Supraparticles for Bare-Eye H₂ Indication and Monitoring: Design, Working Principle, and Molecular Mobility

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Indicators for H₂ are crucial to ensure safety standards in a green hydrogen economy. Herein, the authors report micron-scaled indicator supraparticles for real-time monitoring and irreversible recording of H₂ gas via a rapid eye-readable two-step color change. They are produced via spray-drying SiO₂ nanoparticles, Au—Pd nanoparticles, and indicator-dye resazurin. The resulting gas-accessible mesoporous supraparticle framework absorbs water from humid atmospheres to create a three-phase-system. In the presence of H₂, the color of the supraparticle switches first irreversibly from purple to pink and further reversibly to a colorless state. In situ infrared spectroscopy measurements indicate that this color change originates from the (ir)reversible H₂-induced reduction of resazurin to resorufin and hydroresorufin. Further infrared spectroscopic measurements and molecular dynamics simulations elucidate that key to achieve this functionality is an established three-phase-system within the supraparticles, granting molecular mobility of resazurin. Water acts as transport medium to carry resazurin molecules towards the catalytically active Au—Pd nanoparticles. The advantages of the supraparticles are their small dimensions, affordable and scalable production, fast response times, straightforward bare-eye detection, and the possibility of simultaneously monitoring H₂ exposure in real-time and ex post. Therefore, H₂ indicator supraparticles are an attractive safety additive for leakage detection and localization in a H₂ economy.

1. Introduction

A green hydrogen (H₂) economy based on H₂ as an energy carrier is considered a promising approach to address the steadily growing energy demand in a carbon-free and sustainable way. Due to the diffusion and combustion characteristics of H₂ in air, high safety standards are crucial at every point of use to prevent devastating accidents. As the presence of H₂ cannot be perceived by human senses, the widespread use of sensors and indicators for H₂ will play a key role for the confidence of the end user. Thus, sensing agents are indispensable for the transition towards a renewable energy society based on a green H₂ economy.

Coming from niche applications mostly in industry or medical applications, the recent demand led to the development of an immense number of different detection pathways and sensor types for H₂, which all have their own merits and drawbacks as summarized in the following
review articles.[5,7,9,12–16] In particular, optical H₂ sensors offer a great potential to detect leakages as they operate without electrical contacts. Most importantly, they are intrinsically safe in explosive atmospheres by eliminating the risk of sparks.[17,18] Additionally, optical detection allows for spatially resolved[9,10,19] and remote H₂ sensing via optical fibers,[15,16,20] Classical optical H₂ sensors require a sensing material, for example, a thin film[21–23] or nanoantenna,[19,24] a light source, an optical fiber, and an electronic control device to convert the optical signal into a readable signal response.[17,26]

The introduction of sensors with a chromaticity response enables bare-eye H₂ detection via a clear color change of the sensor material. This eases the readout in particular for untrained personnel and reduces the cost for the sensor fabrication. To date, many different chemochromic metals,[25,26] for example, Y[11,20,27] metal alloys[28,29] or metal sulfides,[37] or oxides, such as TiO₂[30–32] ZnO, MoO₃[9,10,18,33] and WO₃[22,34–36] were combined with catalysts such as Pt and Pd to yield eye-readable H₂ indicators. Additionally, a visual hydrogen detector based on a stimuli-responsive Pd–Cr–Ti nanomembrane was reported.[37] Yet, the vast majority of gasochromic H₂ sensors are applied via complicated fabrication processes[35] as thin films on specific substrates comprising a fragile multi-layer structure.[11,17,22,23,25,28,29]

To achieve the highest possible flexibility in terms of application, small-scaled gasochromic additives fulfill many of the desired requirements for a competitive H₂ sensor.[5,14,15,19] However, most of them require a high content of expensive Pd,[18,30,16,38] show just a slightly noticeable color change,[38,16,38] have long recovery times,[16] and can be applied as powders, inks, paints, or coatings. Thereby, they can function as an eye-readable sensor at any relevant object during H₂ production, transport, and storage.

Established gasochromic additives for H₂ detection include WO₃-Pd,[35,36] MoO₃-Pd,[18] and TiO₂-supported PdO[30–32] pigments, as well as PdO@ZnO nanoparticles (NPs).[38] These systems fulfill many of the desired requirements for a competitive H₂ sensor.[5,14,15,19] However, most of them require a high content of expensive Pd[18,30,16,38] show just a slightly noticeable color change,[38,16,38] have long recovery times,[16] and only moderate response times (>60 s).[18,36] Others are vulnerable to fluctuating environmental parameters.[32] Moreover, the established pigments allow either for real-time monitoring of H₂ with a reversible color change[35,36] or indication and recording of a H₂ leakage via an irreversible optical response.[18,38] Both real-time monitoring of H₂ for immediate leakage detection and irreversible indication for leakage localization, for example, in a pipeline system, expost are of great interest for a safe green H₂ economy. Thus, a gasochromic additive uniting both is desired.

To intensify the visual color change of gasochromic H₂ indicators, a combination of functional dye molecules and catalysts offers great potential for bare-eye detection.[40–44] Among the indicator dyes suitable for real-time monitoring of H₂,[41–43] the resazurin/resorufin dye system is particularly attractive due to its two-step redox reaction: first an irreversible reaction and second a reversible one.[41–45] Hence, a H₂ indicator based on resazurin/resorufin may allow for real-time monitoring and irreversible indication of H₂ exposure via a two-step color change reaction. Note that the use of redox-dye/catalyst combinations as visual H₂ indicators is restricted to the liquid phase[45] or hydrogels,[46] as it requires a three-phase system. This is due to the transport of H₂ as reactive H₂ species from the catalytically active metal surface to the indicator dye molecules or vice versa. Therefore, to date, the application potential for H₂ sensors based on redox-dye/catalyst combinations has not been exploited, yet bears great potential that should be unlocked.

A material system unifying all essential functional units (catalytically active NPs, redox-active dye, and three-phase boundary) in a flexibly applicable additive will significantly expand the horizon of gasochromic H₂ detection.

Mesoporous particles offer a defined pore structure as well as a high specific surface area and are ideally suited as a potential additive material.[47,48] The solid porous framework provides a confined space for capillary condensation of water[49,50] that enables the transport of aqueous molecular solutes[51] that is, dyes,[52] while remaining readily accessible for small gas molecules.[53,54] As an alternative to conventional synthesis routes,[48,55] the assembly of NPs into a hierarchical suprastructure was established as a versatile fabrication route for mesoporous particles with designed confined space and particular advantages for catalysis applications, which result from the cooperative interplay of the NP building blocks.[56] To create these so-called supraparticles (SPs),[57] forced assembly strategies are particularly attractive. They allow for flexible combinations of different nanoparticulate and molecular building blocks almost independent of the respective surface chemistry.[54,58–60] This flexibility offers the potential to customize a smart gasochromic additive towards a specific application via a toolbox-like approach to adjust the functional features of the indicator.

Herein, we report on the design, fabrication, and working principle of gasochromic H₂ indicator particles based on a redox-dye that is capable of simultaneously monitoring and recording the presence of H₂ with a fast, eye-observable color change. As a signal element, we exploit the resazurin/resorufin dye system, which is combined with catalytically active Au–Pd NPs in the confined space of mesoporous silica SPs via a scalable forced assembly process. The visible color change results from the cooperative interplay of the functional building blocks within the micron-sized supraparticulate entity. The system presented herein provides a fast signal response for the detection of H₂, a scalable and affordable synthesis as well as flexible fields of application. This renders the indicator SPs attractive for various applications in a future green H₂ economy.

2. Results and Discussion

2.1. Design, Fabrication, and Characterization of H₂ Indicator SPs

The herein introduced H₂ indicator SPs consist of three functional elements, two different nanoparticulates, and one molecular building block. Combined in one supraparticulate entity via spray-drying, they yield a bare-eye readable H₂ detection (Figure 1). The three essential building blocks are bimetallic Au–Pd NPs (Figure 1a), SiO₂ NPs (Figure 1b), and the redox-dye resazurin (Figure 1c).

Au–Pd NPs are selected as a model catalyst material serving for H₂ activation due to their feasible synthesis and catalytic performance as discussed in previous studies.[43,61–62] The Au–Pd NP synthesis was slightly modified as compared to procedures published before.[43,62] The obtained NPs exhibit a flower-like shape (transmission electron microscopy [TEM] micrograph,
Figure 1. Building blocks, fabrication, and morphological characterization of H₂ indicator SPs: digital photographs and TEM micrographs of a) Au–Pd NP and b) SiO₂ NP dispersion; c) digital photograph of an aqueous resazurin dye solution; d) schematic representation of the SP fabrication via droplet evaporation (using spray-drying as tool) into a free-flowing purple powder; SEM micrographs of e) a SP and f) its surface.

Figure 1a) with sizes ranging from 15 to 50 nm (dynamic light scattering [DLS] measurements, Figure S1, Supporting Information) corroborating the results of the work by Han and coworkers[62] that provides a more detailed analysis of the NP phase structure. Inductively coupled plasma-optical emission spectrometry (ICP-OES) measurements reveal an Au–Pd NP composition of Au₄Pd₆ (Table S1, Supporting Information).

SiO₂ NPs show good performance as support material for chemical gas indicators while being commercially available and economically feasible.[54] The used commercial SiO₂ NPs are of spherical shape (TEM micrograph, Figure 1b) and exhibit a particle size distribution of ≈10 to ≈30 nm (DLS measurements, Figure S1, Supporting Information). As a chemochromic signal element for the envisioned SP system, the molecular building block resazurin is chosen due to its attractive two-step (ir)reversible redox reaction.[43] In an aqueous solution with neutral to alkaline pH, resazurin is present in its anionic form and shows a purple-bluish color resulting from the strong π* transition of the phenoxazin-3-one and the weak nπ* transition of the N-oxide (Figure 1c, UV–vis spectrum, Figure S2, Supporting Information).[63]

The three introduced building blocks are united in a forced droplet evaporation approach (spray-drying, schematically depicted in Figure 1d). Briefly, an atomizer generates small droplets of the mixed NP dispersion that are subsequently introduced into a hot chamber. Due to the induced solvent evaporation, the incorporated NPs and dye molecules are forced together to ultimately form a supraparticulate entity.[58,60]

Scanning electron microscopy (SEM) analyses (Figure 1e, overview images: Figure S3, Supporting Information) confirm that the forced self-assembly process of the different building blocks results in raspberry-like micron-scaled particles with small interstitial pores between the assembled NPs (Figure 1f). Laser light diffraction measurements (Figure S4, Supporting Information) reveal a particle size distribution of the produced SPs ranging from 1.9 (d₀.1) to 11.5 µm (d₀.9) with a mean value of 5.5 µm (d₀.5). The Au–Pd NPs loading of the H₂ indicator SPs amounts to ≈0.04 wt% (ICP-OES measurements, Table S1, Supporting Information).

In order to further characterize the pore structure of such SPs, N₂ adsorption measurements at 77.4 K were performed. The evaluated SP samples consisted of SiO₂ NPs (SiO₂),...
SiO2 NPs with Au–Pd NPs (SiO2+Au–Pd), and SiO2 NPs with Au–Pd NPs and resazurin (RES, 0.05 wt%, and 1 wt%, respectively). While the SiO2 and the SiO2+Au–Pd SPs were prepared to investigate the influence of the addition of the individual components during the SP fabrication on the resulting pore structure, the SiO2+Au–Pd+RES(1 wt%) SPs were specifically synthesized for a mechanistical study, which is discussed in Section 2.2. Figure 2a, shows the N2 isotherms for the above mentioned samples. All samples exhibit a type IV isotherm, indicative of mesoporous materials which exhibit pore condensation accompanied by hysteresis. A typical feature of a type IV isotherm is a final saturation plateau, here extending from the relative pressure ($p/p_0 - 1$) 0.8 to 1, indicating complete filling of the mesopores. This allows one to calculate the total pore volume from the plateau region (Table 1).

Such mesopores are resulting from the interstitial space between the assembled NP building blocks (especially SiO2 NPs) which is generated during the solvent evaporation. Interestingly, the shape of the isotherms is identical in all cases, with a slight decrease of the adsorbed volume as the different building blocks (especially resazurin) are incorporated into the SiO2-based SPs. The observed hysteresis loop for the type IV adsorption isotherms can be characterized as a hybrid between type H1 and type H2 according to the IUPAC classification. This indicates the presence of some pore restrictions leading to pore blocking effects during pore evaporation/desorption. Hence, the pore size distribution curves shown in Figure 2b were calculated by applying a dedicated nonlocal density functional theory (NLDFT) method to the adsorption branch, by assuming cylindrical SiO2 mesopores and by taking into account the delay in condensation due to metastable pore fluid. Additional textural properties are compared in Table 1.

It can be observed that surface area as well as pore volume barely decrease with the addition of Au–Pd NPs. It must be noted, that the amount of catalyst NPs added to the SiO2 NPs is very small (0.04 wt%) and their particle size similar, thus the interstitial space remains unchanged. Furthermore, the samples containing the dye molecules reveal a small but progressive decrease of the surface area which is more evident in the

![Figure 2](image-url)

**Figure 2.** Structural characterization of H2 indicator SPs systems made of SiO2 NPs, SiO2 NPs with Au–Pd NPs, and SiO2 NPs with Au–Pd NPs and resazurin (RES, 0.05 wt%, and 1 wt%, respectively): a) N2 isotherms at 77 K. Full symbols indicate adsorption branch and empty symbols indicate desorption branch; b) nonlocal density functional theory (NLDFT) pore size distributions; c) thermogravimetrical analysis (TGA) measurements of H2 indicator SPs after the activation process in humid atmosphere and vacuum-drying, respectively; d) H2O isotherms at 298 K.

| Sample | SiO2 | SiO2+Au–Pd | SiO2+Au–Pd+RES (0.05 wt%) | SiO2+Au–Pd+RES (1 wt%) | SiO2+Au–Pd+RES (3 wt%) |
|--------|------|------------|---------------------------|------------------------|------------------------|
| S BET/m² g⁻¹ | 130  | 127        | 122                       | 107                    | 85                     |
| V pore/cm³ g⁻¹ | 0.190 | 0.188      | 0.186                     | 0.175                  | 0.167                  |

*Total pore volume obtained at a $p/p_0 - 1$ of 0.95.*
sample containing 1 wt% of resazurin, with a $S_{\text{BET}}$ reduction of 17% (see Table 1). For the sake of clarity, an additional sample was prepared with a higher amount (5 wt%) of resazurin, (Figure S5a,b, Supporting Information). It can be observed that, as the content of resazurin is increased, the accessible surface area decreases since more pores are getting blocked, which are no longer accessible to N$_2$ (see Supporting Information for a detailed discussion).

Pure SiO$_2$ SPs reveal a pore size distribution, covering a range between 4 and 12 nm (Figure 2b). As expected, the addition of small amounts of Au–Pd NPs (SiO$_2$+Au–Pd) does not modify the pore structure. Furthermore, the samples with the dye molecule (SiO$_2$+Au–Pd+RES) also preserve the pore size, despite the pore volume getting reduced (more intensively for the 1 wt% resazurin sample). This reduction is clearly appreciated in the cumulative pore volume analysis (Figure S6, Supporting Information). At this point it is important to explain how the resazurin is located and distributed. The dye molecules are most likely deposited at the external surface of the SiO$_2$ NPs, without directly penetrating into the mesopores (interstitial space). Such pores remain empty and accessible to N$_2$. This explains that pore size is not altered, but the volume becomes smaller, with some of the pores blocked (particularly the small ones).

To achieve the desired H$_2$ indicator functionality in the confined space of the manufactured SPs, a three-phase-system needs to be created by filling up the mesopores with a liquid transport medium for molecular solutes. This is achieved by exposing the supraparticle powder to a humid atmosphere in a sealed desiccator, later also referred to as ex situ H$_2$O dosing (schematically depicted in Scheme S1, Supporting Information).

To determine the amount of stored transport medium inside the pore structure of the SPs, we compare thermogravimetrical analysis (TGA) data of SPs subjected to ex situ H$_2$O dosing and vacuum-drying (Figure 2c). The recorded mass losses of both samples deviate in the temperature range from 30–110 °C. At higher temperatures, the samples behave similarly again. It is noteworthy that no mass loss attributed to the incorporated resazurin dye is recorded in this temperature range (TGA measurement of pure resazurin dye, Figure S7, Supporting Information). Thus, we attribute the mass loss to the evaporation of stored water from the SP sample exposed to ex situ H$_2$O dosing, amounting to $\approx$0.3 wt% (determined at 200 °C).

Water isotherms at 298 K were performed to evaluate the water adsorption capacity of the materials (Figure 2d) since a humid atmosphere is important for the correct functionality of the material as H$_2$ gas detector (it is later shown that in the absence of humidity, resazurin cannot be reduced to resorufin/hydroresorufin). All isotherms show a very similar plateau at a $p/p_0$ close to 1 indicating that SiO$_2$ SPs are able to adsorb up to 20 wt% of water in agreement with the evaporation of water from SPs that were exposed to ex situ H$_2$O dosing in a desiccator (Scheme S1, Supporting Information). The H$_2$O adsorption measurements also exhibit type IV isotherms with a hysteresis indicating pore condensation of water in the mesoporous.

Furthermore, despite the addition of the dye molecules on the SiO$_2$ SPs do not modify their water adsorption capacity (pore volume is rather similar). It is very interesting to notice that the presence of resazurin on the SiO$_2$ generates effective stronger attractive interactions of water molecules with the adsorbent surface. This is indicated by the fact that the pore condensation is shifted to smaller $p/p_0$ volumes.

According to these results, the H$_2$ indicator SPs absorb water from a humid atmosphere in their sponge-like mesoporous structure during the ex situ H$_2$O dosing. As the solid framework is readily accessible for gases, this yields the desired three-phase-system.

We study the response of the produced indicator SPs to the presence of H$_2$ by placing the powder in a vial and exposure to H$_2$ from a gas bag (flow rate: $\approx$20 mL s$^{-1}$) (Figure 3a, see experimental section for more details, full video is accessible online). No response to the presence of H$_2$ was detected in case of the SPs obtained directly after spray-drying (as-prepared state, Figure S8, Supporting Information). Contrarily, a fast and distinct color change reaction upon exposure to H$_2$ was observed for the SPs treated previously by ex situ H$_2$O dosing (Figure 3b,c).

First-time exposure to H$_2$ leads to a two-step color change (Figure 3b): after 1 s of H$_2$ dosing, the color of the powder changes from purple to pink followed by a second color change from pink to colorless after 2 s. This colorless state is conserved as long as the H$_2$ exposure maintains constant. After the H$_2$ exposure is stopped (10 s), the powder recovers its pink color within the next 3 s. Upon further H$_2$ dosing, the color of the powder switches between colorless and pink displaying the presence (colorless) and absence (pink) of real-time H$_2$ exposure, respectively (Figure 3c). Fast recovery times (3–4 s) are observed.

The results obtained from these experiments demonstrate that the ex situ H$_2$O dosing procedure as well as the combination of the three functional elements in one supraparticle (reaction of SPs without Au–Pd NPs, Figure S9, Supporting Information) are key for the functionality of the H$_2$ indicator SPs. Further, the results convincingly show that the SP powder exhibits the expected (ir)reversible two-step color change reaction, which is suitable for simultaneously monitoring the presence of H$_2$ in real-time (Figure 3c) with appropriate cycle stability (Figure S10, Supporting Information) as well as recording its presence ex post (Figure 3b). These two color-change reactions agree with the reported redox reaction of the utilized resazurin dye and are not observed upon exposure to other reducing gases, for example, NH$_3$ or CH$_2$O vapor (Scheme S2 and Figure S11, Supporting Information). According to literature, resazurin is reduced irreversibly to resorufin. Further H$_2$ dosing leads to the reversible formation of hydroresorufin.$^{[43–45]}$

2.2. In Situ DRIFTS – Reaction Mechanism and Influence of H$_2$O Content

To shed more light on the H$_2$-induced conversion of the incorporated resazurin dye and the effect of the ex situ H$_2$O dosing process (see Section 2.1 and Scheme S1, Supporting Information) on the latter, in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) was performed. The DRIFTS reactor is connected to a gas dosing system, which supplies Ar, H$_2$, and H$_2$O-saturated Ar (H$_2$O/Ar). Importantly, the setup runs in a remote-controlled fashion and the complete optical
path remains evacuated during the experimental procedure. Overall, this provides maximum reproducibility and stability of the system. A schematic of the setup is displayed in Figure 4a.

Prior to the IR measurements, the SPs were exposed to different pretreatments (Figure 4b): one sample was subjected to the above-described ex situ H$_2$O dosing in a desiccator. All other samples were dried in vacuo (~1 mbar, at least 1 h) and, thereafter, the samples were subjected to an in situ H$_2$O dosing procedure. Here, the H$_2$O exposure time was varied systematically (0, 2, 20, and 64 h) to probe the influence of the water content. Finally, a gas dosing sequence was performed to monitor and compare the color change reaction of the H$_2$ indicator SPs on a molecular level (Figure 4c, see Experimental Section for a detailed description). After an initial Ar and H$_2$O/Ar dosing step (10 min), two consecutive cycles of 33.3 vol% H$_2$ dosing for 60 min and Ar dosing for 90 min were applied at constant H$_2$O backpressure to probe the reduction of resazurin as well as the (ir)reversible formation resorufin and/or hydroresorufin.

To differentiate between the structurally closely related dyes resazurin, resorufin, and hydroresorufin, we focus on characteristic vibrational bands as described in the following. For a complete peak assignment based on density functional theory (DFT) and transmission infrared spectroscopy (TIRS), the reader is referred to Figure S12, Supporting Information.

Figure 5a illustrates the reaction network and highlights characteristic vibrational modes. Note that difference spectra with respect to resazurin were recorded. Thus, the presence (negative, downwards pointing bands) and absence (positive, upwards pointing bands) of characteristic vibrational modes allows us to draw conclusions on the speciation of the dye in the SPs. For resazurin, characteristic N=O and C=O stretching bands (ν(N=O), ~1500 cm$^{-1}$, highlighted in brown; and ν(C=O), ~1600 cm$^{-1}$, highlighted in orange) were observed. For resorufin, characteristic C=N=C stretching (ν(C=N=C), ~1600 cm$^{-1}$, highlighted in red) and ν(C=O) stretching bands (~1610 cm$^{-1}$, highlighted in orange) were obtained. Finally, the presence of the N-H stretching and deformation modes (ν(N-H)+δ(N-H), ~1510 cm$^{-1}$, highlighted in brown) and the absence of ν(C=O) indicate the formation of hydroresorufin.

Figure 5b displays results obtained during the Ar/H$_2$ dosing sequence on SPs, which were subjected to ex situ H$_2$O dosing in a desiccator prior to the experiment. It includes a color-coded intensity plot, selected averaged spectra, and the integration of the characteristic bands. Note that the ex situ H$_2$O dosing is identical to the sample discussed in Section 2.1. In the following, the trend of the characteristic vibrational modes listed above is discussed: in the beginning, no bands are visible. At the onset of H$_2$ dosing, a positive band at ~1500 cm$^{-1}$ and negative bands at ~1600 and ~1460 cm$^{-1}$ evolve. With continuous H$_2$ dosing, a negative band at ~1510 cm$^{-1}$ and a positive band at ~1600 cm$^{-1}$ form, whereas the band at ~1460 cm$^{-1}$ vanishes. Upon Ar dosing, a positive band at ~1500 cm$^{-1}$ and negative bands at ~1600 and ~1460 cm$^{-1}$ evolve. During the second H$_2$ and Ar dosing sequence, the behavior of the bands is identical to the first cycle except for the evolution of the initial peaks at the onset of the H$_2$ dosing sequence.

Based on the assignment of the characteristic vibrational modes presented above, we interpret the results as follows: in the beginning, no peaks are visible in the DRIFT spectra as only resazurin is present. At the onset of the first H$_2$ dosing sequence, resorufin forms as indicated by the negative band at ~1460 cm$^{-1}$ (ν(C=N=C); highlighted in red). Continuous H$_2$ dosing further reduces resorufin to hydroresorufin. This is proven by the presence of ν(N-H)+δ(N-H) (~1510 cm$^{-1}$; highlighted in brown) and the simultaneous absence of ν(C=O) (~1600 cm$^{-1}$; highlighted in orange). Upon switching to the Ar
dosing sequence, resorufin forms again. This is indicated by the occurrence of negative bands at \( \approx 1460 \) (\( \nu(C-N-C) \); highlighted in red) and \( \approx 1610 \, \text{cm}^{-1} \) (\( \nu(C=O) \); highlighted in orange). In agreement with the literature, the formation of the resazurin starting material is not observed again.[43–45] During the second \( \text{H}_2 \) and \( \text{Ar} \) dosing sequence, an identical behavior is displayed. In particular, \( \text{H}_2 \) and \( \text{Ar} \) dosing leads to the reversible formation of hydroresorufin and resorufin, respectively, which is in agreement with previous studies.

Next, the influence of the \( \text{H}_2\text{O} \) content in the \( \text{H}_2 \) indicator system is addressed via a systematic increase of the in situ \( \text{H}_2\text{O} \) exposure time of vacuum-dried samples prior to the gas dosing sequences. In line with the discussion above, the speciation in the SP system is followed qualitatively via the respective integrated peak areas in Figure 5c (the color-coded intensity plots and selected spectra can be found in Figures S13–S16, Supporting Information). Without water dosing (0 h, Figure S13, Supporting Information), no characteristic bands form upon \( \text{H}_2 \) dosing. This shows that resazurin is not reduced in the SP system in the absence of water, which affirms the necessity of a three-phase-system as discussed previously (Section 2.1, Figure S8, Supporting Information).

For the SPs exposed to in situ \( \text{H}_2\text{O} \) dosing for 2 h (Figure S14, Supporting Information), characteristic bands evolve in the DRIFT spectra. A negative band at \( \approx 1460 \, \text{cm}^{-1} \) forms and increases in intensity over time. Additionally,
positive bands at ≈1500 and ≈1600 cm$^{-1}$ form, with the band at ≈1500 cm$^{-1}$ vanishing reversibly upon exposure to H$_2$. Thus, resazurin is converted to resorufin upon H$_2$ dosing after in situ H$_2$O dosing for 2 h. Due to the decrease of the peak area of the band at ≈1500 cm$^{-1}$, it is concluded that there is only slight further reduction to hydroresorufin if any. Instead, an accumulation of resorufin is observed as indicated by the constantly growing band at ≈1460 cm$^{-1}$ (ν(C=N-C); highlighted in red).

Figure 5. In situ DRIFTS on H$_2$ indicator SPs: a) reaction network of resazurin, resorufin, and hydroresorufin with characteristic vibrational modes highlighted; b) color-coded intensity plot, selected DRIFT spectra, and integrated peak areas of characteristic bands for the sample exposed to ex situ H$_2$O dosing; c) integrated peak areas of the samples exposed to in situ H$_2$O dosing only.
Referring to the samples exposed to in situ H₂O dosing for 20 h and 64 h (Figures S15 and S16, respectively, Supporting Information), a more similar behavior as compared to the sample subjected to the ex situ H₂O dosing procedure is perceived (Figure 5b). Note that only the peak intensities vary. Upon H₂ dosing, the formation of a positive band at ≈1600 cm⁻¹, the vanishing of the band at ≈1460 cm⁻¹, and the formation of a negative band at ≈1500 cm⁻¹ are observed. Upon Ar dosing, the positive band at ≈1600 cm⁻¹ decreases in intensity, whereas a negative band evolves at ≈1460 cm⁻¹. In addition, the band at ≈1500 cm⁻¹ vanishes. These trends are observed again during the second H₂ and Ar dosing sequence. Thus, the reversible formation of resorufin and hydroresorufin induced by the H₂ and Ar dosing sequences is followed by DRIFTS after in situ H₂O dosing for 20 h and 64 h.

Furthermore, the SP sensitivity to H₂ was successfully probed at a reduced H₂ concentration of 16.7 vol% (refer to Figure S17, Supporting Information).

This series of samples demonstrates that the efficiency of the consecutive reduction of resazurin to resorufin/hydroresorufin strongly correlates with the water content in the supraparticulate system. To shine more light on the influence of water on the system, molecular dynamics (MD) simulations were performed and the results are summarized in the following.

2.3. MD Simulations – H₂O-Induced Molecular Mobility

To follow the H₂O-induced molecular mobility of resazurin in the mesoporous silica SP framework, two simulation models referring to different wetting conditions were investigated: a SP in the as-prepared state and a SP after in situ or ex situ H₂O dosing. In both MD simulations, the weakly polar resazurin molecules quickly dissociate from the SiO₂ surface at a time scale of only 60–70 ps. Instead, the H₂O molecules form strong salt-bridges to the silica ions in addition to hydrogen bonds with the hydroxide groups. Upon about 100 ps additional simulation time, the model featuring a water film (i.e., the model that mimics a SP in the as-prepared state) showed segregation of the resazurin molecules to the water/vapor interface (Figure 6a). On a much slower pace, the diffusion of resazurin molecules along the water surface lead to association of the segregated compound and eventually to the formation of an aggregate comprising all resazurin molecules in the model.

On the other hand, the model of a vapor-free silica/water/silica sandwich arrangement, that mimics SPs after H₂O dosing, indicated the solvation of resazurin, albeit few (pairwise) association events could also be observed within the 2 ns scale of the performed MD runs (Figure 6b). While the simulation model is likely addressing an over-saturated resazurin solution, the data still suggests the mobility of dispersed resazurin molecules in the vapor-free system. This stands in strong contrast to the water-vapor interface, which showed rapid resazurin segregation and aggregation and, thus, rather limited resazurin availability for interactions with the water phase or the NPs in the mesoporous material. Consequently, it is concluded that a high degree of hydration of the SPs mesoporous network structure—affecting the filling of entire pores by water and thereby, creating a three-phase-system—is best suited to enable resazurin hydrogenation.

Bringing together the experimental results and the data obtained from MD simulations, the following mechanism for the color change reaction of the H₂ indicator SPs is suggested (Figure 7): the mobility of resazurin molecules is granted by the condensation of water within the mesoporous SP framework during the H₂O dosing process. This enables the movement of indicator dye species toward the Au–Pd NP surfaces. Subsequently, these H₂ atoms react with the resazurin molecules in their direct environment leading to their (ir)reversible reduction to...
resorufin/hydroresorufin accompanied by the observed eye-readable two-step color change.

3. Conclusion

In conclusion, we have synthesized and investigated a particulate additive for real-time monitoring and irreversible recording of the presence of H\textsubscript{2} gas, detectable by the bare eye. This supraparticulate system consists mostly of inexpensive components and is synthesized through a simple and scalable manufacturing process. Our findings are summarized as follows:

(1) SPs consisting of SiO\textsubscript{2} and Au−Pd NPs as well as the indicator dye resazurin were assembled via a scalable droplet evaporation approach using spray-drying. The resulting mesoporous supraparticulate framework absorbs and stores water from a humid atmosphere resulting in a three-phase-system. Upon exposure to H\textsubscript{2} gas, a fast, distinct, eye-readable (ir)reversible two-step color change reaction of the SPs is observed.

(2) In situ DRIFTS measurements demonstrate that this color change originates from the H\textsubscript{2}-induced (ir)reversible reduction of resazurin to resorufin/hydroresorufin. Based on a series of samples, we demonstrate that the water content within the mesoporous SP framework is key for their functionality and ensures the efficient reduction of resazurin. If the water content is too low, resazurin is not reduced or is reduced to resorufin only. Contrarily, an irreversible reduction to resorufin and reversible formation of hydroresorufin was observed, when the water content is high enough.

(3) MD simulations demonstrate that the mobility of resazurin dye molecules in a SP with low water content is limited due to segregation and aggregation processes. In contrast, the mobility of dye molecules is similar to that of bulk water solutions at a high water content. Based on this molecular mobility, the H\textsubscript{2} indicator functionality of the SP emerges as water acts as a transport medium to carry resazurin molecules towards the Au−Pd catalyst NPs that are embedded into the porous SP framework.

The presented H\textsubscript{2} indicator SPs enable a wide variety of applications as they can be applied as a smart additive. Furthermore, the combination of spatially resolved real-time monitoring and irreversible recording of H\textsubscript{2} gas, renders them especially attractive as safety aid in a future green H\textsubscript{2} economy. Following this mechanistic study, we will focus on practical aspects for future applications, such as the effects of temperature and gas impurities on the sensing properties of the SPs.

4. Experimental Section

\textbf{Materials and Reagents:} Resazurin sodium salt (C\textsubscript{12}H\textsubscript{6}N\textsubscript{4}NaO\textsubscript{4}), sodium citrate (C\textsubscript{6}H\textsubscript{5}Na\textsubscript{3}O\textsubscript{7}, ≥99%), and gold(III) chloride trihydrate (HAuCl\textsubscript{4}⋅3 H\textsubscript{2}O, ≥99.9%) were purchased from Sigma Aldrich. Potassium hexachloropalladate(IV) hexahydrate (K\textsubscript{2}PdCl\textsubscript{6}⋅6 H\textsubscript{2}O, 99%) was purchased from Alfa Aesar. Aqueous ammonia solution (28.0–30.0% NH\textsubscript{3} basis) was purchased from Merck and formaldehyde solution (CH\textsubscript{2}O, ≥37% with 8–12% methanol) was purchased from Carl Roth. Silica NPs (Köstrosol 2040, K2040) in the form of an aqueous NP dispersion containing 40 wt% silica were received from Chemiewerke Bad Köstritz. All chemicals were used without further purification. Water was deionized before use.

\textbf{Au-Pd NP Synthesis:} Au−Pd NPs were synthesized in a seedless one-pot sodium citrate coreduction reaction as described in more detail elsewhere\cite{41,62} with slight modifications. In a typical experiment, 1.6 mg (4.2 \textmu mol) gold(III) chloride trihydrate and 3.3 mg (8.3 \textmu mol) potassium hexachloropalladate(IV) hexahydrate were dissolved in 50 mL water and heated to 100 °C under reflux cooling. Subsequently, 3 mL of an aqueous sodium citrate solution (2 wt%) were added under vigorous stirring. The reaction mixture was left to boil with constant stirring for 15 min. The resulting black NP dispersion was cooled down to room temperature, purified via centrifugation (13 000 rpm, 35 min) and dispersed in water using ultrasonication.

\textbf{Fabrication of H\textsubscript{2} Indicator SPs:} H\textsubscript{2} indicator SPs were prepared in a one-step spray-drying process from a mixed NP dispersion. To 2.5 g of an aqueous SiO\textsubscript{2} NP dispersion (containing 40 wt% of SiO\textsubscript{2} NPs [1 g], stabilized with sodium hydroxide, pH ~10), 2 mL of the prepared Au−Pd NP dispersion and 0.5 mL of an aqueous resazurin solution (1 mg mL\textsuperscript{-1}) were added. For the in situ DRIFTS, the pore structure investigations and the functional testing, SP samples using 10 and 50 mL of the aqueous resazurin solution (1 mg mL\textsuperscript{-1}) and SPs without Au−Pd NPs using 10 mL of the aqueous resazurin solution (1 mg mL\textsuperscript{-1}) were prepared in the same manner. The obtained mixture was stirred for 5 min before spray-drying the obtained NP mixture using a lab-scale spray-dryer (Büchi).
Labrotechnik AG, B290 mini connected to a dehumidifier B-296). The spray-drying parameters were set to a pump rate of 200 mL h⁻¹, an inlet temperature of 110 °C resulting in an outlet temperature of ~54 °C, an aspirator power of 85% resulting in a volume flow of ~33 m³ h⁻¹ (~70 mbar under pressure) and a N₂ gas flow of ~470 L h⁻¹. A purple-colored, free-flowing powder was obtained. For control experiments, SPs consisting of SiO₂ NPs as well as SiO₂ and Au–Pd NPs were prepared following the procedure described above.

Materials Characterization: TEM was performed on a JEM-2010 (JEOL) using an acceleration voltage of 200 kV (Au–Pd NPs) and on a LEO 912 Omega (Zeiss) with 80 kV (SiO₂ NPs), respectively. Carbon coated copper TEM grids were used for sample preparation. Hydrodynamic particle size distributions were determined from diluted NP dispersion by DLS using a Zetasizer Nano (Malvern Panalytical) after a sonication step. ICP-OES was carried out using an iCAP 6000 emission spectrometer (Thermo Scientific). For determination of the H₂ indicator SP composition, 351.1 mg of the powder were dissolved in 250 mL aqua regia and analyzed utilizing ICP-OES standards for Au and Pd. SEM analyses were conducted on a JSM-F100 (JEOL) using an acceleration voltage of 4 and 1 kV, respectively, and a secondary electron detector. The particles were prepared on a carbon pad. Particle size distribution of the spray-dried SPs were obtained from laser light diffraction measurements using a Mastersizer 2000 (Malvern Panalytical). Prior to the measurement, the particles were dispersed in water under mechanical stirring and sonication using a Hydro 2000S (Malvern Panalytical). TGA was carried out in synthetic air atmosphere (10 mL min⁻¹ O₂, 40 mL min⁻¹ N₂) with a heating rate of 10 K min⁻¹ in the temperature range from 30 to 1000 °C using a TG 209 F1 Libra (Netzsch). To determine the water content of the activated SPs, the particles were dried at 110 °C and 40 mbar overnight and activated according to the previously described procedure.

High-resolution nitrogen (77.4 K) isotherm measurements were performed using an Autosorb-iQ sorption instrument (Anton Paar Quantatec). Water adsorption experiments were performed at 298 K with a volumetric (manometric) sorption analyzer (Vistar, Anton Paar). Water adsorption experiments were always performed on a fresh sample from the same homogeneous batch that was used for nitrogen adsorption experiments. Before each sorption measurement the samples were outgassed for 12 h under turbomolecular pump vacuum at 150 K and then weighed under an inert atmosphere. The UV–vis absorption spectra of an aqueous resazurin solution (0.05 mm, pH 10) was measured with a UV-2600 spectrometer (Shimadzu).

Ex Situ H₂O-Dosing and Functional Testing of H₂ Indicator SPs: The ex situ H₂O-dosing of the H₂ indicator SPs was performed by placing the powder together with a 100 mL beaker filled with water in a sealed desiccator in an oven at 50–60 °C for 24 h (Scheme S1, Supporting Information).

For the investigation of the particles color change reaction, the powder was placed in a 7 mL glass vial and exposed to H₂ gas (>99.9%, Air Liquide) from a 2 L gas bag connected to a syringe (1 mL). The experiments were carried out in an open system at air and room temperature. In order to follow the (ir)reversible color change of the powder, the gas bag (Fisher Scientific) was opened and closed for three cycles of ~10 s. Experimental details regarding further functional testing, for example, the selectivity study, are provided in the Supporting Information. Digital photographs and videos were taken with an Alpha 6000 (Sony).

In Situ IR Spectroscopy: The in situ DRIFTS measurements were performed with a Vertex 80v Fourier transform infrared (FTIR) spectrometer (Bruker). It is equipped with a KB beam splitter and a liquid N₂ cooled HgCdTe-detector. The Praying Mantis DRIFTS accessory and the high temperature reaction chamber (both from Harrick) is located in the extended sample compartment of the spectrometer. This home-built extension supplies all electrical and gas dosing feedthroughs. Thus, the sample compartment and the optical path is evacuated during IR measurements, which results in an outstanding long-term stability. The DRIFTS reactor is equipped with a type K thermocouple and two CaF₂ windows. Additionally, the reaction chamber is connected to the gas dosing system and a bubbler system dedicated to the in situ dosing of liquids. In this work, Ar (Linde, >99.999%) and H₂ (Linde, >99.999%) were used. In addition, Ar saturated with H₂O was dosed via the bubbler system. The H₂O reservoir was kept at room temperature and we refer to this gas feed as H₂O/Ar in the following. In general, gas flows up to 20 mL min⁻¹ and pressures between 1 mbar and 20 bar were regulated by mass flow and pressure controllers (both from Bronkhorst). Precise and reproducible experimental procedures, that is, control of temperature, pressure, gas composition, and gas flows, is possible as the system runs in a remote-controlled fashion.

Note that to obtain appropriate signal intensities in the DRIFTS measurements, H₂ indicator SPs with an increased resazurin dye concentration (1 wt%) were investigated. Prior to the IR measurements, the investigated SPs were either activated in a desiccator (ex situ H₂O dosing, Scheme S1, Supporting Information) or dried in vacuo (~1 mbar, at least 1 h). Thereafter, the samples were subjected to an in situ H₂O dosing for 0, 2, 20, and 64 h, respectively. Finally, a gas dosing sequence was conducted as described in the following (Figure 4c). Note that the total pressure was kept at 1 bar during all experimental steps. First, Ar (2.8 mL min⁻¹) and H₂O/Ar (5.6 mL min⁻¹) were dosed at 1 bar for 10 min. Under these conditions, a background spectrum was recorded (resolution = 2 cm⁻¹; acquisition time = 10 min). Thereafter, DRIFT spectra were recorded continuously (resolution = 2 cm⁻¹; acquisition time = 0.5 min). For the sample exposed to ex situ H₂O dosing, the temporal resolution was doubled. However, the ratio of sample scan time (acquisition time = 0.25 min) to background scan time (acquisition time = 5 min) was kept constant as compared to the measurements for the samples treated by in situ H₂O dosing. Subsequently, the samples were exposed to a mixture of H₂ (2.8 mL min⁻¹) and H₂O/Ar (5.6 mL min⁻¹) for 60 min (referred to as H₂ dosing sequence in the following) to induce the reduction of resazurin to resorufin and/or hydrosorufin. This step was followed by an Ar (2.8 mL min⁻¹) and H₂O/Ar (5.6 mL min⁻¹) dosing interval of 90 min (referred to as Ar dosing sequence in the following). To probe the reversibility of the induced changes, a second, identical sequence of H₂ dosing (60 min) and Ar dosing (90 min) was performed, subsequently. Post-data treatment included baseline-correction. For selected spectra shown later on, 5 spectra were averaged to improve the signal-to-noise ratio.

MD Simulation Details: All molecular dynamics simulations were performed with the LAMMPS software package and VMD was used for displaying and analysis of generated trajectories. The integration time step was chosen as 1 fs. Temperature and pressure were controlled by the Nose-Hoover thermostat with a damping factor of 1 ps and barostat with a damping factor of 200 ps, respectively. All force-field parameters were adapted from Becit et al.,[7] namely modelling the silicon-oxide interactions by the CMASS94 model from Matsui et al.[68] and employing the tailor-made potentials from Ciacchi et al.[69] for interactions involving hydroxide and water. All charges and force-field parameters are listed in full detail in the Supporting Information of our previous work.[3] For the short-ranged Buckingham potentials we used a distance cutoff of r_c = 1.1 nm, whereas r_c = 1.2 nm was applied to all other interactions. Long range electrostatics were described by the damped-shifted-force Coulomb approach with a damping factor of 0.5 nm⁻¹.[70]

For the MD simulations, a hydroxylated silica surface model according to pH = 7 was used in accordance with a previous study.[71] Therein, a charge-neutral 8 x 8 x 4 aₐ unit cell of non-chelated (001) and (00-1) surfaces was melted and then quenched into an amorphous silica/silanol core-shell system. 2D periodic boundary conditions were applied normal to the pristine [001] direction. Next, five resazurin molecules were docked to the obtained silica slab of 4 nm thickness (5027 H₂O) was added. In turn, silica wetting by a vapor-free water phase
was mimicked by a 3D-periodic silica-water-silica sandwich model of $7.2 \times 7.7 \times 7.7$ nm$^3$ dimensions ($7102$ H$_2$O). Initial relaxation of the water molecules was performed at fixed resazurin and silica positions before exploring full relaxation by unconstrained MD simulations. The temperature was kept at 300 K and for the 3D-periodic model a pressure of 1 atm was applied.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

Data Availability Statement
The data that support the findings of this study are available in the supplementary material of this article.

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