

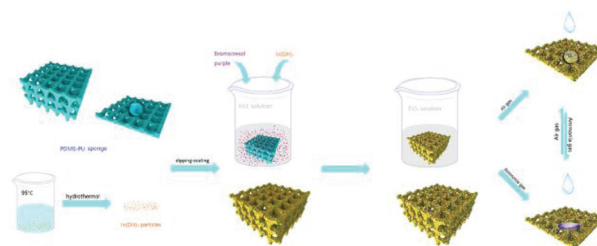
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1

A dual ammonia-responsive sponge sensor: preparation, transition mechanism and sensitivity

Jiahong Guo, Zhiwei Bai, Yonglei Lyu, Jikui Wang* and Qiang Wang

Yellowish and superhydrophobic ammonia-responsive sponge which fabricated by dipping–coating method changes to purple and superhydrophilic when exposed to ammonia condition.



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First (given) name(s)	Last (family) name(s)	ResearcherID	ORCID
Jiahong	Guo		0000-0002-9188-2242
Zhiwei	Bai		
Yonglei	Lyu		
Jikui	Wang		
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A dual ammonia-responsive sponge sensor: preparation, transition mechanism and sensitivity†

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Q1

Jiahong Guo,^a Zhiwei Bai,^a Yonglei Lyu,^b Jikui Wang*^a and Qiang Wang^c

PDMS-PU (polydimethylsiloxane-polyurethane) sponge decorated with $\text{In}(\text{OH})_3$ (indium hydroxide) and BCP (bromocresol purple) particles is shown to be a room-temperature ammonia sensor with high sensitivity and excellent reproducibility; it can accomplish real-time detection and monitoring of ammonia in the surrounding environment. The superhydrophobic and yellowish $\text{In}(\text{OH})_3$ -BCP- TiO_2 -based ammonia-responsive (IBT-AR) sponge changes to a purple superhydrophilic one when exposed to ammonia. Notably, after reacting with ammonia, the sponge can recover its original wettability and color after heating in air. The wettability, color and absorption signal of IBT-AR sponge have been measured for sensing ammonia using the water contact angle, macroscopic observation and UV-vis absorption spectrometry, respectively. The minimum ammonia concentrations that can be detected by the sponge wettability, color and absorption signal are 0.5%, 1.4 ppm and 50 ppb, respectively. This kind of sponge with smart wettability and color is a promising new ammonia detector.

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Introduction

Given the rapid development of industry, agriculture, and the automotive revolution, atmospheric environmental pollution has become one of the most serious issues, which has attracted considerable attention.^{1,2} Frequent utilization of water heaters, air conditioners and piped gas has aggregated the release of gas, which poses a threat to the environment, ecosystem and human health. Ammonia (NH_3) is a toxic gas with strong and pungent odor, and it is harmful to the human organs; ammonia is widely used in fertilizer production, food processing, *etc.*^{3–6} Therefore, relevant development has raised a series of restrictive requirements for ammonia concentration. Generally, the immediately dangerous to life or health concentration (IDLH) is stipulated to be 300 ppm by the American National Institute for Occupational Safety and Health. The specified threshold limit value in the workplace is 50 ppm as stipulated by the Occupational Safety and Health Administration (OSHA).⁷ Ammonia in water at a concentration of $25 \mu\text{g L}^{-1}$ is known to be toxic to organisms.⁸ Therefore, it is

necessary to design and fabricate a sensitive and room-temperature-efficient gas sensor, which can detect, monitor and remove NH_3 in real time from the surrounding environment.

Over the past few years, some materials have been continuously proposed for NH_3 detection and absorption including electrochemical materials,⁹ near-IR absorption materials,¹⁰ metal oxide semiconductors¹¹ and fiber optic sensors;¹² among these, metal oxide semiconductors and fiber optic sensors have attracted much interest due to their microstructural defects, which are beneficial for oxygen ion formation and easy observation. In the presence of a testing gas, the conductivities of the chemical gas sensors based on semiconducting metal oxides, such as GO (graphene oxide),^{13–15} TiO_2 ,^{16–18} ZnO ,^{19–21} In_2O_3 ,^{22,23} SnO_2 ,²⁴ WO_3 ,^{25,26} vary. However, some metal oxide gas sensors have limited practical applications as they only operate at high temperature and thus are not suitable for normal environments.^{27,28} In addition, the recovery performance of the gas sensors is poor because the gas requires long time periods for desorption.^{29,30} Thus, it remains a great challenge to propose novel gas sensors with different response mechanisms.

Surface wettability change and color change are sensitive to the surroundings but have rarely been utilized in harmful atmosphere detection. Currently, some ammonia gas sensors with excellent sensitivity based on wettability and color change have been successfully obtained. Zhu *et al.* prepared a polyaniline (PANI)-coated fabric by *in situ* doping polymerization, and they found that when the PANI-coated fabric was exposed to ammonia gas, the wettability changed from superhydrophobic (doped state) to superhydrophilic (de-doped state).³¹ Wang

^aShanghai Key Laboratory of Advanced polymeric Materials, Key Laboratory for Ultrafine Materials of Ministry of Education, School of Materials Science and Engineering, East China University of Science and Technology, Shanghai 200237, PR China. E-mail: wang326@ecust.edu.cn

^bDepartment of Chemistry, University of Turku, Vatselankatu 2, 20500 Turku, Finland

^cSofima Automotive Filter (Shanghai) Co., Ltd, Shanghai, 201707, China

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et al. synthesized $\text{In}(\text{OH})_3$ -PDMS sponges by surface modification and proved that the surface wettability can switch reversibly between superhydrophobicity and superhydrophilicity while detecting ammonia.²³ Trinkel *et al.* investigated an ammonia optical sensor with a pH-sensitive dye (bromophenol blue); the color of the sensor changed reversibly from yellow to blue with the increasing concentration of ammonia.³² Claudia fabricated an optical sensor that immobilized rhodamines, and the sensor turned colorless when it was exposed to ammonia gas.⁸ Tao *et al.* developed sensitive, reversible ammonia sensing probes using an organic reagent (bromocresol purple), and the originally yellow compound changed to blue when it was reacted with ammonia.³³ However, some obstacles need to be overcome to further improve the gas sensitivity performance and expand the application range: operability at room temperature, compatibility between stability and sensitivity, and humidity influence.

Indium hydroxide [$\text{In}(\text{OH})_3$] and its oxides are good semiconductor materials with excellent optical properties and photocatalytic activities.^{34,35} Besides, $\text{In}(\text{OH})_3$ shows subacidity in an aqueous atmosphere, due to which it interacts weakly with $\text{NH}_3\cdot\text{H}_2\text{O}$ molecules.³⁶ Thus, $\text{In}(\text{OH})_3$ is considered to be a leading ammonia-responsive candidate; the mechanism principally includes continuous monitoring of the direct changes in wettability with respect to adsorption and desorption of the target gas molecules. Optical methods are based on either the intrinsic IR-absorption of gaseous ammonia or selective reaction of a reagent with ammonia to give a detectable color, which can be used for single shot tests. Bromocresol purple (BCP), an organic dye with large surface area, has attracted great attention due to its high number of active sites and superior conductivity. In addition, BCP can detect ammonia in an aqueous solution, which makes it a potential candidate for ammonium detection.^{37,38}

Herein, a dual reversible ammonia-responsive sensing sponge was fabricated using $\text{In}(\text{OH})_3$ and BCP as ammonia wettability indicator and color indicator, respectively. In air conditions, the sponge showed superhydrophobicity and yellowish color, whereas it exhibited superhydrophilicity and purple color when exposed to ammonia conditions. Therefore, the preparation of a sponge with easy distinguishability, high sensitivity and excellent repeatability may pave the way toward environmental monitoring.

Experimental

Materials

SYLGARD 184 silicone elastomer prepolymer (Sylgard 184A, $M_w = 22\,000\text{ g mol}^{-1}$) and curing agent (Sylgard 184B, $M_w = 15\,000\text{ g mol}^{-1}$) were purchased from Dow Corning. PU sponges were obtained from Co., Ltd (Nangtong, China). Indium chloride (InCl_3), urea [$(\text{NH}_2)_2\text{CO}$] and $\text{NH}_3\cdot\text{H}_2\text{O}$ were purchased from Aladdin (Shanghai, China). *N*-Octane, carbon tetrachloride, concentrated hydrochloric acid (HCl), and ethanol were bought from Lingfeng Chemical Reagent Co., Ltd

(Shanghai, China). BCP (bromocresol purple) and TiO_2 (titanium dioxide) were purchased from Molbase (Shanghai, China).

Preparation of $\text{In}(\text{OH})_3$ micro- and nanoparticles

$\text{In}(\text{OH})_3$ micro- and nanoparticles were fabricated by low-temperature hydrothermal synthesis according to our previously reported method.²³ In a well-sealed glass bottle, 0.8 mmol InCl_3 and 8 mmol $(\text{NH}_2)_2\text{CO}$ were dissolved in deionized water. After heating at 95 °C for 24 h, the obtained $\text{In}(\text{OH})_3$ particles were rinsed with deionized water and ethanol to remove any possible contamination. The sample was then dried in an oven at 70 °C.

Preparation of superhydrophobic and superoleophilic PDMS-PU sponge

Superhydrophobic and superoleophilic PDMS-PU sponges were fabricated based on our previous study.³⁹ Specifically, commercial PU sponges were immersed in PDMS mixed solution containing *n*-octane and carbon tetrachloride (CCl_4) for a certain period of time. Then, the sponges were taken out and left in air to remove diluents, followed by drying in an oven at 70 °C for 2 h. To improve roughness, the as-prepared sponges were etched in HCl solution and then rinsed with distilled water and ethanol several times. Finally, PDMS-PU superhydrophobic sponges were obtained after drying in an oven at 80 °C.

Fabrication of $\text{In}(\text{OH})_3$ -BCP- TiO_2 -based ammonia-responsive (IBT-AR) sponge

The obtained $\text{In}(\text{OH})_3$ micro- and nanoparticles and BCP particles were dispersed in 1 M HCl aqueous solution for 2 h to form a homogenous yellowish solution. Then, a piece of PDMS-PU sponge was soaked in the above solution with continuous stirring for 24 h at room temperature. After rinsing with ethanol and deionized water, the $\text{In}(\text{OH})_3$ -BCP ammonia responsive (IB-AR) sponge was dried in an oven at 80 °C. Finally, IB-AR sponge was immersed in TiO_2 solution for a certain period of time and dried at 80 °C to obtain $\text{In}(\text{OH})_3$ -BCP- TiO_2 -based ammonia-responsive IBT-AR sponge.

Characterization

The morphologies of as-prepared sponges were investigated by field emission scanning electron microscopy (FESEM S-4800) under an electron beam with an accelerating voltage. All samples were coated with a thin layer of gold for better conductivity. X-ray energy dispersive spectrometer (EDS) attached to the SEM was used for the examination of the chemical composition of sponges. The surface chemical composition of sample was analysed *via* X-ray photoelectron spectroscopy (XPS) using constant pass energy mode with a value of 100 eV. X-ray diffraction (XRD) was performed on Rigaku D/Max B. Ultraviolet and visible-light (UV-vis) absorption spectra of samples were obtained on a Shimadzu Model UV-2550 UV-vis spectrophotometer. The surface wettability of the sponges was studied *via* contact angle measurement with JC2000D3. Each sample was measured at least three times.

Results and discussion

Fig. 1 illustrates the fabrication process of $\text{In}(\text{OH})_3$ -BCP- TiO_2 -based ammonia-responsive (IBT-AR) sponge. In accordance with our previous literature,³⁹ the IBT-AR sponge was prepared by dipping a PDMS-PU sponge in HCl mixed solution containing BCP and $\text{In}(\text{OH})_3$, followed by dipping in TiO_2 solution. The dipping order of HCl mixed solution and TiO_2 solution influenced the wettability of the obtained sponge. Compared with the procedure where the PDMS-PU sponge was dipped into TiO_2 solution first and then into the HCl mixed solution, a reverse procedure where the PDMS-PU sponge was first dipped into the HCl mixed solution and then into the TiO_2 solution produced samples with better wettability. Also, pre-dipping in TiO_2 solution improved sponge wettability, which was ascribed to the improvement in roughness; the subsequent HCl dipping rinsed off some of the TiO_2 particles and resulted in $\text{In}(\text{OH})_3$ and BCP particles being coated on the surface of the sponge, both of which weakened the wettability

of the sponge. The reverse dipping order ensured that TiO_2 particles were coated on the surface of the sponge, which enhanced the roughness. Therefore, the optimum dipping order is dipping PDMS-PU sponge into HCl mixed solution first and then into TiO_2 solution. Finally, the yellowish IBT-AR sponge covered with BCP and $\text{In}(\text{OH})_3$ showed ammonia-responsive wettability and color due to ammonia reacting with $\text{In}(\text{OH})_3$ and BCP.

X-ray diffraction analysis (XRD) of $\text{In}(\text{OH})_3$ particles was carried out for phase identification, and the results are shown in Fig. 2a. Clearly, all the diffraction peaks were easily assigned to the body centered cubic (bcc) phase of $\text{In}(\text{OH})_3$ [JCPDS 76-1463]. The sharp and strong diffraction peaks showed that the sample was a well-crystallized sample. Fig. 2b shows the elemental analysis of $\text{In}(\text{OH})_3$, which is obtained by energy dispersive X-ray spectroscopy (EDS). In this EDS curve, the existence of In and O elements proved the successful preparation of the sample. In addition, the In/O atomic ratio was about 1:3, which was consistent with the theoretical In/O atomic ratio of $\text{In}(\text{OH})_3$.

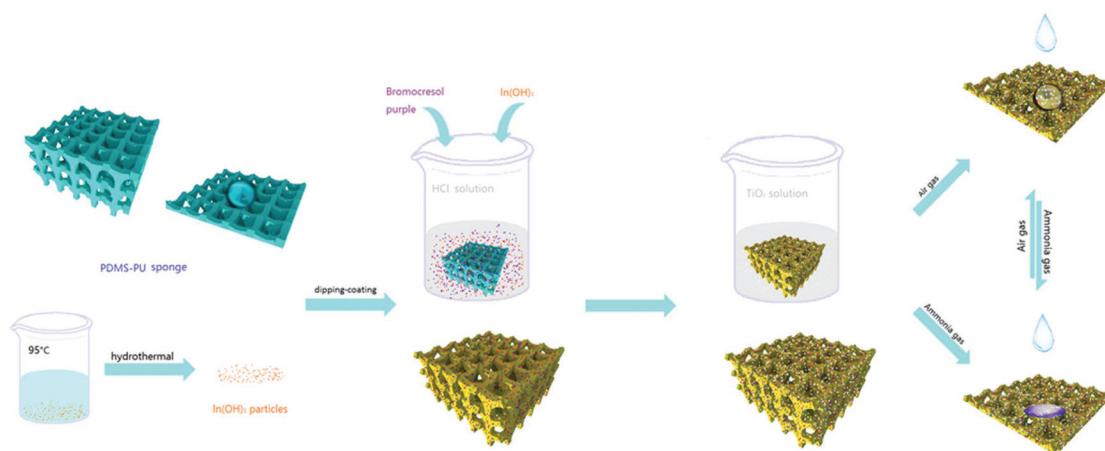


Fig. 1 Fabrication process of IBT-AR sponges.

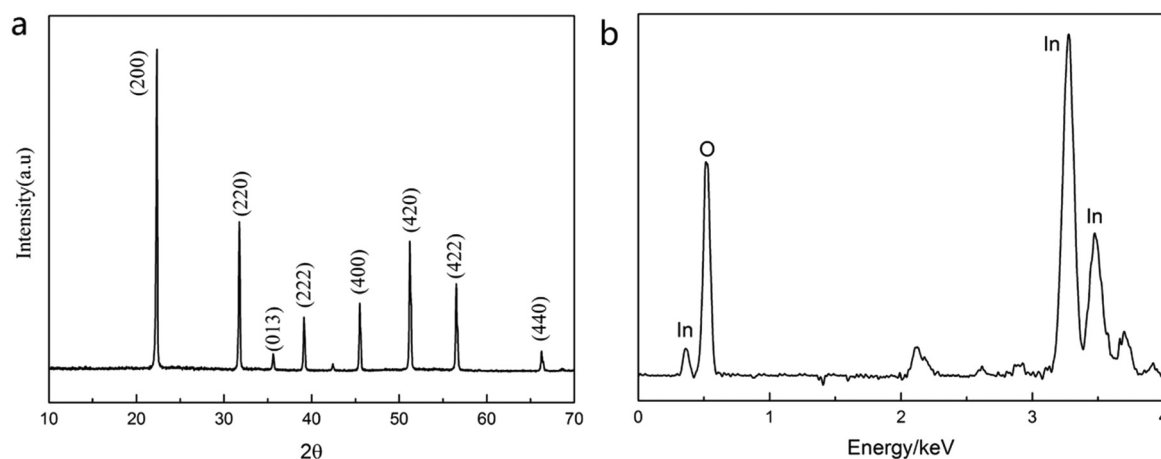


Fig. 2 XRD and EDS patterns of $\text{In}(\text{OH})_3$. (a) XRD spectrum of $\text{In}(\text{OH})_3$ with good crystallization. (b) EDS spectrum shows particles mainly composed of indium and oxygen.

Fig. 3(a) and (b) show EDS and XPS spectra of IBT-AR sponge, respectively; both reveal the presence of In, C, Ti, O, Br, Si and S elements, which proves that $\text{In}(\text{OH})_3$ and BCP have adhered on the PDMS-PU sponge. Compared with other elements, the S element of BCP ($\text{C}_{21}\text{H}_{16}\text{Br}_2\text{O}_5\text{S}$) had very low concentration and thus, its peak was difficult to detect. Therefore, the enlarged S 2p image is seen as an inset in the XPS spectrum, which shows the S element peak appearing at 170 eV. These results prove that the IBT-AR sponge was successfully fabricated.

Fig. 4(a)–(h) show the structural morphologies of $\text{In}(\text{OH})_3$, BCP, IB-AR sponge and IBT-AR sponge. $\text{In}(\text{OH})_3$ particles fabricated by the low-temperature hydrothermal synthesis have multiple stacked structures including microcubes and nanorods. BCP particles have smooth and cubic structures with irregular sizes, which are similar to those of $\text{In}(\text{OH})_3$ microcubes.

The sponge surface becomes rougher after $\text{In}(\text{OH})_3$ and BCP coating on PDMS-PU sponge, and $\text{In}(\text{OH})_3$ and BCP microstructures can also be found in the enlarged image. Moreover, after decorating by TiO_2 solution, it can be observed that the sponge skeletons possess uniformly coated particles including $\text{In}(\text{OH})_3$, BCP and TiO_2 , which greatly increase the surface roughness; this further results in excellent ammonia sensitivity.

When the sponge comes in contact with aqueous ammonia, the ammonia molecule diffuses into the porous structure and reacts with BCP dye immobilized in the sponge. Hence, in principle, a conventional sponge with BCP dye despite hydrophilic or hydrophobic wettability can be used for detecting and monitoring ammonia in aqueous solution directly. However, there are two main problems while using a hydrophilic sponge to detect ammonia in water. First, BCP

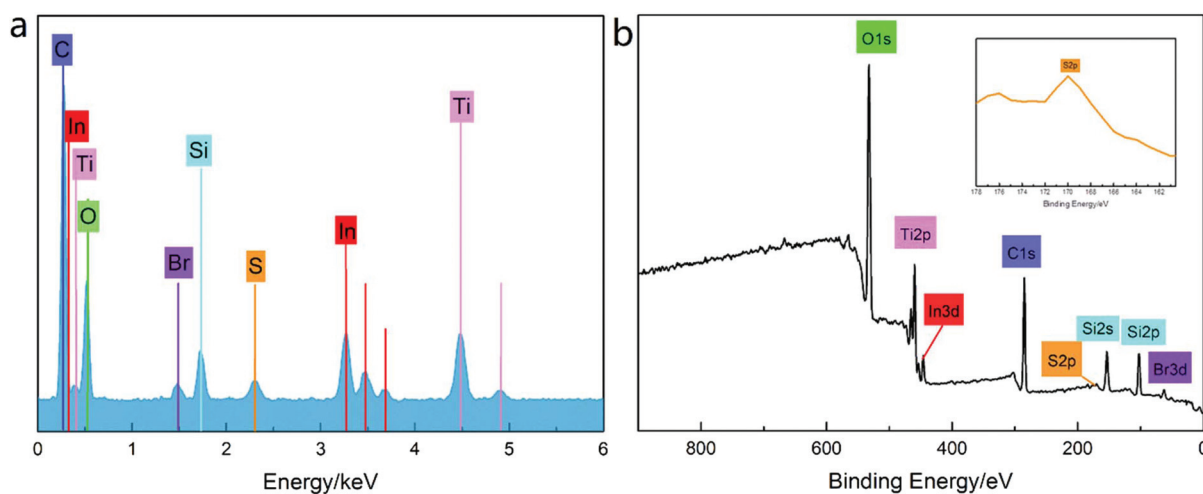


Fig. 3 EDS and XPS spectra of IBT-AR sponge. (a) EDS spectrum of IBT-AR sponge. (b) XPS spectrum of IBT-AR sponge; inset is the enlarged view of S 2p peak.

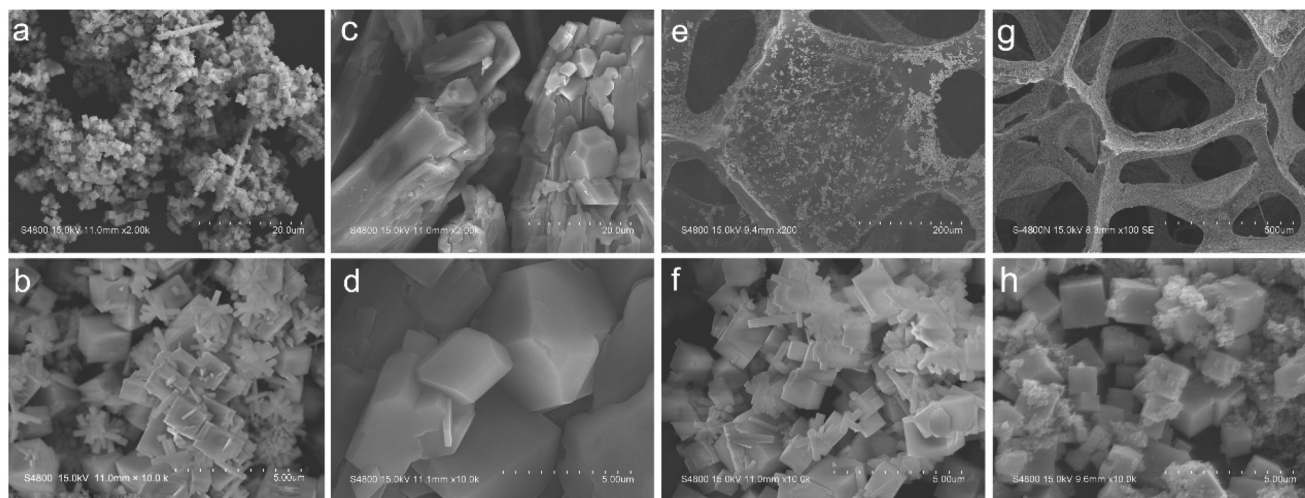


Fig. 4 SEM images of $\text{In}(\text{OH})_3$, BCP, IB-AR sponge and IBT-AR sponge with different magnifications. (a, b) $\text{In}(\text{OH})_3$; (c, d) BCP; (e, f) IB-AR sponge; (g, h) IBT-AR sponge.

would re-dissolve into water slowly when a BCP-coated sponge is soaked in ammonia solution for a long time, and its color would change continuously during the entire sensing process due to the re-dissolution of the BCP dye into the solution. Second, the BCP dye can react with metal ions existing in water to form a stable complex. In addition, some metal ions in solution can consume BCP dyes and reduce the efficiency greatly. Therefore, in this study, sponges must be modified with PDMS layers to block liquid water from entering into the sponge and to increase the efficiency. Fig. 5(a) is the image of different liquid droplets including water, HCl and ammonia on the IBT-AR sponge. The water and HCl droplets form beads, but the aqueous ammonia droplet is easily absorbed

into the sponge. Fig. 5(b) and (c) are the water and ammonia (1 M) contact angles of IBT-AR sponge. When a water droplet was placed on the IBT-AR sponge surface, it appeared spherical, and the static water contact angle was $162^\circ \pm 1.5^\circ$, indicating the superhydrophobic behaviour of the IBT-AR sponge. After placing an aqueous ammonia droplet on the sponge surface, the droplet was absorbed into the sponge, and the static water contact angle was measured to be 0° . Additionally, the IBT-AR sponge had low sliding angle, and the water rolled quickly after it was placed on sponge (See movie in ESI†).

Fig. 6 is the shape change comparison of IBT-AR sponge before and after bending or twisting. After bending or twisting, the IBT-AR sponge always recovered its primary shape, which

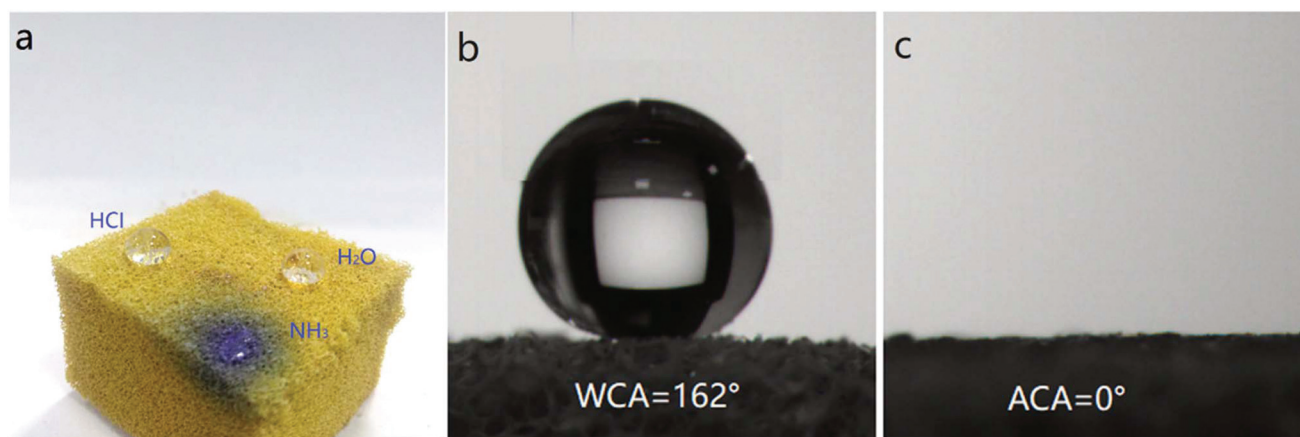


Fig. 5 Wettability of IBT-AR sponge. (a) Image of different liquid droplets including HCl, water and ammonia on IBT-AR sponge. (b) Water contact angle of IBT-AR sponge. (c) Ammonia contact angle of IBT-AR sponge.

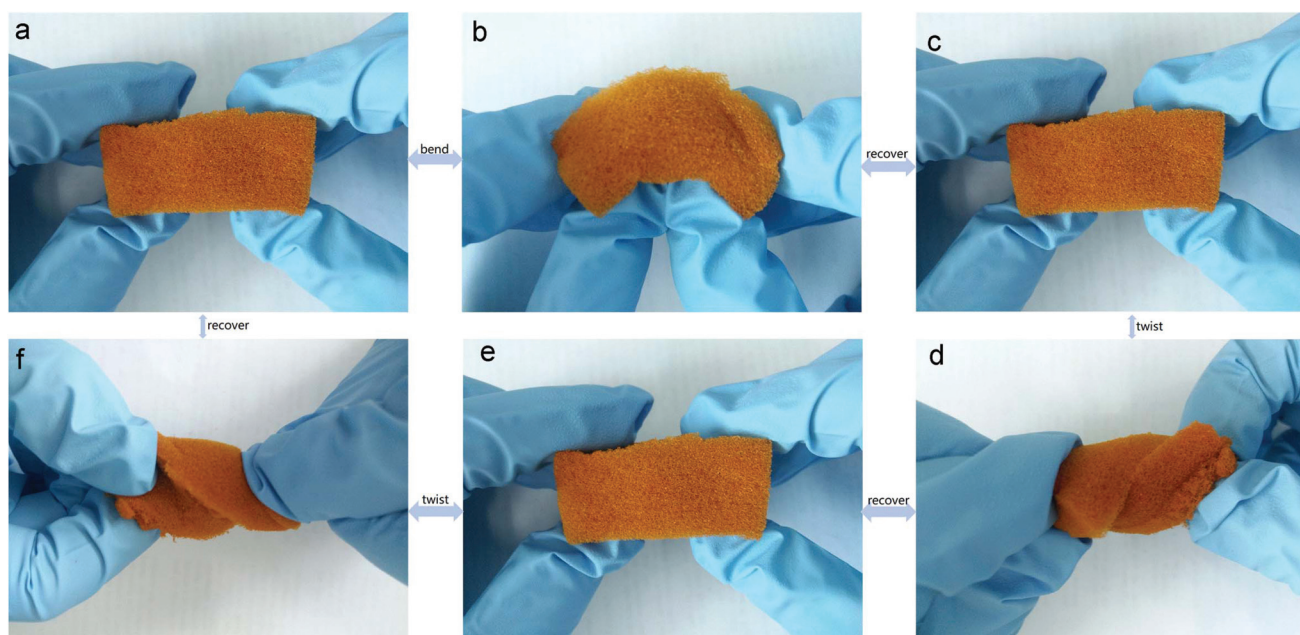


Fig. 6 The apparent shape changes of IBT-AR sponge after bending and twisting. (a) Shape of original sponge; (b) shape of sponge after bending; (d, f) shape of sponge after twisting; (c, e) shape of sponge after releasing force.

proved that the presence of external force has no influence on the apparent shape of the sponge.

BCP is an organic dye which can react with ammonia to form a BCP-ammonia salt. In this study, the reaction results are examined by UV-vis absorption spectrometry. BCP of IBT-AR sponge absorbs light with peak absorption at around 440 nm, whereas BCP-ammonia salt absorbs light with peak absorption at around 595 nm. Fig. 7 shows the absorption spectra of the IBT-AR sponge exposed to ammonia environments with different ammonia concentrations. When ammonia comes in contact with IBT-AR sponge, ammonia molecules diffuse into the sponge and react with BCP immobilized on the IBT-AR sponge skeletons. Fig. 8 is the reversible reaction equation between BCP and ammonia. The reaction process promotes the increase in BCP-ammonia salt concentration and reduction in BCP concentration. Therefore, the absorption peak intensity of BCP-ammonia salt increases and the absorption peak intensity of BCP decreases. With the increase in ammonia concentration, absorption at around 595 nm increases, and the absorption at around 440 nm decreases.

Fig. 9 shows the reversible reaction between ammonia and $\text{In}(\text{OH})_3$. When IBT-AR sponge is exposed to ammonia solution, hydrogen atoms are easily removed because $\text{In}(\text{OH})_3$ shows subacidity in aqueous solution. The hydroxyl groups in the polar $\text{NH}_3 \cdot \text{H}_2\text{O}$ molecules tend to capture hydrogen atoms of $\text{In}(\text{OH})_3$ because of the strong basicity of $\text{NH}_3 \cdot \text{H}_2\text{O}$. Thus, the hydrogen atoms form a strong combination with $\text{NH}_3 \cdot \text{H}_2\text{O}$

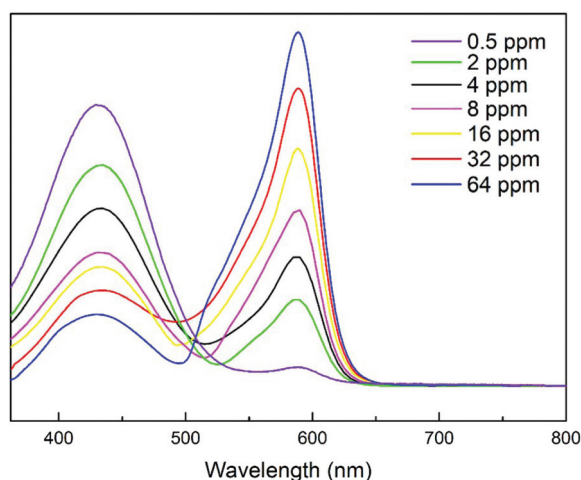


Fig. 7 Absorption spectra of IBT-AR sponge exposed to ammonia environments with different ammonia concentrations.

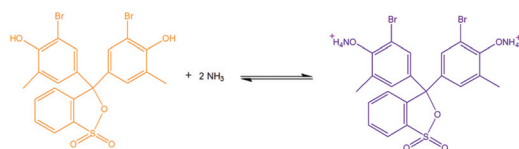


Fig. 8 Reversible color reaction between ammonia and BCP.

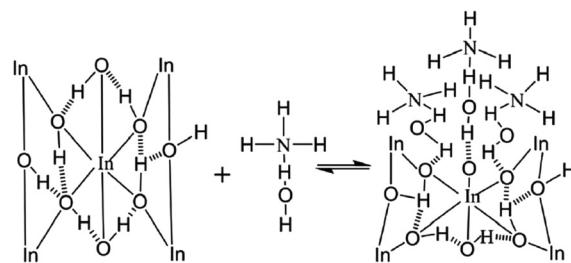


Fig. 9 Reversible reaction between ammonia and $\text{In}(\text{OH})_3$.

molecules. $\text{In}(\text{OH})_3$ micro and nanoparticles are randomly dispersed in the skeleton of the sponge, which increases the direct contact area between $\text{NH}_3 \cdot \text{H}_2\text{O}$ and $\text{In}(\text{OH})_3$. Therefore, $\text{NH}_3 \cdot \text{H}_2\text{O}$ molecules fixed on $\text{In}(\text{OH})_3$ can form an ammonia hydroxide layer on $\text{In}(\text{OH})_3$ particles, which greatly increases the surface free energy. Thus, after placing ammonia solution on IBT-AR sponge, the ammonia solution droplets penetrate into the pores and displace the trapped air to the wet sponge surface, creating a superhydrophilic sponge with a water contact angle of 0° .

To detect the ammonia wettability sensing properties based on the as-prepared IBT-AR sponge, systematic measurements were carried out in specific ammonia solution for 2 h at room temperature. Fig. 10(a) shows the curve of water contact angles with different ammonia concentrations. When the $\text{NH}_3 \cdot \text{H}_2\text{O}$ concentration increased, the water contact angles decreased from 162° to 0° , and the minimum detectable $\text{NH}_3 \cdot \text{H}_2\text{O}$ concentration was 0.5%, which was due to the breaking of hydrogen bonds being possible only when the $\text{NH}_3 \cdot \text{H}_2\text{O}$ concentration is more than 0.5%. Fig. 10(b) shows the reversible superhydrophobic–superhydrophilic conversion and color change of IBT-AR sponge. Interestingly, by heating the superhydrophilic sponge at 80°C for a certain period of time, the weak bonds between $\text{NH}_3 \cdot \text{H}_2\text{O}$ molecules and $\text{In}(\text{OH})_3$ were gradually broken, and the $\text{NH}_3 \cdot \text{H}_2\text{O}$ molecules escaped from the surface. Thus, the sponge surface wettability recovered to superhydrophobicity again. Furthermore, the sponge maintained excellent ammonia wettability sensitivity properties after 15 cycles of detection and heat treatments.

Color change is also one of the most important parameters in this study. According to the reaction equation between BCP and ammonia (Fig. 8), pristine IB-AR sponges are yellowish, but having detected the existence of ammonia, the color quickly changes to purple. The minimum $\text{NH}_3 \cdot \text{H}_2\text{O}$ concentration that changed the sponge color to purple is 1.4 ppm; the minimum $\text{NH}_3 \cdot \text{H}_2\text{O}$ concentration that can be detected by UV-vis absorption spectrometry is 50 ppb. Similarly, the sponge color can change back to yellowish after standing in air for a period of time. After 15 detection and air standing cycles, IBT-AR sponge maintained good ammonia color sensitivity (Fig. 10b).

Combining the two above-mentioned properties, we deduced that IBT-AR sponge can detect the existence of ammonia *via* its wettability and color. Fig. 10(a) shows the

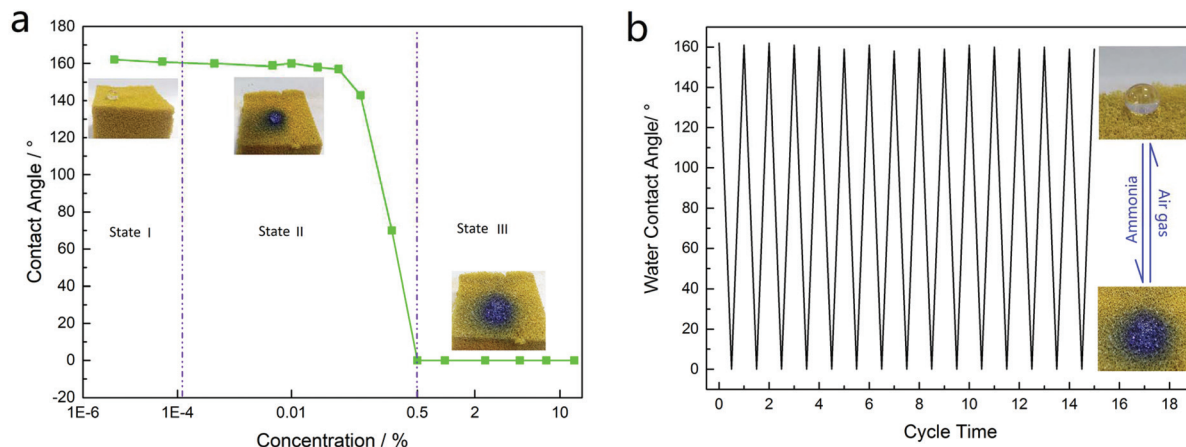


Fig. 10 (a) Plots of water contact angles with different ammonia concentrations; insets are three different representative wettability and color of IBT-AR sponges. (b) Reversible surface wettability and color change when IBT-AR sponge is exposed alternatively to ammonia and air.

water contact angle curve variation with different ammonia concentrations, and the inset images are sponge appearances with different ammonia concentrations. According to different ammonia responses, this curve can be divided into three regions. When the ammonia concentration is over 0.5% (State III), the water contact angle of the sponge decreases to 0°, and color turns to purple as $\text{NH}_3 \cdot \text{H}_2\text{O}$ reacts with $\text{In}(\text{OH})_3$ and BCP completely. When the $\text{NH}_3 \cdot \text{H}_2\text{O}$ concentration is in the range from $1.4 \times 10^{-4}\%$ to 0.5% (State II), the sponge color changes to purple, but the wettability exhibits no significant decline because $\text{NH}_3 \cdot \text{H}_2\text{O}$ can react with BCP completely but reacts with $\text{In}(\text{OH})_3$ only partly. When the $\text{NH}_3 \cdot \text{H}_2\text{O}$ concentration is lower than $1.4 \times 10^{-4}\%$ (State I), the wettability and color of the sponge both exhibit no change because $\text{NH}_3 \cdot \text{H}_2\text{O}$ cannot react with $\text{In}(\text{OH})_3$ and BCP. Thus, based on the above results, it can be deduced that at certain $\text{NH}_3 \cdot \text{H}_2\text{O}$ concentrations, $\text{NH}_3 \cdot \text{H}_2\text{O}$ can react with $\text{In}(\text{OH})_3$ and BCP partly or completely, and BCP has more sensitivity towards $\text{NH}_3 \cdot \text{H}_2\text{O}$.

For dry NH_3 response, the mechanism of IBT-AR sponge's color change is similar to that of $\text{NH}_3 \cdot \text{H}_2\text{O}$ response, whereas the mechanism of wettability change is different. After coming in contact with dry NH_3 gas, yellowish BCP dye reacts with ammonia to form a purple ammonium salt. The color change of IBT-AR sponge is measured with varying NH_3 concentrations. The results show that the minimum NH_3 concentration that can be detected by color change is 5.0 ppm, which is higher than that in $\text{NH}_3 \cdot \text{H}_2\text{O}$. Fig. 11 is the plot of water contact angles varying with humidity in NH_3 atmosphere. The water contact angle decreases as humidity increases, which shows that the surface wettability of IBT-AR sponge is related to ammonia humidity, and $\text{NH}_3 \cdot \text{H}_2\text{O}$ molecules play a crucial role in improving the hydrophilicity of the sponge. While detecting dry NH_3 concentration according to wettability change of IBT-AR sponge, small wettability difference has been observed. It should be mentioned that there is no completely dry environment at room temperature. Besides, as is referred before, color change is more sensitive to ammonia than wet-

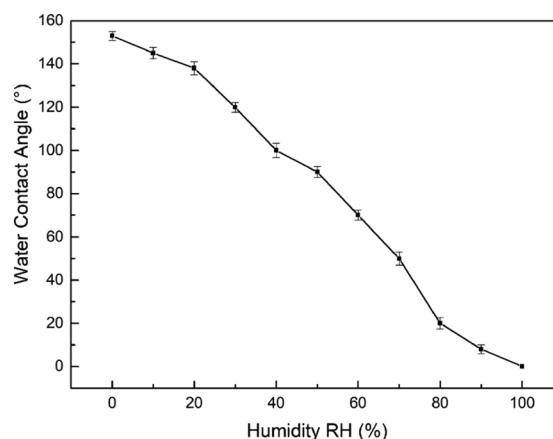


Fig. 11 The plot of water contact angles of IBT-AR sponge varying with humidity in NH_3 atmosphere.

ability change. Thus, we can detect the existence of NH_3 based on the IBT-AR sponge surface color and wettability change.

In addition to sensitivity, specificity and stability are also important factors of sensors. When ammonia was introduced into a cabinet with IBT-AR sponges, the sponge surface color changed to purple gradually. When distilled water droplets were dropped on the sponge, they were quickly adsorbed. However, when other kinds of gases such as H_2 , O_2 , CO_2 with the same concentration (32 ppm) were introduced for a certain period of time, wettability and apparent color of IBT-AR sponges exhibited no change. These results proved that the IBT-AR sponge has good specificity and sensitivity for $\text{NH}_3 \cdot \text{H}_2\text{O}$.

The stability of a sensor is the sensitivity difference of the sensor before and after its placement at room temperature for a certain period of time. After 45 days, the color of IBT-AR sponge surface always changed to purple gradually when ammonia gas at a concentration of 16 ppm was introduced

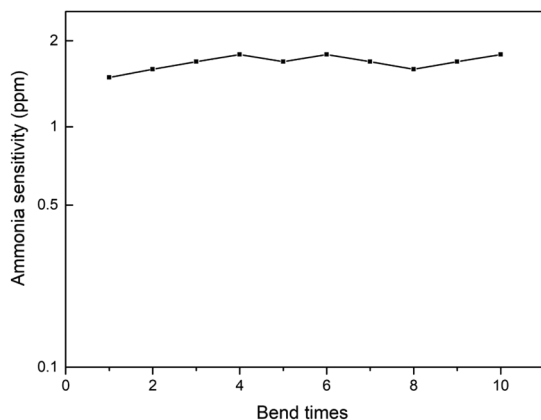


Fig. 12 Plot of ammonia sensitivity varying with the bend times increase.

into the cabinet. When the ammonia gas with the concentration of 2.0% was introduced into cabinet and kept for 2 h, the wettability of sponge surface changed to superhydrophilic. Moreover, when distilled water droplets were placed on this sponge, these water droplets were adsorbed quickly. Fig. 12 is the plot of $\text{NH}_3\cdot\text{H}_2\text{O}$ sensitivity when the number of bending times was increased. From the curve, we can see that the ammonia sensitivity of the IBT-AR sponge almost had no difference after bending 10 times, which showed that the IBT-AR sponge exhibited good long-time response performance. Due to excellent sensitivity, specificity, stability and reversibility, the IBT-AR sponge can be utilized to estimate the ammonia concentration, which is beneficial for ammonia pollution detection.

Conclusions

In summary, superhydrophobic IBT-AR sponges are successfully fabricated by decorating $\text{In}(\text{OH})_3$, BCP and TiO_2 particles on the surface of a PDMS-PU sponge. Based on the reversible ammonia reactions with $\text{In}(\text{OH})_3$ and BCP, the superhydrophobic and yellowish sponge can change to a superhydrophilic and purple one simply by storing in an ammonia hydroxide atmosphere. More importantly, the superhydrophilic and purple sponge can convert back to superhydrophobic and yellowish one after heating in air. The minimum ammonia concentration that can be detected is 50 ppb. Due to low cost, easy manipulation and good repeatability of the superhydrophobic IBT-AR sponge, it may possess potential for applications in detecting and monitoring toxic gas *via* surface wettability and color change.

Conflicts of interest

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