

Highly sensitive hydrogen gas sensor based on a capacitor-like Pt/TiO₂/Pt structure with large-scale nanoporous top electrode

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ABSTRACT

Metal-oxide semiconductor gas sensors with capacitor-like Pt/TiO₂/Pt electrode arrangement and very narrow (~100 nm wide) top electrodes were shown to exhibit extremely high responses ($R_{\text{air}}/R_{\text{H}_2} = \sim 10^7$ at 10 000 ppm H₂) to hydrogen even at room temperature. It is thanks to the very high electric field intensity and the narrow top electrode, which allows for hydrogen diffusion under the electrode. Moreover, they are capable of resistive switching within the same sensing structure, which allows them to operate as gasistors, i.e. gas sensors with intrinsic memristive memory. Such sensors however suffer from two major drawbacks: the very high baseline resistance (>1 TΩ at 0 ppm H₂) which renders response to low H₂ concentrations unmeasurable, and the necessity to use e-beam lithography in the fabrication process. Here we present a sensor which eliminates both of the problems. It is based on a similar capacitor-like Pt/TiO₂/Pt structure, but with a large-scale nanoporous top Pt electrode. It is shown that the sensor can detect 3 ppm of H₂ gas in dry air even at room temperature, while providing extremely high response to higher H₂ concentrations (~10⁹ at 10000 ppm H₂). Humidity decreases the sensor response moderately, particularly at room temperature. We also demonstrate that the sensor is capable of resistive switching, although the device resistance after the electroforming process becomes too low to be effectively used as gasistor.

1. Introduction

Zero-carbon energy carriers are gaining importance, particularly in the context of storage and transport of renewable energy [1]. Hydrogen is a promising candidate for high density energy storage and transport due to its suitable physical properties. Considering hydrogen's flammability and small easy-diffusing molecules [2], reliable H₂ gas sensing has become essential. Chemiresistive gas sensors, which detect reducing or oxidizing gases by measuring the change of resistance of metal oxide semiconductors (MOS) – typically SnO₂ or TiO₂ – offer a reliable and cost-effective way of H₂ detection [3,4]. However, currently available MOS gas sensors with comb-like electrodes depicted in Fig. 1(a) typically operate at elevated temperatures of 200–400 °C [6,7], which increases the power consumption and manufacturing costs significantly. To overcome this issue, a transition to the nanoscale has proven to be a feasible way [5,8]. Chemiresistive gas sensors with nanostructured gas-sensing material (e.g. nanowires, nanoparticles, or thin films) are

well known for their high sensitivity and fast response rates [9]. A high surface-to-volume ratio and easy diffusion of the target gas can be achieved in structures such as nanotubes [10,11] and nanowires [12,13]. In the case of thin-films-based sensors, a porous metal oxide rather than compact is preferred to increase the detection performance [14–16]. Following the downsizing trend, a novel type of sensor with the Pt/TiO₂/Pt capacitor-like electrode arrangement and nanoscale top electrode, depicted in Fig. 1(b), was reported to operate at room temperature [8]. Fast detection and high response (~10⁷ at 10 000 ppm H₂) were achieved by using a thin (30 nm) nanocrystalline TiO₂ film and very narrow (~100 nm) top electrode (TE) [17]. This arrangement ensures very high electric field intensity and enables diffusion of H₂ into the TiO₂ located under the TE. The combination of a strong electric field and H₂ within the same volume of the TiO₂ layer changes the electron transport mechanism from thermionic emission to hot electron drift, adding an additional sensing mechanism and increasing the total sensor response. In this previous work of ours the narrow TE was fabricated by

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electron beam lithography, which increases the production costs and limits the application potential of such sensors. Moreover, the sensors with such narrow top electrodes exhibit extremely high baseline resistances ($>1\text{ T}\Omega$), way above the measurement limit of most setups. Such high baseline resistance limits the measurable response of the sensors, particularly to low H_2 concentrations.

We aim to solve both above-mentioned problems (the use of e-beam lithography and the very high baseline resistance) by replacing the narrow top electrode (Fig. 1(b)) by a large-scale porous TE (Fig. 1(c)). This goal could be achieved by using an electrically conductive and permeable composite membrane for the TE [18]. Another approach could be to use self-assembled nanospheres as a shadow mask [19]. In this work, we focus on a technologically even less complicated method, where the nanoporous top Pt electrode (Fig. 1(c)) is prepared by standard reactive magnetron sputtering of Pt in $\text{Ar} + \text{O}_2$ atmosphere and subsequent annealing. The final TE has a structure of interconnected Pt islands [20,21] (see Fig. 1(f)). Since the necks between the Pt islands have a width of $\sim 100\text{ nm}$, the nanoporous TE maintains the advantages of the narrow TE but provides much larger electrode area (in our case $\sim 200 \times 200\text{ }\mu\text{m}^2$). The large electrode area decreases the baseline resistance by several orders of magnitude, significantly enhancing the sensitivity, particularly at low H_2 concentrations. The use of a nanoporous TE thus enhances the sensor performance and eliminates the necessity to use e-beam lithography at the same time. The technology of preparing such porous Pt electrodes with high surface-to-volume ratio, suitable e.g. for fuel cells, was originally reported by works of Cho et al. [21] and Jung et al. [22]. Here, we have adopted and optimized the technology to prepare a large-scale nanoporous Pt TE in the capacitor-like Pt/TiO₂/Pt gas sensing structure. To the best of our knowledge, this is the first report of this type of hydrogen gas sensor with large-scale nanoporous TE prepared via deposition of metastable PtO_x and subsequent annealing.

We have focused on TiO₂-based sensors for two reasons. First, both

TiO₂ and SnO₂ exhibit very high response to H_2 . In particular, the response of capacitor-like Pt/TiO₂/Pt sensors to 1% H_2 can be as high as 7 orders of magnitude. Second, the investigated capacitor-like sensing structures are expected to be capable of resistive switching, which is also of our interest (see below) and is particularly well explored for TiO₂-based memristive cells [23–25]. In addition, such sensing structures were shown to function as gasistors (gas sensors with intrinsic memristive memory) [26–29]. Therefore, we also evaluate the resistive switching properties of the prepared devices.

2. Materials and methods

The sensing Pt/TiO₂/Pt structure with nanoporous Pt TE (Fig. 1(c and d)) was prepared on c-cut sapphire substrate. The 20 nm thick, $\sim 200\text{ }\mu\text{m}$ wide Pt bottom electrode was prepared by DC magnetron sputtering through a shadow mask. After shielding the contact pads of the electrode, the 50 nm thick TiO₂ layer was deposited by reactive magnetron sputtering from Ti target in $\text{Ar} + \text{O}_2$ atmosphere. The nanoporous $\sim 200\text{ }\mu\text{m}$ wide Pt TE, transverse to the bottom electrode, was prepared as follows. First, a metastable PtO_x layer was deposited by reactive magnetron sputtering from Pt target in $\text{Ar} + \text{O}_2$ atmosphere through the same shadow mask as the bottom electrode. The deposition time was 150 s at the sputtering voltage of 430 V, power of 1 W/cm^2 , Ar partial pressure of 0.164 Pa and total deposition pressure of 0.97 Pa. Subsequently, the whole Al₂O₃/Pt/TiO₂/PtO_x stack was annealed at 550 °C for 1 h in ambient air. During the annealing, the PtO_x decomposed and formed a metallic nanoporous Pt electrode. As a result, the TE changed its resistance by 3 orders of magnitude from 50 k Ω to 20 Ω . The SEM cross-section image (Fig. 2(a)) of the annealed stack and the AFM topography image (Fig. 6(a)) of the porous TE revealed an interconnected network of Pt islands with height of several tens of nm and, pore sizes of roughly 200 nm and the width of the Pt necks of roughly $\sim 100\text{ nm}$. The annealing step also increased and stabilized the TiO₂

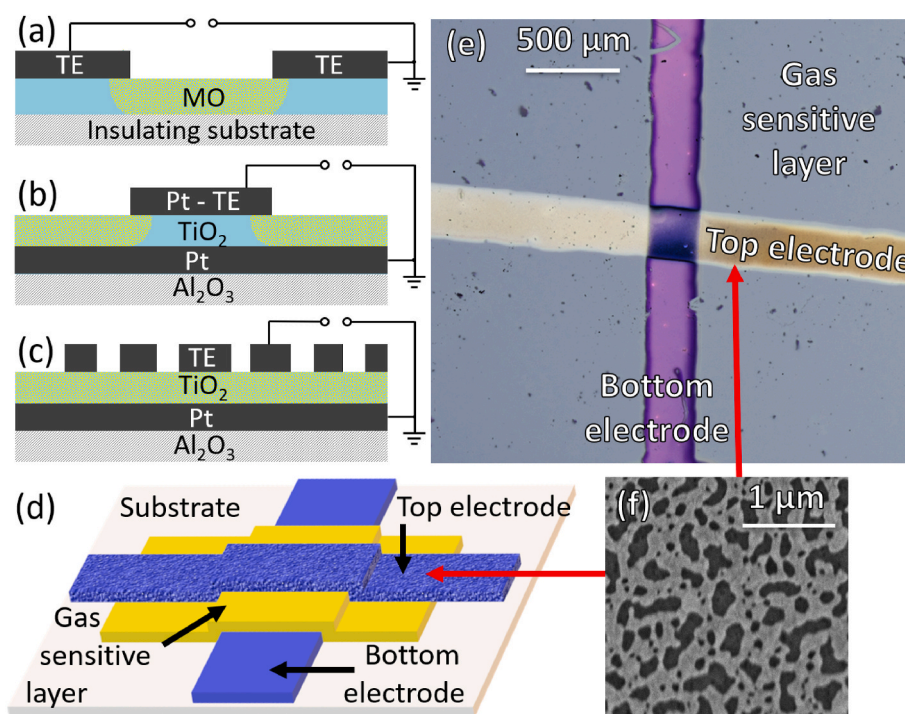


Fig. 1. Cross-sectional diagram of (a) a standard MOS gas sensor with comb-like electrode arrangement, (b) sensor with capacitor-like Pt/TiO₂/Pt arrangement, and (c) sensor with capacitor-like Pt/TiO₂/Pt arrangement and nanoporous Pt TE. The H_2 diffusion through the TE is inhibited, the green areas denote the areas of TiO₂ where the H_2 can diffuse. (d) Schematic diagram of the capacitor-like structure. (e) Top view of the prepared sensor with large-scale TE and the electrode cross section area of $200 \times 200\text{ }\mu\text{m}^2$. (f) Top view SEM image of the porous TE. For clarity, the dimensions in panels (a–d) are not to scale. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

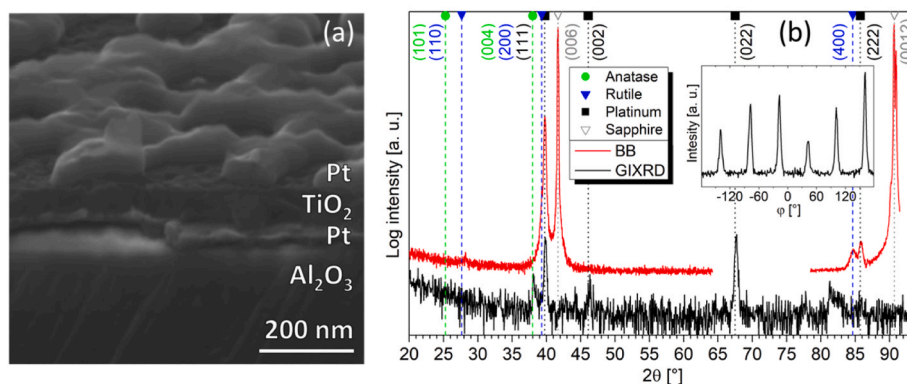


Fig. 2. (a) SEM cross-section scan of the annealed $\text{Al}_2\text{O}_3/\text{Pt}/\text{TiO}_2/(\text{nanoporous})$ Pt stack displaying the morphology of the layers and the porosity of the TE created by decomposition of the PtOx layer. (b) XRD pattern of the annealed sensor #2. Rutile 200 and 400 diffractions in the symmetrical (BB) scans (top patterns) show a preferential orientation of TiO_2 grains. The ϕ -scan (inset) together with the grazing incidence (GIXRD, bottom pattern) indicate the biaxial texture of the TiO_2 layer.

crystallinity and smeared the TiO_2/Pt interfaces which otherwise would form a strong Schottky barrier [30]. Based on the XRD data of reference samples prepared in the same way but without the TE, the TiO_2 layer consists of mixture of rutile/anatase phases with an average coherence domain (grain) size of ~ 15 nm.

To demonstrate the robustness of this method, another series of samples was fabricated using the same arrangement and fabrication process, but with different PtOx deposition and annealing parameters. To maximize the porosity of the TE and at the same time maintain its electrical conductivity (the interconnected Pt islands), we optimized the annealing temperatures (550 – 700 °C) and PtOx thickness (35 – 90 nm). The final PtOx layer of the sensors (further referred to as sensor #2 and #3) with the thickness of 40 nm was deposited with the same sputtering power of 1 W/cm² for 70 s at a voltage of 490 V in mixed Ar + O_2 atmosphere with Ar partial pressure of 0.190 Pa and the total pressure of 0.340 Pa. The samples were then annealed at 660 °C for 1 h in ambient air. According to XRD patterns in Fig. 2(b), the TiO_2 recrystallized predominantly to the rutile phase with a biaxial texture. The coherent domain size of 17 ± 2 nm was derived from 200 to 400 rutile diffractions by Williamson-Hall analysis [31,32]. Further details on XRD analysis of the TiO_2 layer in a $\text{Pt}/\text{TiO}_2/\text{Pt}$ stack can also be found in our previous works [33,34].

The H_2 gas sensing characterization was performed in a constant gas flow regime at 100 sccm (standard cubic centimeters per minute), while the sensor was placed in a closed chamber inserted in a furnace with PID-controlled temperature. The H_2 concentration was adjusted by mixing a pure synthetic air with a pre-mixed $10\,000$ ppm H_2 (for H_2 concentration between 300 and $10\,000$ ppm) or 100 ppm H_2 (for H_2 concentration between 3 and 100 ppm) in synthetic air using two mass flow controllers (Vögtlin Instruments). The relative humidity (RH) was adjusted by controlling the flow through a wet branch with a water bubbler and measured by a RH sensor (Honeywell HID-4000) located beyond the chamber outlet, where the gas was already cooled down to room temperature. The resistance was measured by Keithley 6485 Picoammeter/Voltage source providing an upper resistance measurement limit of ~ 1 TΩ. Bias voltage of $U_B = +0.5$ V was used for all R (time) (dynamic gas response) characteristics measured at 100 °C and at room temperature. For measurements at 150 °C, U_B of $+0.1$ V was used to avoid sample damage. The response S was evaluated as $(R_0 - R_g)/R_g$, where R_0 is the baseline resistance at 0 ppm H_2 and R_g is the resistance at the end of the H_2 exposure window. The response time constant τ_{res} was

obtained from exponential decay fit of the resistance $R = R_g + A \cdot e^{-\left(\frac{t-t_0}{\tau_{\text{res}}}\right)}$ at the initial part of the H_2 window (at least 20 data points). The recovery time constant τ_{rec} was obtained from the exponential decay

fit of the resistance $R = R_0 - B \cdot e^{-\left(\frac{t-t_0}{\tau_{\text{rec}}}\right)}$ at the initial part of the air window after the H_2 was removed from the atmosphere (at least 20 data points). Prior to each measurement the sensor was heated to 250 °C at 100 sccm flow of pure synthetic air to desorb water and other residual species. The electroforming process and resistive switching were performed in current controlled mode using Keithley 6221 current source and Keithley 2000 voltmeter. In all measurements the bottom electrode was grounded, and the top electrode was biased.

3. Results and discussion

Fig. 3 shows the dynamic responses of the sensor to H_2 concentrations ranging from 3 to $10\,000$ ppm in dry conditions ($\text{RH} = 0\%$). At 100 °C (Fig. 3(a and b)) the sensor reliably detects H_2 concentration as low as 3 ppm ($S = 0.3$). At $10\,000$ ppm H_2 the resistance drops down from the baseline resistance of 240 GΩ down to 155 Ω, yielding a response of $S = 1.5 \times 10^9$. An even higher response magnitude (3.1×10^9) to $10\,000$ ppm H_2 was observed at room temperature (RT). The higher response at RT stems from the significantly higher baseline resistance R_0 and comparable final resistance R_g at $10\,000$ ppm H_2 , as shown in Fig. 3(c). The lowest detected concentration at RT was 100 ppm as shown in Fig. 3(d). At RT the baseline resistance is much higher compared to 100 °C, probably above our measurement limit of ~ 1 TΩ. As such, it is likely that even at RT the sensor responds also to H_2 concentrations lower than 100 ppm, yet the resistance changes are not measurable.

The response value S as a function of the H_2 concentration c on a log-log scale is plotted in Fig. 3(e). At RT the linear fit implies a power law dependence, i.e. $S \sim c^\alpha$ with $\alpha = 4.5$. Similar power dependence with $\alpha = 1.6$ is observable also at 100 °C for low concentrations. At higher concentrations the response saturates. The saturation of response for higher concentrations has been reported before for metal-oxide gas sensors [35,36], although in our case the serial resistance of the Pt electrodes (~ 120 Ω) possibly plays a role as well. At last, we note that the actual response of the sensor is likely higher since completely steady resistance is not reached within the 1.5 h (100 °C) or 2 h (RT) window, particularly for lower H_2 concentrations.

Fig. 3(e) demonstrates nearly linear dependency of the response time constant τ_{res} on H_2 concentration on a log-log scale. The sensor reaches τ_{res} of 1.5 s for $10\,000$ ppm H_2 at 100 °C and slightly higher τ_{res} of 4.6 s at RT. The recovery time constant τ_{rec} significantly increases at high H_2 concentrations, which can be partially caused by response saturation effects. Another contributing factor is the combined resistance of electrodes, which is ~ 120 Ω. Therefore, at least at $10\,000$ ppm H_2 the initial part of the recovery is likely hidden below the serial resistance cutoff.

Since TiO_2 -based gas sensors typically respond to humidity as well

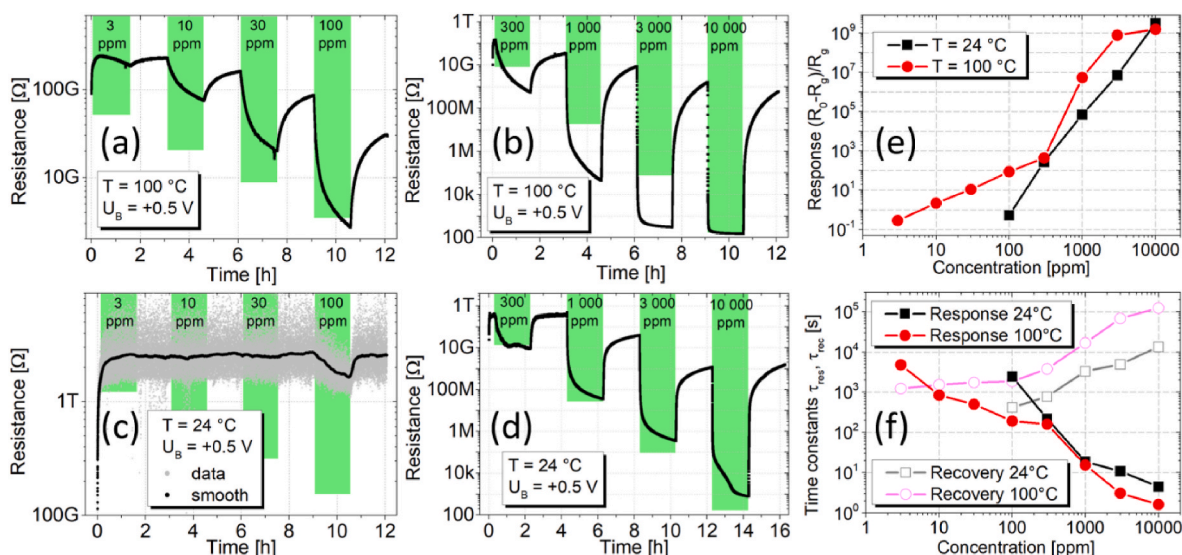


Fig. 3. $R(\text{time})$ characteristics of a sensor with porous TE in dry conditions at 100 °C (a), (b) and at RT (c), (d) measured at bias voltage of +0.5 V. Calibration curves (e) and response and recovery time constants (f) were extracted from panels (a)–(d). Data in panel (c) were smoothed over 20 data points by a 50% percentile filter. Original data are displayed in gray color. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

[16], the sensor performance at elevated humidity is crucial for practical applications and is addressed below. From dynamic response to 300–10 000 ppm H_2 at 100 °C and at 60% RH in Fig. 4(a) we can see a decrease of the baseline resistance R_0 by a factor of ~ 10 compared to dry conditions. The humidity also hinders the resistance drop caused by hydrogen. This results in lower response values, as seen in the calibration curve in Fig. 4(c), although the R_g at 10 000 ppm H_2 reached nearly the same value as in dry conditions. The response at elevated humidity at RT is shown in Fig. 4(b). A strong influence of the humidity is apparent from the calibration curves (solid lines) in Fig. 4(c) as a gradual decrease of both the response and the detection limit. The lowest detected H_2 concentrations were 300 ppm at 19% RH, 1000 ppm at 34% RH and 3000 ppm at 50% RH. At the RH of 32% and the H_2 concentration of 10 000 ppm, the sensor reached response of $S = 1.1 \times 10^4$, which is one order of magnitude higher compared to sensors based on similar TiO_2 layers with standard comb-like electrodes (1.5×10^3) [36].

The presence of moisture substantially impacts the rate of resistance

changes. In condition with 60% RH, the sensor responds slower to hydrogen, leading to lower response values measured at the end of the 90-min H_2 windows. However, after the hydrogen is removed, the resistance recovers faster compared to dry conditions. These trends, visible in Fig. 4(a and b), are further confirmed by the extracted time constants depicted in Fig. 4(d and e). In the measured concentration range of 300–10 000 ppm the response time constants are higher, and the recovery time constants are lower compared to dry conditions. These observations may be explained by a high density of water molecules on the grains' surface that prevent the H_2 from diffusing deeper into the TiO_2 layer, thus, less time is needed to recover to the initial condition.

Let us now comment on the sensing mechanism and the role of the TE in our Pt/ TiO_2 /Pt structure. In ambient air, inter-grain barriers are formed in the nanocrystalline TiO_2 layer due to the negative surface charge generated by the chemisorbed oxygen species [37]. These barriers with height of up to ~ 1 eV cause very low conductivity of the TiO_2 layer, governed by the thermionic emission of electrons, leading to the

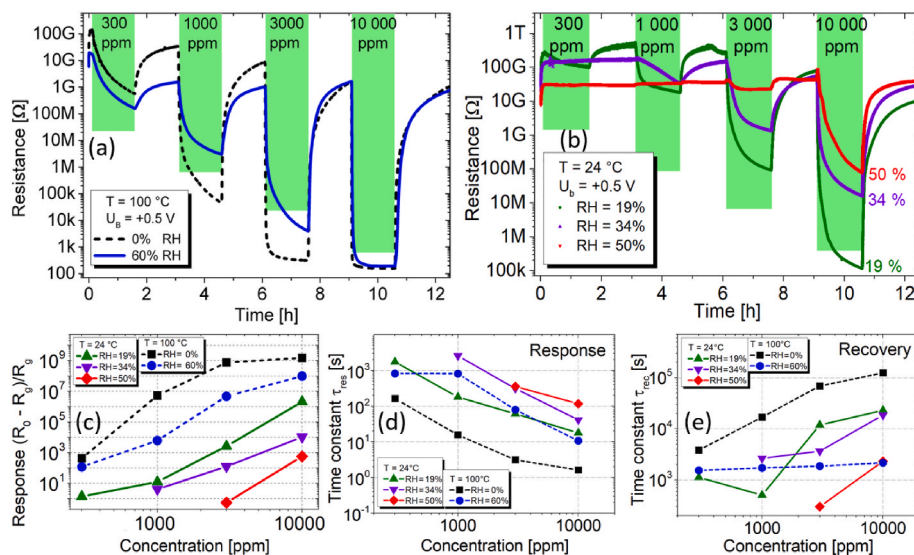


Fig. 4. Sensing performance for 300–10 000 ppm H_2 at elevated humidity. (a) Dynamic response at 100 °C for RH of 60% compared to dry conditions and (b) at RT for RH of 19%, 34% and 50% compared to dry conditions. (c) Calibration curves, (d) response time constants τ_{res} and (e) recovery time constants τ_{rec} at 100 °C (dashed lines) and RT (solid lines) extracted from the data in panels (a) and (b).

high baseline resistance R_0 . When H_2 is introduced, it consumes the chemisorbed oxygen species, decreasing the negative surface charge density and consequently reducing the height of the inter-grain energy barriers to 0.36 eV at 10 000 ppm H_2 . This mechanism is in accord with the $R(T)$ curves (Fig. 5(a)) and Arrhenius plots (Fig. 5(b)) constructed from the measured $R(T)$ curves.

It is important that the TE is very narrow (or nanoporous), as this allows for diffusion of H_2 into the TiO_2 volume located beneath the TE. Moreover, the electric field intensity in the same TiO_2 volume between the electrodes is very high even at small bias voltages (e.g. 0.5 V) thanks to the very small (50 nm) inter-electrode distance in the capacitor-like sensor arrangement. This may give rise to additional sensing mechanism, i.e. additional drop of the resistance in the presence of hydrogen. It is caused by a change of the electron transport mechanism from the above-described thermionic emission to hot electron drift [9], which results in a supplementary resistance drop (response to hydrogen) that can be as high as 3 orders of magnitude. However, using a single narrow (~ 100 nm) TE leads to a small sensor area of $0.1 \times 100 \mu m^2$, which causes an extremely high baseline resistance R_0 way above our measurement limit of ~ 1 T Ω . The use of such narrow TE thus limits the measurable response, as part of the resistance change is hidden in the low current noise. This is particularly critical at low H_2 concentrations, where even the R_g can be above the measurement limit, thus inhibiting the response completely.

The use of $\sim 200 \mu m$ wide nanoporous TEs in this work increased the sensor area from $0.1 \times 100 \mu m^2$ to $200 \times 200 \mu m^2$, i.e. by a factor of 4000 (not considering the 25–50% porosity). This resulted in a lower baseline resistance, which significantly enhanced the detection limit, enabling the sensor to detect H_2 concentrations as low as 3 ppm at $100^\circ C$ and 100 ppm at RT. The larger sensor area also increased the response. For instance, at $100^\circ C$ the sensor resistance at 10 000 ppm H_2 dropped down to $R_g \sim 150 \Omega$, resulting in a response of 1.5×10^9 , compared to 10^7 in the case of sensor with ~ 100 nm wide TE [9]. This enhancement is attributed to the fact that also the initial part of the response is measurable in the case of large nanoporous TE.

To demonstrate that the excellent H_2 gas sensing properties of the presented sensors are not tied to one specific set of fabrication parameters of the nanoporous TE, another set of sensors was prepared. This set was fabricated using a higher Ar/ O_2 ratio, lower total pressure during the PtO_x layer deposition, and higher annealing temperature of $660^\circ C$ (see the Materials and Methods section).

The AFM topography of both sensors is compared in Fig. 6 and reveals higher porosity of the TE for sensors annealed at $660^\circ C$. It also shows a higher density of very narrow (~ 100 nm) necks interconnecting the Pt areas, which is expected to be beneficial for the sensing performance as confirmed by the $R(\text{time})$ characteristics of the sensor #2 shown in Fig. 6. To get closer to the saturated resistance values we increased the measurement temperature from 100 to $150^\circ C$ and

prolonged the cycle windows at RT from 1.5 to 2 h. Moreover, the increase in temperature brings the baseline resistance R_0 safely below the measurement limit of our setup even for a smaller bias voltage of $+0.1$ V. At $150^\circ C$, the dynamic response measurements were thus conducted at the bias voltage of 0.1 V to (i) utilize the whole resistance measurement range; (ii) avoid possible sample damage and (iii) show that the sensor is fully capable of operating at lower voltages, i.e. at lower power consumption.

The dynamic response of sensor #2 shows excellent sensitivity across a wide range of H_2 concentrations at $150^\circ C$. The sensor clearly detects H_2 concentration as low as 3 ppm with $S = 0.95$, and the response saturates at $S = 1.4 \times 10^8$ at 3000 ppm as can be seen in Fig. 7(e). Moreover, at $150^\circ C$ the sensor performs well even at elevated humidity of 60% RH with slightly decreased response but similar response rate. Moreover, it is still capable of detecting 3 ppm of H_2 .

The excellent sensitivity of sensor #2 is maintained also at RT as can be seen in Fig. 7(c and d). Surprisingly, the response values for low concentration (3–300 ppm) are slightly higher compared to those obtained at $150^\circ C$. However, the response and recovery time constants are significantly longer. Indeed, the main drawback of the RT operation is the slow recovery process, particularly at higher H_2 concentrations. Fig. 7(d) shows that after exposing the sensor to 1000 ppm H_2 , the resistance does not return to R_0 even after prolonged time window of 14 h. The sensor is thus clearly not suitable for sensing higher (above 100 ppm) concentrations of H_2 at RT. In addition, at RT the presence of water vapor considerably decreases the response magnitude. Nevertheless, the sensor is still capable of detecting 10 ppm of H_2 at room temperature and relative humidity of 50%.

Since chemiresistive gas sensors are typically more or less sensitive to a large group of reducing and oxidizing gases, selectivity of the studied sensors towards H_2 is an important factor. The selectivity of our sensors was investigated by measuring the response to a representative reducing gas – methane (CH_4), to which the TiO_2 -based sensors exhibit a high response [38,39]. Since the two above-studied sensors were electroformed to perform resistive switching measurements (see below), the dynamic response to CH_4 was measured on sensor #3 prepared in the same way as sensor #2. Fig. 8(a) shows a comparison of the sensor's response to 10 000 ppm of CH_4 and 1000 ppm H_2 in synthetic air at $150^\circ C$. One can see that the response to CH_4 is indeed very small ($S = 0.1$). No measurable response to CH_4 up to 10 000 ppm has been observed at RT.

The much lower response to CH_4 compared to H_2 is most likely due to the sensor arrangement in which the diffusion of gas molecules into the TiO_2 volume in between the TE and BE is crucial. For gases with small molecules and high diffusivity, such as H_2 , molecules can easily reach the region under the top electrode and diffuse throughout the TiO_2 layer, yielding a high response. On the other hand, bigger molecules that reach only the geometrical surface of the TiO_2 layer do not significantly alter

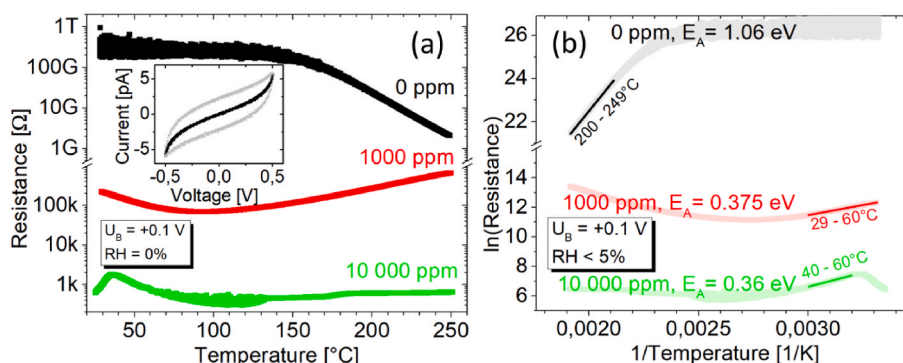


Fig. 5. (a) Resistance vs. temperature cooling curves measured at $U_B = +0.1$ V. The inset shows the current-voltage dependence of the sensor at 0 ppm H_2 and $100^\circ C$. The black curve is an average of current from increasing and decreasing sweeps (gray) shifted due to capacitive hysteresis. (b) Arrhenius plot with highlighted areas of the linear fitting.

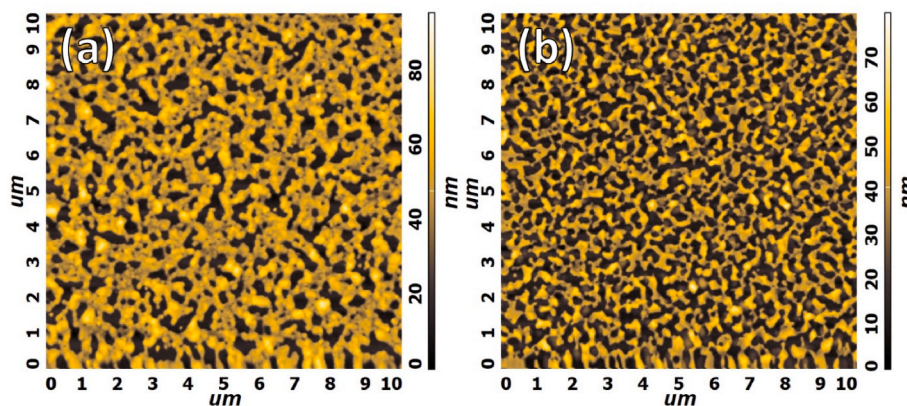


Fig. 6. AFM topography image of the top electrode prepared by magnetron sputtering in mixed Ar + O₂ atmosphere with (a) a total pressure of 0.94 Pa, subsequently annealed at 550 °C and with (b) a total pressure of 0.34 Pa, subsequently annealed at 660 °C.

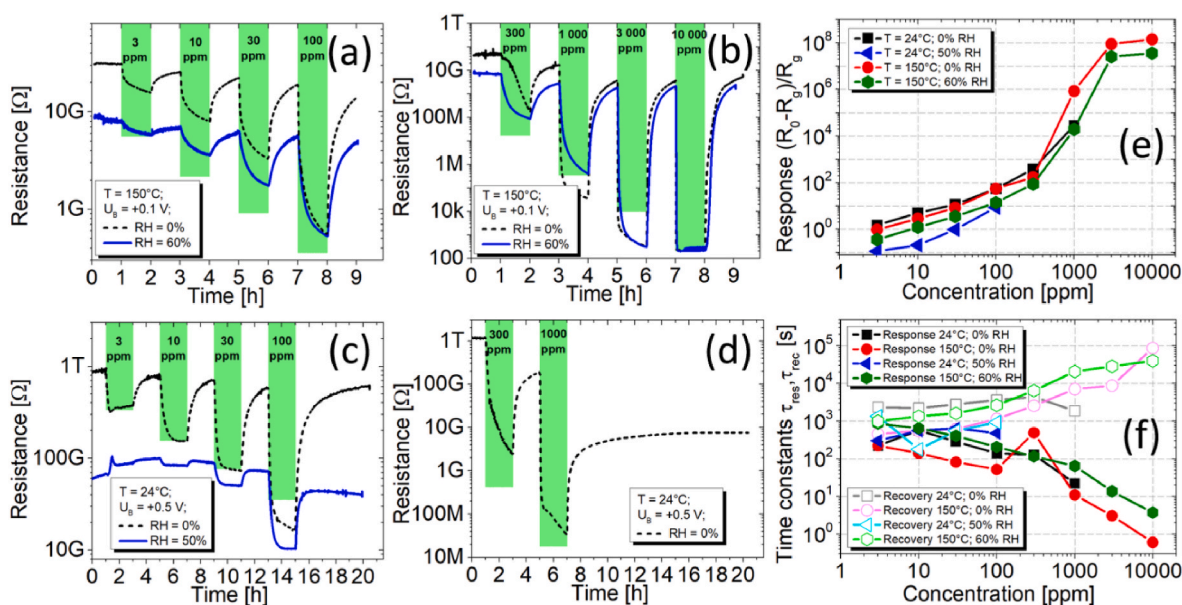


Fig. 7. R(time) characteristics of the sensor with porous TE annealed at 660 °C measured (a), (b) at 150 °C in dry conditions and at RH of 60% and (c), (d) at RT, in dry conditions and at RH of 50%. The calibration curves along with response and recovery time constants, extracted from panels (a)–(d) are shown in panels (e) and (f), respectively.

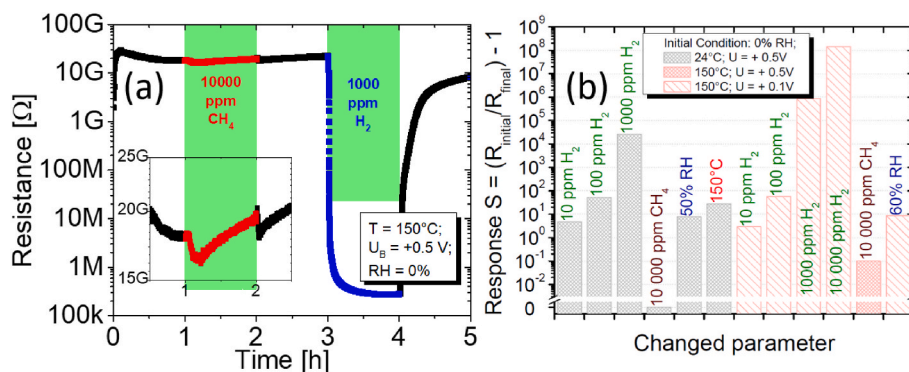


Fig. 8. (a) Selectivity of sensor #3 (fabricated in the same way as sensor #2) at 150 °C and dry conditions. Response to 10 000 ppm of CH₄ (red curve) and 1000 ppm of H₂ (blue curve) is shown. (b) Comparison of the sensor's response to H₂, humidity and CH₄ at different temperatures. The initial conditions are defined as 0 ppm H₂, 0 ppm CH₄, 0% RH, and 24 °C (gray columns) or 150 °C (red columns). All data in this panel are taken from measurements of sensor #2 shown in Fig. 7, except for the response to methane, which is taken from the measurement of sensor #3 shown in panel (a). (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

the conductivity of the capacitor-like Pt/TiO₂/Pt stack. The presented sensors are thus expected to be selectively sensitive to H₂, as has been shown on the example of CH₄.

Fig. 8(b) summarizes the cross-sensitivity to methane and to various measurement conditions (temperature, relative humidity). In this figure, all data are taken from measurements of sensor #2 shown in Fig. 7, except for the response to methane, which is taken from the measurement of sensor #3 shown in Fig. 8(a). We note that the response of sensor #3 to 1000 ppm H₂ at 150 °C is comparable to sensor #2. The y-axis (log-scale) depicts the response to the changed parameter defined as $S = (R_{\text{initial}} - R_{\text{final}}) / R_{\text{final}}$, where R_{initial} is the resistance at 0 ppm H₂, 0 ppm CH₄, 0% RH, and 24 °C (gray columns) or 150 °C (red columns), and R_{final} is the resistance in the environment with given conditions. The comparison of the responses clearly shows practically negligible cross-sensitivity to the humidity, temperature, or methane for the H₂ concentrations of 1000 ppm and higher. For lower H₂ concentrations, the influence of humidity and temperature becomes comparable to the H₂ response, and stabilization or compensation of operating conditions is required to ensure correct quantitative measurements.

To verify the repeatability of the sensor's response, R(time) characteristics of repeated exposure to two selected H₂ concentrations were measured at 150 °C and at RT in dry air. First, response to repeated exposure to 2-h windows of 1000 ppm H₂ was measured at 150 °C (Fig. 9(a)). The dynamic response exhibits periodic resistance changes of very similar magnitude even if a prolonged 4-h window with 0 ppm H₂ is introduced between the cycles, indicating reasonable repeatability of the response. At RT, response to repeated exposure to 2-h windows of 10 ppm H₂ was measured and is shown in Fig. 9(b). The dynamic response clearly exhibits monotonic decrease of the baseline resistance as well as the resistance at the end of H₂ window, which is caused by the incomplete recovery of the sensor at RT within the 2-h window. This effect is more pronounced at higher concentrations and is caused by the asymmetry of response/recovery rates (see Fig. 7(f)) due to the asymmetry of the diffusion rate of H₂ and O₂ into the TiO₂ layer. The slow out-diffusion of the created H₂O after exposure to hydrogen contributes to the effect as well. We note that after a heating cycle to 250 °C the baseline resistance returns to the initial value.

The long-term stability of the presented sensors was not studied as they were electroformed to perform resistive switching measurements (see below). We however note that decrease of the response, particularly at lower (<3000 ppm) H₂ concentrations, was observed in sensors prepared in a similar way as sensor #2, but with higher TiO₂ thickness (70 nm) and slightly different annealing process, after being stored for 8 months in ambient air.

Apart from the high sensitivity, another advantage of the sensors with capacitor-like arrangement is that they are also capable of resistive switching, i.e., they can be operated as memristors. This has been already demonstrated on similar sensing structures where the gas sensing and resistive switching was combined to form a gas sensor with

intrinsic memristive memory, known as “gasistor” [26–29]. To explore whether the sensors with large-scale nanoporous top electrodes prepared in this study are suitable for such memristive applications, the electroforming process was performed on some of the sensors and their resistive switching (RS) properties have been studied. For comparison, we also show RS properties of similar structures fabricated in the same way, but with a continuous (non-porous) and relatively narrow (5 μm wide) top electrode.

Fig. 10 shows the electroforming process and RS behavior of capacitor-like Pt/TiO₂/Pt sensors with different designs of the top electrode (TE). While panel (a) shows RS in the sensor with cross-section area of 200 × 200 μm² and large nanoporous Pt TE, panel (b) shows RS in the sensor with 5 × 200 μm² electrode area and a continuous (non-porous) Pt TE prepared via lift-off photolithography. After the electroforming process is performed in positive polarity (blue curves in Fig. 10), we observe hysteretic I(V) curves typical for bipolar resistive switching in both cases. In the case of large porous TE, the sensor switches from the low resistance state (LRS, R = 1.3 kΩ) to high resistance state (HRS, R = ~4.5 kΩ) in the positive polarity. In the latter case of the sensor with 5 μm wide TE, the transition from LRS (R = 7 kΩ) to HRS (R = 117 kΩ) takes place in the negative polarity, and both resistance states have significantly higher resistances.

Fig. 10(a) clearly shows that resistive switching in the sensor with large porous electrode prepared from a metastable PtO_x is possible. However, the HRS resistance of 4.5 kΩ is very low for sensing purposes and reliable gasistor functionality. As described in Ref. [26], the device after forming can be viewed as a parallel connection of the non-memristive gas sensor and a non-sensing memristor. Therefore, it responds to a target gas only when the resistance of the gas sensor is lower than (or at least comparable to) the resistance of the memristor. From this reason, the HRS resistance is a critical value from the sensing point of view.

The low resistance of HRS in Fig. 10(a) most likely originates from the large amplitude of the forming current that flowed through the sensor and created a conducting channel with a low resistance [40,41]. In contrast, the three-orders lower forming current in Fig. 10(b) led to a higher resistance of both HRS and LRS. According to Ref. [42], the critical parameter (besides the used current compliance) that determines the resistance after the forming process is the electrode area, which also determines the capacitance of the metal/metal-oxide/metal structure. This is in accord with Fig. 10, where the sensor with 20-times smaller cross-sectional electrode area exhibits RS with higher resistances of the LRS and HRS. In addition, the smaller electrode area is also beneficial for decreasing the dispersion of the switching voltage at which the transition from HRS to LRS and vice versa occurs [40,43].

In summary, the capacitor-like metal/metal-oxide/metal sensing structure with large-scale nanoporous Pt TE can also function as a memristive device. However, to obtain a sufficient response to a target gas, the structure must be formed into a HRS with resistance higher than

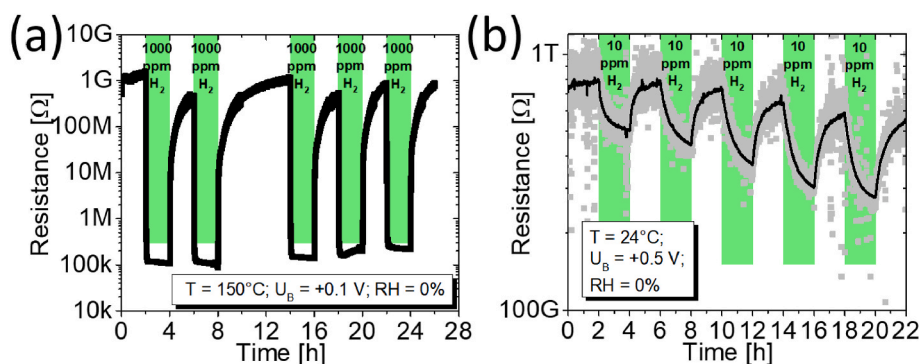


Fig. 9. R(time) characteristics of the sensor fabricated in the same way as sensor #2 repeatedly exposed to (a) 1000 ppm H₂ at 150 °C and 0% RH and (b) 10 ppm H₂ at RT and 0% RH.

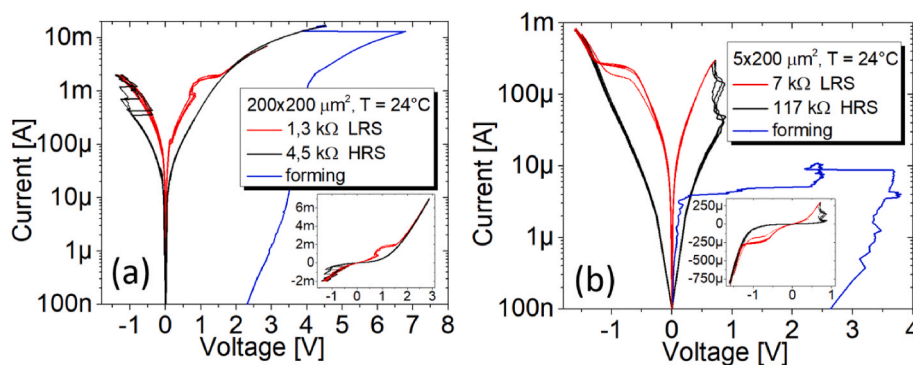


Fig. 10. $I(V)$ characteristics of the sensor (after electroforming) with (a) porous TE with the overlay area of $200 \times 200 \mu\text{m}^2$ and (b) with compact Pt TE with an overlay area of $5 \times 200 \mu\text{m}^2$. After the forming process, both of them exhibit hysteretic $I(V)$ curves typical for bipolar resistive switching. The insets show the same data but in linear scale. Resistance values of the HRS and LRS have been obtained from linear fit of the $I(V)$ curves in the range of $[-0.1 \text{ V}; +0.1 \text{ V}]$.

R_g at the desired concentration. A possible way to meet this requirement is to significantly decrease the electrode cross-section area. This would however bring us back to the problem of too high baseline resistance of the sensor and the necessity of using advanced lithographic methods. The problem of low HRS resistance could also be addressed by modification and optimization the electroforming process. Forming the structure in a different way, e.g. by very short voltage pulses [44] could potentially lead to much higher HRS resistance. Such optimization of the electroforming process is however beyond the scope of this work and will require further study.

4. Conclusions

To conclude, we have prepared highly sensitive hydrogen gas sensors based on a capacitor-like Pt/TiO₂/Pt structure with large-scale nanoporous top Pt electrode and characterized their hydrogen gas sensing properties at various temperatures and humidity levels. The nanoporous top Pt electrodes were prepared by annealing the PtO_x precursor layer deposited by a standard reactive magnetron sputtering through a shadow mask. The nanoporous top electrode, consisting of Pt islands interconnected by ~ 100 nm wide necks, allows for easy diffusion of H₂ into the sensing layer between the top and bottom electrodes. The large area of electrodes decreases the baseline resistance of the device, while the close proximity (50 nm) of the electrodes ensures very high electric field intensity even at low bias voltages (0.5 V). This allows the sensor to detect H₂ concentrations as low as 3 ppm in dry air even at room temperature, while providing extremely high response to higher H₂ concentrations (10^9 at 10 000 ppm H₂). Humidity moderately decreases the sensor response, particularly at room temperature. This type of structure is also used as a resistive switching cell and has the potential to function as a gasistor (gas sensor with intrinsic memristive memory). Therefore, some of the sensors were electroformed, and we have demonstrated that they are capable of reversible switching between the high and low resistance states. However, the resistance of the electroformed sensor with large area electrodes is too low for gas sensing (gasistor) applications and further study is needed to adjust the electroforming process accordingly.

CRediT authorship contribution statement

Michal Patrnciak: Writing – review & editing, Writing – original draft, Project administration, Methodology, Investigation. **Marek Vidiš:** Writing – review & editing, Writing – original draft, Supervision, Software, Methodology, Investigation, Formal analysis, Data curation. **Lubomír Staňo:** Writing – review & editing, Methodology, Investigation, Formal analysis. **Ihor Shpetnyy:** Supervision, Methodology, Investigation, Funding acquisition. **Tomáš Roch:** Investigation, Data curation. **Branislav Grančič:** Methodology, Formal analysis. **Leonid**

Satrapinsky: Investigation. **Pavol Ďurina:** Investigation. **Marián Mikula:** Resources, Methodology. **Tomáš Plecenik:** Writing – review & editing, Writing – original draft, Supervision, Project administration, Investigation, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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