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# Mesoporous supraparticles with a tailored solid–liquid–gas interface for visual indication of H<sub>2</sub> gas and NH<sub>3</sub> vapours†

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**Dual-gasochromic supraparticles that undergo rapid eye-readable and gas-specific colour changes upon reaction with hydrogen or ammonia are reported. This functionality is achieved by tailoring the solid–liquid–gas interface within the mesoporous framework of supraparticles via spray-drying.**

Gasochromic materials that visually indicate the presence of toxic, flammable, or explosive gases through a change in their absorbance become increasingly relevant. Their optical readout facilitates remote and spatially resolved gas detection without a power supply. In addition, optical signal transduction makes an operation in explosive atmospheres possible by eliminating electrical contacts, *i.e.*, the risk of sparks.<sup>1</sup> Hydrogen (H<sub>2</sub>) gas and ammonia (NH<sub>3</sub>) vapours are currently relevant as targets for gasochromic detectors. They are considered promising energy carriers to foster the decarbonisation of our energy system. However, both gases pose danger to humans due to the high flammability range of H<sub>2</sub>/air mixtures<sup>1</sup> and the toxicity of NH<sub>3</sub>.<sup>2,3</sup> Therefore, any unintended release during the production, transport, or usage of both gases must be immediately detected and the leakage precisely localized.

A gasochromic particle that can be incorporated as an additive into diverse materials and indicate the presence of both gases through rapid, eye-readable, and gas-specific colour

changes at every point of use, *i.e.*, a dual-gasochromic particle, has the potential to meet this demand.

Despite the large variety of gasochromic materials available for H<sub>2</sub> gas<sup>4,5</sup> and NH<sub>3</sub> vapours,<sup>6–8</sup> respectively, no dual-gasochromic particle for these two species has been reported to the best of our knowledge. It is important to mention that electrical dual-gas detectors for H<sub>2</sub> and NH<sub>3</sub><sup>9</sup> or multi-gas detector arrays<sup>7,10</sup> were established but not in the form of one flexibly applicable, gasochromic particle. Most materials for visual H<sub>2</sub> detection are based on the activation of H<sub>2</sub> molecules at catalytically active noble metal surfaces and the subsequent reduction of organic<sup>11</sup> or inorganic chromophores.<sup>4,12</sup> NH<sub>3</sub> vapours are typically detected by impregnating organic pH indicator dyes into porous host materials and exploiting the basic nature of NH<sub>3</sub> as a proton acceptor.<sup>8</sup> Both types of gasochromic materials incorporate functional chromophores into porous support materials. Recently, we introduced supraparticles (SPs) as a new class of (meso)porous support materials for gasochromic indicators.<sup>13</sup> SPs are hierarchical assemblies of nanoparticle (NP) building blocks with a consistent structural motif,<sup>14</sup> offering a highly customizable material design.<sup>13,15–17</sup> The established gasochromic SPs exploit (ir)reversible colour changes of incorporated Reichardt's betaine dye or resazurin (RES) for the detection of NH<sub>3</sub> vapours<sup>13</sup> and H<sub>2</sub> gas,<sup>15–18</sup> respectively. However, the NH<sub>3</sub>-indicator SPs cannot detect H<sub>2</sub>, and *vice versa*.<sup>18</sup> Thus, the development of a SP for the visual detection of both gases is still an open challenge.

Herein, we report a pioneering example of a dual-gasochromic SP for H<sub>2</sub> gas and NH<sub>3</sub> vapours. Aiming for such a SP, we elaborated a suitable material design that involves the selection of appropriate building blocks and the adjustment of the chemical microenvironment within the solid–liquid–gas interface, provided by the porous framework of the SP. We found that a suitable dye species must undergo distinguishable colour change reactions upon reduction and deprotonation, respectively. Furthermore, we demonstrate that a suitable microenvironment can be created by spray-drying of a mixed dispersion containing SiO<sub>2</sub> NPs, Pt NPs, the chosen dye molecules, and an acid (H<sub>2</sub>SO<sub>4</sub>),

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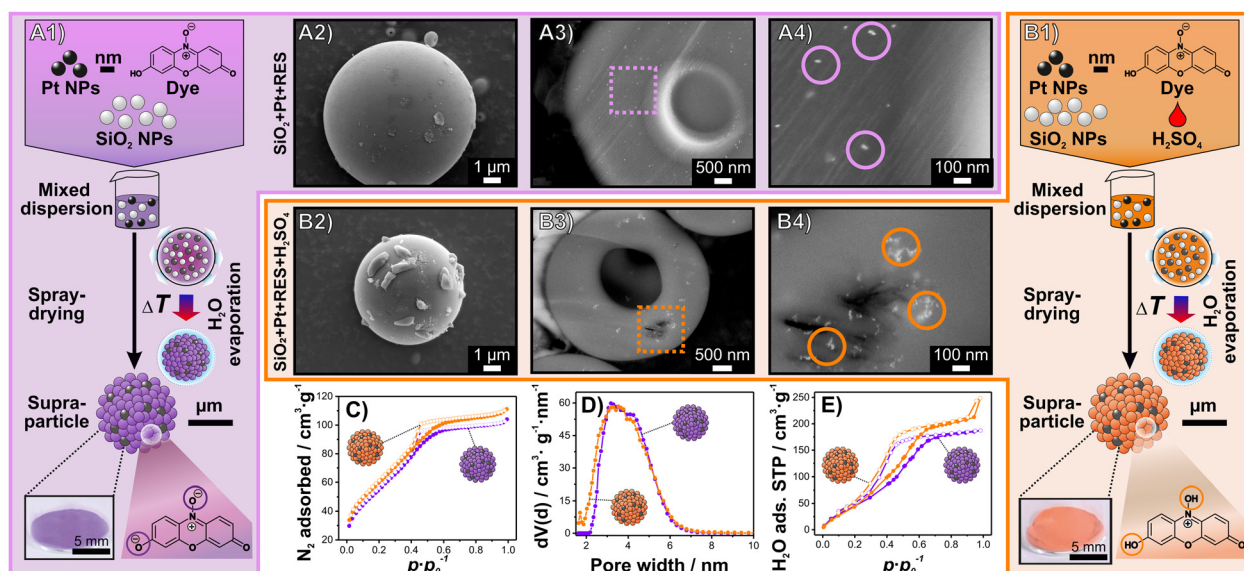


functioning as an additional key component. The resulting SPs achieve the targeted functionality through the interaction of  $H_2$  with the incorporated Pt NPs and  $NH_3$  with the acidic liquid phase within the gas-accessible pores of the SP. Both reactions at the solid-gas and liquid-gas interface induce a gas-specific colour change of the comprised dye molecules *via* reduction or deprotonation, respectively. From a broader perspective, the confined space within such mesoporous SPs provides a reaction environment similar to solution chemistry with the following advantages: exotic precursor combinations can be united almost independently of their surface-chemistry using forced assembly. The resulting SP powders can be easily incorporated as active material into sensor devices<sup>19</sup> or as pigment in coatings and clothing.<sup>18</sup>

The first step to create a dual-gasochromic SP for  $H_2$  gas and  $NH_3$  vapours was the identification of suitable chromophore systems and reaction conditions. Therefore, we probed the colour response of various indicator dye solutions by mixing them with  $NH_3$  solution or  $H_2$  gas (Fig. S1, ESI†). The main findings can be summarized as follows: Pt NPs with a size of roughly 5–10 nm (dynamic light scattering, DLS, Fig. S2, ESI†) are required for the  $H_2$ -induced reduction of dye molecules by providing active hydrogen at their surface.<sup>11</sup> Many dyes require an acid (*e.g.*, the presence of  $H_2SO_4$ ) to realize a strong colour change upon reaction with  $NH_3$  solution. An indicator dye species suitable for the envisaged SPs must undergo distinguishable colour responses upon deprotonation, induced by an increase in the pH value of its surrounding medium, and additionally also due to the reduction by active hydrogen. Among all tested indicator dyes (see ESI†), resazurin (RES) and methyl red (MR) are most suitable for the visual indication of both  $H_2$  and  $NH_3$ .

In the second step, we created a SP that provides the required chemical microenvironment by forced assembly of the identified key elements, *i.e.*, Pt NPs, dye molecules,  $H_2SO_4$ , and framework-building  $SiO_2$  NPs ( $\approx 5$ –15 nm, DLS, Fig. S3, ESI†) *via* spray-drying (Fig. 1A1 and A2). In this process, the different building blocks are united in a mixed dispersion, fed through a nozzle and atomized into small droplets. These droplets enter a hot chamber, which induces the evaporation of the solvent thereby forcing the assembly of all components at the liquid-gas interface, yielding a SP entity. Spray-drying is a continuous, high-throughput and industrially established process, which makes its scalability possible.<sup>20</sup> Herein, we achieved a SP production capacity of  $12\text{ g h}^{-1}$  using a lab-scale spray dryer.

For a proof-of-concept study, we exemplarily used RES as an indicator dye as it is well studied by others<sup>11</sup> and us.<sup>15–18</sup> We focused in our study on how the addition of  $H_2SO_4$  to the mixed dispersion prior to spray-drying influences the morphology, structure, texture and functionality of the resulting SPs. The mixed dispersion of the reference SP system containing  $SiO_2$  NPs, Pt NPs and RES had a pH  $\approx 10$  due to the NaOH-stabilisation of the  $SiO_2$  NP dispersion. The other mixed dispersion had a pH  $\approx 2$  due to the addition of  $H_2SO_4$ . The performed spray-drying processes of the two mixed dispersions yielded homogenous, free-flowing powders with a purple and orange colour, respectively (Fig. 1A1 and B1). These colours correspond to the deprotonated (purple) and protonated species of RES (RES- $H^+$ , orange), respectively,<sup>21</sup> matching the colours and UV-vis spectra of the aqueous solutions of RES (Fig. S1, ESI†). Scanning electron microscopy (SEM) imaging (Fig. 1A2 and B2) and laser diffraction measurements (Fig. S4, ESI†) revealed that neither the morphology nor the size



**Fig. 1** Synthesis of SPs *via* spray-drying without (A1) and with the addition of  $H_2SO_4$  (B1) and related SEM images of SPs without  $H_2SO_4$  (A2–A4) and with  $H_2SO_4$  (B2–B4): overview images (A2, B2), images of SP cross-sections using backscattered electron detection at different magnifications (A3–4, B3–4). Bright spots partially highlighted with coloured circles indicate the Pt NPs.  $N_2$  ad-/desorption isotherms at 77 K (C). Full symbols indicate adsorption branch and empty symbols indicate desorption branch. Non-local density functional theory (NLDFT) pore size distribution (D).  $H_2O$  ad-/desorption isotherms at standard temperature (298 K) and pressure (STP) (E).

distribution of the SPs are significantly altered by the addition of  $\text{H}_2\text{SO}_4$ . Both types of SPs show a spherical or doughnut-like morphology and a size distribution ranging from  $\approx 2$  to  $\approx 8 \mu\text{m}$ . As the Pt NPs are essential for the detection of  $\text{H}_2$ ,<sup>16</sup> we studied their distribution within the SP framework *via* SEM imaging of SP cross-sections using back-scattered electron detecting to obtain elemental contrast. Without the addition of  $\text{H}_2\text{SO}_4$ , the Pt NPs are well dispersed throughout the entire SP (Fig. 1A3) and partially form small agglomerates (Fig. 1A4). In contrast, the addition of  $\text{H}_2\text{SO}_4$  to the mixed dispersion results in the formation of larger Pt NPs agglomerates within the SP that, in turn, are distributed throughout the entire SP (Fig. 1B3 and B4). The enhanced agglomeration of the citric acid stabilised Pt NPs is attributed to the  $\text{H}_2\text{SO}_4$ -induced destabilisation of the colloidal dispersion.<sup>22</sup>

Similarly, the interstitial pores between the assembled NPs of the SP framework are essential for the targeted functionality.<sup>15</sup> The mesopores are intended to provide the required micro-environment within the solid-liquid-gas interface that consists of solid NPs, liquid pore water that is adsorbed in humid atmospheres<sup>15</sup> and the surrounding gas atmosphere. Therefore, we investigate the effect of the addition of  $\text{H}_2\text{SO}_4$  to the mixed dispersion prior to spray-drying on the textural properties and the water adsorption capacity of the resulting SPs. Details of the conducted  $\text{N}_2$  ad-/desorption at 77 K and  $\text{H}_2\text{O}$  ad-/desorption measurements at 298 K are provided in the ESI† (Fig. S5), while the main findings can be summarized as follows: both SPs are mesoporous, which is indicated by their almost identically shaped type IV  $\text{N}_2$  isotherms (Fig. 1C).<sup>23</sup> Their non-local density functional theory (NLDFT) pore size distribution is narrow ( $\approx 2\text{--}6 \text{ nm}$ ) with minor differences likely associated with the colloidal destabilization induced by  $\text{H}_2\text{SO}_4$  (Fig. 1D). Additionally, the presence of  $\text{H}_2\text{SO}_4$  in the SPs increases the total water adsorption capacity and causes a small shift of the relative pressure range at which water condensation occurs to smaller values (Fig. 1E). We attribute these changes mainly to the hygroscopic nature of  $\text{H}_2\text{SO}_4$ .<sup>24</sup>

Next, we probed the gasochromic functionality of the two SP powder samples by exposing the SP powders to  $\text{H}_2$  gas for  $\approx 20 \text{ s}$  and  $\text{NH}_3$  vapours for  $\approx 3 \text{ s}$ , respectively – optionally, also after *ex situ*  $\text{H}_2\text{O}$  dosing in a climate chamber (1 h,  $30^\circ\text{C}$ , 98% r.h.) to increase the amount of water in the pores.<sup>15</sup> The SP powder without  $\text{H}_2\text{SO}_4$  showed the previously reported rapid, eye-readable, two-step (ir)reversible colour change upon  $\text{H}_2$  dosing (Fig. 2A1, after *ex situ*  $\text{H}_2\text{O}$  dosing).<sup>15–17</sup> First exposure to  $\text{H}_2$  leads to the irreversible reduction of deprotonated RES (purple) to deprotonated resorufin (RF, pink), followed by a reversible reduction to hydroresorufin (hRF, colourless) upon further  $\text{H}_2$  dosing (Fig. 2A2). The condensed water in the mesopores grants the mobility of the incorporated dye molecules. This dye mobility enables their migration to the surface of the Pt NPs, where they can be reduced by active hydrogen when  $\text{H}_2$  gas is present.<sup>15</sup> SP powder without *ex situ*  $\text{H}_2\text{O}$  dosing did not show a complete conversion to colourless hRF due to a lower dye mobility (Fig. S6, ESI†). However, as the RES molecules in SPs without  $\text{H}_2\text{SO}_4$  are deprotonated, no colour change is observed upon dosing  $\text{NH}_3$  vapours (Fig. 2A3).

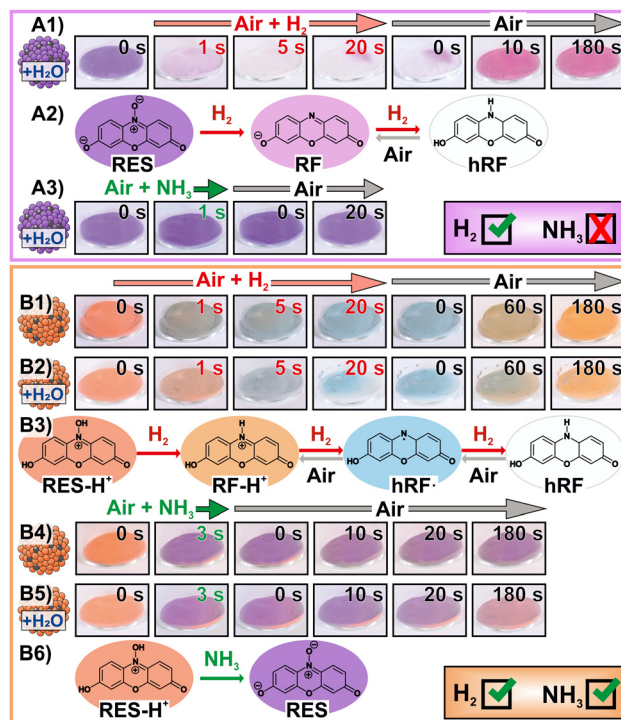


Fig. 2 Gasochromic functionalities of SP powders without (A) and with  $\text{H}_2\text{SO}_4$  added (B): snapshots before, during and after  $\text{H}_2$  dosing of SPs after *ex situ*  $\text{H}_2\text{O}$  dosing (A1) and related reaction network (A2). Snapshots of the same SPs before, during and after  $\text{NH}_3$  dosing (A3). Snapshots before, during and after  $\text{H}_2$  dosing of SPs containing  $\text{H}_2\text{SO}_4$  before (B1) and after *ex situ*  $\text{H}_2\text{O}$  dosing (B2) and related reaction network (B3). Snapshots of the same SPs before (B4) and after *ex situ*  $\text{H}_2\text{O}$  dosing (B5) before, during and after  $\text{NH}_3$  dosing and related reaction network (B6).

In contrast, SP powder containing Pt NPs,  $\text{SiO}_2$  NPs, RES and  $\text{H}_2\text{SO}_4$  showed rapid, eye-readable, gas-specific colour change reactions upon exposure to  $\text{H}_2$  or  $\text{NH}_3$  vapours (Fig. 2B, more snapshots provided in Fig. S7, ESI†). First reaction with  $\text{H}_2$  irreversibly reduced the orange  $\text{RES-H}^+$  to the slightly brighter  $\text{RF-H}^+$  (Fig. 2B1–B3). This is confirmed by distinct changes in their absorption and fluorescence spectra (Fig. S8, ESI†). Further  $\text{H}_2$  dosing led to blue powder due to the formation of a scarcely reported stable radical state of hRF (hRF $\cdot$ , Fig. 2B3).<sup>21</sup> When the dye mobility was high enough, hRF $\cdot$  was further reduced by  $\text{H}_2$  dosing to colourless hRF (Fig. 2B2). After stopping  $\text{H}_2$  dosing, the colourless SP powder (hRF) turned blue (hRF $\cdot$ ), before reaching a final orange colour ( $\text{RF-H}^+$ ). It is important to mention that the colouration of these SPs occurred much slower (up to 180 s) compared to their reduction ( $\approx 5\text{--}10 \text{ s}$ ) and the colouration of SPs without  $\text{H}_2\text{SO}_4$  ( $\approx 5\text{--}10 \text{ s}$ ). We attribute this slow reversibility to the stability of the blue hRF $\cdot$  radical in air.

In contrast to  $\text{H}_2$  dosing,  $\text{NH}_3$  vapours induced a rapid, visual colour change of SPs containing  $\text{H}_2\text{SO}_4$  from orange to purple (Fig. 2B4 and B5) due to deprotonation of  $\text{RES-H}^+$  to RES (Fig. 2B6). This reaction is caused by a pH increase of the liquid phase in the mesopores of the SPs that is likely induced by the adsorption and dissolution of gaseous  $\text{NH}_3$  species. The





proposed mechanisms are supported by a control SP sample containing SiO<sub>2</sub> NPs, RES, H<sub>2</sub>SO<sub>4</sub> but no Pt NPs, which showed no response to H<sub>2</sub> but an identical colour change to NH<sub>3</sub> dosing (Fig. S9, ESI†). The NH<sub>3</sub>-induced colour change of the SP powders is partially irreversible, as the initially orange colour related to RES-H<sup>+</sup> was never fully recovered (Fig. 2B4 and B5). Comparing the reversibility of the colour change upon repeated NH<sub>3</sub>/air dosing revealed a slightly higher degree of reversibility for SPs after *ex situ* H<sub>2</sub>O dosing compared to pristine SPs (Fig. S10, ESI†). The enhanced amount of water after H<sub>2</sub>O dosing increases the amount of NH<sub>3</sub> required to alter the pH of the liquid phase in the mesopores.

Besides testing separate H<sub>2</sub> and NH<sub>3</sub> dosing, the SPs containing Pt NPs, SiO<sub>2</sub> NPs, RES and H<sub>2</sub>SO<sub>4</sub> were subjected to simultaneous exposure to both target species. Details of this investigation are found in the ESI† (Fig. S11), while the main finding of this investigation can be summarized as follows: NH<sub>3</sub> poisons the incorporated Pt NPs,<sup>25</sup> which results in impaired H<sub>2</sub>-induced reduction of the dye species, when both NH<sub>3</sub> and H<sub>2</sub> are present. Therefore, upon dosing of H<sub>2</sub> and NH<sub>3</sub>, either pink RF is formed, when H<sub>2</sub> reacts with the SPs first, or deprotonated purple RES, when the SPs react first with NH<sub>3</sub>.

Next, we studied the adjustability of the conceptualised SPs and synthesized SPs containing MR as indicator dye. SPs with MR also showed eye-readable, gas-specific colour change reactions upon exposure to H<sub>2</sub> gas or NH<sub>3</sub> vapours (Fig. S12, ESI†). Preliminary quantitative *in situ* UV-vis measurements (Fig. S13, ESI†) demonstrate that dual-gasochromic SPs carrying RES or MR also undergo strong colour changes when they are exposed to ≈ 2 vol% H<sub>2</sub> in N<sub>2</sub> (*i.e.*, below the lower flammability limit of 4 vol%) or ≈ 620 ppm NH<sub>3</sub> in N<sub>2</sub> (*i.e.*, below the limit at which human health issues occur<sup>2,3</sup>).

In conclusion, we synthesised and characterised the first dual-gasochromic SPs that undergo rapid, eye-readable, gas-specific colour changes upon reaction with H<sub>2</sub> gas or NH<sub>3</sub> vapours. We revealed the parameters that affect the visual response and characteristics of the SPs. We demonstrated that only SPs assembled from SiO<sub>2</sub> NPs, Pt NPs, suitable dye species (RES or MR) and H<sub>2</sub>SO<sub>4</sub>, achieve the desired functionality. Thereby, the addition of H<sub>2</sub>SO<sub>4</sub> caused just minor changes to the morphology and texture of the SPs but improved the water adsorption capability and ultimately made the desired two gas-specific colour changes *via* scarcely reported reactions possible. The functionality of the SPs results from the synergistic interplay of all four types of building blocks within the solid-liquid-gas interface of their mesoporous framework (Fig. S14, ESI†). This interplay includes the adsorption and condensation of water in the mesopores, the dissociation of H<sub>2</sub> at the surface of Pt NPs and the mobility of incorporated indicator dye

molecules in the liquid phase. The later move through and react with the surface of the solid framework, *e.g.*, *via* hydrogenation. Furthermore, we herein demonstrated the possibility of adjusting the pH of the liquid phase in the mesopores during SP synthesis *via* H<sub>2</sub>SO<sub>4</sub> addition as well as afterward through the interaction with NH<sub>3</sub> vapours. The dual-gasochromic SPs are therefore a pioneering example for the emergence of new functionalities by exploiting the customisation of the solid-liquid-gas interface within the mesopores of a micron-sized SP.

The contribution of all authors according to the CRediT system is listed in the ESI.† All authors have approved the final version of the manuscript.

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## Conflicts of interest

There are no conflicts to declare.

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