorporation in the metallic photonic crystal. The sensor head with the sample and the whole electronics for the sensor are placed on a circuit board. Future designs will be further miniaturized to fulfill the industrial requirements concerning supply voltage and output current. This makes the whole device a plug-and-play sensor that can be used by many of our partners in the “hydrogen economy”.

Outlook

The concept can be extended towards an “all-optical hydrogen sensor”. This will give the opportunity to spatially separate the detection and analysis of the measurement, which adds to the level of safety.