Light-activated inorganic CsPbBr$_2$I perovskite for room-temperature self-powered chemical sensing$^\dagger$

Hongjun Chen,$^\dagger$ Meng Zhang,$^\dagger$ Xiao Fu,$^\dagger$ Zelio Fusco,$^\dagger$ Renheng Bo,$^\dagger$ Bobo Xing,$^\dagger$ Hieu T. Nguyen,$^\dagger$ Chog Barugkin,$^\dagger$ Jianghui Zheng,$^\dagger$ Shujuan Huang,$^\dagger$ Anita W. Y. Ho-Baillie,$^\dagger$ Kylie R. Catchpole$^\dagger$ and Antonio Tricoli$^\dagger$$^\ast$

Halide perovskite materials are excellent light harvesters that have generated enormous interest for photovoltaic technology and an increasing number of other optoelectronic applications. Very recently, their use for miniaturized chemical sensors has shown a promising room-temperature response. Here, we present some insights on the use of CsPbBr$_2$I (CPBI) perovskites for self-powered room-temperature sensing of several environmentally and medically relevant compounds demonstrating rapid detection of down to concentrations of 1 ppm. Notably, the photocurrent of these self-powered CPBI-based devices increases under exposure to both reducing (e.g. acetone, propane) and oxidizing (e.g. NO$_2$, O$_2$) gas molecules and decreases rapidly upon reverting to an inert atmosphere. In situ photoluminescence (PL) analysis of the CPBI during exposure to oxidizing molecules reveals a strongly increased PL intensity and longer lifetime indicating a prevalent role of CPBI trap states in the sensing mechanism. These findings provide new insights for the engineering of perovskite-based materials for their future chemical sensing applications.

Introduction

In addition to their rapidly increasing use for environmental monitoring,$^1$ chemical sensors are becoming a key technology for the future development of medical diagnostic technologies.$^2$ For instance, analysis of disease-related biomarkers in the breath provides a powerful approach for the contactless monitoring and diagnostics of numerous diseases such as diabetes,$^3$ asthma,$^4$ breast cancer$^5$ and kidney disorders.$^6$ The strict requirements of environmental monitoring and medical diagnostics are driving the engineering of novel materials with sufficiently high sensitivity and selectivity for measuring trace concentrations of analytes in complex gas mixtures. Amongst other key research focuses, the development of self-powered materials that can transduce chemical interactions on their surface in electrical signals at room temperature has the potential to resolve the need of providing miniaturized and/or wearable power sources and complex sensor designs.$^2$

Nanostructured metal oxide semiconductors (MOSs) have sufficient sensitivity for the measurement of numerous gas molecules, which are of increasing relevance for environmental monitoring and medical diagnostics.$^1,7$ However, the high operation temperature requirement (200–500 °C)$^{1,8}$ of MOS-based devices increases the device complexity limiting their use for miniaturized healthcare and environmental sensors. Although UV light can activate the sensing reactions of some wide-bandgap semiconductors at room-temperature,$^9$–$^{11}$ these materials suffer from insufficient low limit of detection (LOD), and slow response and recovery times. Furthermore, even under UV irradiation, an external power source is required to apply the bias for the transduction of the sensing signal.

To overcome these challenges, self-powered chemical sensors based on ZnO nanowires,$^{12}$ ZnO and Si nanowires,$^{13}$ and organic surface functionalization of p-Si/n-ZnO diodes$^{13}$ have been developed demonstrating the detection of H$_2$S, ethanol solvent in hexane, and NO$_2$ gas molecules, respectively. However, improvement of the LOD, currently at 100 ppm for H$_2$S and for 0.27 vol% ethanol in hexane, and the slow recovery
times (ca. 600 s), is required for their application to the measurement of many important gas molecules, which are usually present in ppm to ppb concentrations in the environment and in the breath.

Organic–inorganic halide perovskites have attracted enormous interests since their first report in 2009.14 Amongst numerous benefits, they provide a tunable optical band gap,15,16 high carrier mobility and lifetime,17 low exciton binding energy,18 and a broad absorption range with high extinction coefficient. Recently, organic–inorganic halide perovskites have also been attempted for application as chemical sensors. Colorimetric ammonia gas sensors based on the perovskite (CH$_3$NH$_3$)PbI$_3$ were reported to achieve a colour change from brown to colourless, when in contact with ammonia gas.19 Using photoluminescence (PL) analysis, perovskites were demonstrated to respond to moisture and different environmental gases.20–24 Very recently, chemoresistive sensor devices consisting of organometallic halide perovskite films were shown to have potential for the sensing of multiple gases.25,26 Although these devices have demonstrated a promising initial performance for O$_2$ and acetone measurement at room temperature,25,26 their insufficient LOD of 70 ppm for O$_2$ and 20 ppm for acetone and external bias requirement still limits their applicability for many environmental and medical applications.2 We have recently reported a self-powered chemical sensor design based on visible-light activated CsPbBr$_3$ perovskites demonstrating room-temperature sensitivity for O$_2$, acetone and ethanol.27 However, the relatively broad bandgap of these perovskites decreases their visible light absorption limiting the availability of photo-generated electron/hole couples for chemical sensing.27

Here, we report some insights on the application of a narrow-bandgap inorganic halide perovskite, CsPbBr$_3$I (CPBI), for self-powered photo-chemoresistive sensors for the room-temperature sensing of numerous environmentally and medically relevant gas molecules at trace concentrations. CPBI was chosen due to its better stability to environmental exposure than the other mixed Br/I ratio perovskites such as CsPbI$_3$ and CsPbI$_2$Br and having a broader absorption range than that of CsPbBr$_3$. Meanwhile, the findings reported here are also valuable in investigating the influence of mixed anions on the chemical sensing performance of perovskites. The CPBI-based detectors show excellent visible light absorption resulting in superior sensing performance than previous broad bandgap perovskites, and achieving sensing of NO$_2$, acetone, methanol, ethanol, propane, and ethyl benzene gas molecules down to 1 ppm concentrations. Notably, in situ PL analysis and photochemosensitve measurement of the CPBI during exposure to oxidizing molecules reveals a significant and reversible increase in PL intensity and lifetime from 1.12 to 4.04 ns. These findings shed some light on the sensing mechanism of the CPBI, indicating a predominant role of its trap states in the chemical modulation of the photocurrent. We believe that these new insights provide directions for the future engineering of perovskite-based self-powered room-temperature chemical sensors.

Results and discussion

Fig. 1 shows a schematic of the CPBI-based sensor layout and its morphological, structural and optical characterizations. The sensors are composed of one layer of CPBI deposited on one hole-blocking layer of TiO$_2$ on a bottom fluorine-doped tin oxide (FTO) glass substrate, where the bottom electrode is connected. The top electrode is connected to the top surface of the CPBI layer by an Au probe (ca. 0.1 cm$^2$) leaving most of the CPBI surface (ca. 1.4 cm$^2$) accessible to the gas molecules (Fig. S1, inset, ESI†). Fig. 1b shows the energy band diagram of the CPBI device by virtue of well-established band positions in perovskite solar cells.28–32 Under sunlight illumination, the CPBI generates photo-excited electron–hole pairs. Subsequently, the photo-generated electrons transfer from the conduction band of CPBI to the FTO across the hole-blocking TiO$_2$ layer,28–32 while the holes in the valence band of CPBI are collected at the Au probe resulting in a net current flow through the out circuit, from the FTO to the Au without any applied external bias. The resulting photocurrent is utilized to transduce the change in the electrical properties of the CPBI caused by the interaction with the gas molecules.

Fig. 1c and d show the top and cross-sectional SEM images of a representative CPBI device. A compact film, composed of densely packed CPBI grains of ca. 100–500 nm with well-sintered inter-particle necks, is observed (Fig. 1c). The cross-sectional SEM image (Fig. 1d) shows a well-adhering and continuous CPBI layer with an average thickness of ca. 115 nm over the
TiO₂ layer on the FTO surface. The EDS mapping is shown in Fig. S2 (ESI†) and all the elements of Cs, Pb, Br, I and Ti from CPBI and TiO₂ layers can be clearly discerned, respectively. In addition, the elements of Sn and Si from the FTO glass substrate can also be found. However, due to the low-resolution of the EDS and high-voltage electron beam on the CPBI film, the EDS mapping images have a broad scattering without a very clear boundary. All the top view, cross-sectional analysis, and EDS mapping confirm the successful synthesis of a dense CPBI layer with a compact and continuous morphology, which is beneficial in exposing the CPBI surface to the target gas molecules while providing a continuous path for the collection of the photo-excited charge carriers.

Fig. 1e and f summarize the structural and optical characterization of these devices. The XRD patterns of the CPBI/TiO₂/FTO are denoted by three peaks matching the (100), (110) and (200) crystal planes of the monoclinic CsPbBr₃ phase (JCPDS: 18-0364). In comparison to the XRD patterns of the CsPbBr₃, the position of these three peaks shifted to lower angles, due to the lattice expansion caused by the substitution of the bromide (ionic radius 1.96 Å) with the iodide (ionic radius 2.2 Å) ions.²⁷,¹³ In addition, the XRD patterns of the FTO substrate and a tiny XRD peak at 27.4° from the TiO₂ can also be discerned. The stability of CPBI was initially investigated by XRD in environmental air for 1 h for each measurement. The relative XRD peak intensity between the (100) peak of CPBI and the main peak of FTO (located at 2θ = 26.5°) is plotted in Fig. S3 (ESI†) as a function of the storage time in vacuum. The XRD analysis reveals that the CPBI crystal structure is quite stable for at least one month without obvious degradation, in line with previous reports.¹⁶ The optical absorbance spectrum of CPBI shows an onset of the absorbance at ~610 nm with a corresponding bandgap of 2.06 eV. This is quite close to those reported CPBI films fabricated by thermal evaporation.³⁴ The PL spectrum shows a strong emission peak at ~590 nm (2.10 eV),³⁴ which is very close to its optical band edge. These results demonstrate the successful synthesis of CPBI films with excellent optical and structural properties for light absorption and photo-excited carrier transport. If compared with previously reported CsPbBr₃,²⁷ here, the onset of absorbance is redshifted by ca. 60 nm and its bandgap is also reduced by ~0.25 eV after one bromide anion was substituted by an iodide anion in its unit cell structure, suggesting CPBI is a promising perovskite material with narrower bandgap for more light absorption. The optoelectronic properties of these CPBI-based devices were firstly tested in air. As shown in Fig. S1 (ESI†), under simulated sunlight illumination (AM 1.5, 42.3 mW cm⁻²), the devices generate an open circuit potential of 0.9 V and a short-circuit current of 37 nA. The open circuit potential and short-circuit current are close to zero in dark conditions (0.019 V and 0.1 nA, respectively). The resulting photocurrent allows operating these CPBI gas sensors without the need of applying an external bias and also demonstrate better optoelectronic performance than that of the previously investigated CsPbBr₃.²⁷,²⁷

Fig. 2 demonstrates the use of these CPBI devices for the self-powered chemical sensing of VOCs at 35 °C under solar irradiation (AM 1.5, 42.3 mW cm⁻²). Fig. 2a shows a typical dynamic gas sensing response of the CPBI devices. Upon exposure to 4 and 8 ppm of acetone in an inert N₂ atmosphere the photocurrent increases from 8.8 nA to 9.9 nA and 10.2 nA, respectively. Although the response is relatively small in magnitude, the signal to noise ratio is still 20.59, and thus sufficiently high for this limit of detection. Furthermore, considering that the sensors are operated at room temperature without an applied external bias and at a relatively low acetone concentration of 4 ppm, the result is still quite attractive. Additional measurements were done with other devices showing a good reproducibility (Fig. S4, ESI†). In a control experiment, the CPBI device was kept in the dark and its response to acetone was tested. The latter showed no variation in the current up to exposure to, at least, 8 ppm of acetone (Fig. S5, ESI†), indicating that the gas molecule sensing mechanism of the CBPI perovskite relies on light activation. Notably, here, perovskite films were fabricated by a gas-quenching technique,³⁵ which has shown more reproducibility than the conventional anti-solvent method.³⁶ Thus, the CBPI device used in this work had a high reproducibility of the composition, thickness and grain size leading to a similar sensing response across different batches of samples (Fig. S4–S6, ESI†).

Under simulated solar illumination, a LOD of 1 ppm was determined for both acetone and methanol (Fig. S6, ESI†). Furthermore, the CPBI devices revealed a linear response to both VOCs in the tested concentration range from 0 to 8 ppm (Fig. 2b). The sensitivity of the CPBI to other analytes was investigated for methanol, ethyl benzene (ETBZ), ethanol and...
propane (PROP) as exemplary reducing gases, which are relevant for environmental and medical applications.\textsuperscript{3,37–39} It was observed that, for the same concentration, the CPBI responds significantly stronger to acetone and M\textsubscript{t}OH (Fig. 2d) than to the other analytes. The performance of the CPBI sensor has been compared with the state-of-art perovskite based and other photo- and chemoresistive sensors as shown in Table S1 (ESI†). From this table, it is demonstrated that the present CPBI sensor is superior to most of the photo- and chemoresistive sensors in terms of either the response time or LOD. Although the CPBI provides some selectivity toward the detection of acetone and methanol (Fig. 2c), it does however show a response to all the VOCs tested here. The selectivity can be further increased by implementation of pattern recognition analysis with multiple chemoresistive sensors\textsuperscript{40} and the integration of gas selective membranes as for MOS devices.\textsuperscript{41}

Furthermore, the CPBI response to NO\textsubscript{2} was also evaluated as an exemplary oxidizing gas with particular environmental monitoring relevance. Although the sensor response to NO\textsubscript{2} was weaker than that of any of the tested reducing VOCs, it was observed that even under exposure to this oxidizing analyte, the CPBI device’s photocurrent increased. The stronger response to O\textsubscript{2} than to NO\textsubscript{2} is mostly attributed to the significantly lower concentration of the latter (8 ppm) than that of the former (20 vol%). This indicates a different gas sensing mechanism of CPBI devices to that of MOS-based gas sensors, where the current increase or decrease is in the opposite direction for reducing and oxidizing analytes. Furthermore, the response and recovery times of the CPBI devices were in the orders of 100–150 s (Fig. S7, ESI†) and thus significantly faster than the typical response of most MOS sensors (2–25 min) for VOCs detection at room temperature (Table S2, ESI†). It was also observed that the sensor response gradually decreases from 0.16 to 0.09 with the decreasing light intensity from 42.3 to 22.5 mW cm\textsuperscript{−2} (Fig. S8, ESI†), in line with previous observations for CPB-based devices.\textsuperscript{27} When the device was exposed under air with a humidity of around 20–35% in the lab, it rapidly decreased to ca. 23% within the first 10 hours. The device can still retain 11% of the initial sensor response after 34 hours of exposure (Fig. S9, ESI†).

These findings suggest that the gas sensing process of the CPBI might rely on weak physisorption, in line with the results reported by Fang et al. on the physisorption of gas molecules on the perovskite crystal surfaces as revealed by PL measurements\textsuperscript{23} and the investigation revealed by Zheng et al. using first principles and molecular dynamic calculations.\textsuperscript{42} Furthermore, it was observed that for all the gas molecules tested, the CPBI had a significantly stronger photocurrent variation (Fig. 2c) under an inert N\textsubscript{2} atmosphere than in an oxidizing one (i.e., simulated air). This suggests that O\textsubscript{2} competes with the other (reducing or oxidizing) analyte molecules for the CPBI’s active surface sites, resulting in a smaller sensor response. To verify this hypothesis, the photo-chemoresistive and PL response of the CPBI to O\textsubscript{2} was investigated. As shown in Fig. S10 (ESI†), the CPBI devices respond swiftly to alternate exposure to 20% of O\textsubscript{2} in a N\textsubscript{2} atmosphere with a sensor response of 0.81 and a response time of 34 seconds. The \textit{in situ} PL characterization of CPBI under alternate exposure to 20% O\textsubscript{2} and an inert atmosphere was conducted. Fig. 3a and b show a PL spatial map of a CPBI film section. The later reveal a significantly stronger intensity over the whole sample area in 20% O\textsubscript{2} in N\textsubscript{2} than in an inert N\textsubscript{2} atmosphere. This indicates that the O\textsubscript{2} presence facilitates the PL activation of CPBI. The phenomenon is also in agreement with the recent reports on the activation role of O\textsubscript{2} for similar perovskites.\textsuperscript{41,23,43} This effect was further supported by the consecutive measurement of the PL intensity variation of the CPBI under alternate 20% O\textsubscript{2} and pure N\textsubscript{2} exposure. As shown in Fig. 3c, the CPBI film demonstrates a reproducible PL response under a sequential variation of its atmosphere with the PL intensity under an exposure of 20% O\textsubscript{2} being 6 times higher than that under N\textsubscript{2} (Fig. S11, ESI†). Notably, upon O\textsubscript{2} injection, the PL intensity swiftly increased to a maximum value and stabilized, indicating that activation of CPBI in the presence of O\textsubscript{2} is a dynamic process that can be quickly induced in line with the recent literature.\textsuperscript{44} Meanwhile, this reproducible and rapid PL response further suggests that O\textsubscript{2} activation of CPBI is a physisorption-driven phenomenon rather than due to the chemisorption of O\textsubscript{2} molecules on the CPBI surface.\textsuperscript{23}

To gain further insights on how the presence of oxidizing molecules affects the chemical sensing mechanism, time-resolved
PL spectra of the photo-excited CPBI films in oxidizing and inert environments were acquired. The decay time of CPBI measured with 20% O2 in N2 (Fig. 3d) shows an initial fast component with a lifetime of ~4.04 ns and a slower component with a lifetime of ~16.17 ns. In contrast, the PL lifetime of the CPBI in the inert N2 atmosphere is significantly shorter with an initial fast component of ~1.12 ns and a slower component of ~4.49 ns. The shorter PL lifetime suggests high non-radiative recombination, due to the presence of trap states within the CPBI films.45 As a result, the slower decay time in the presence of O2 suggests that O2 molecules can passivate some of the trap states in the CPBI and retard the electron–hole recombination. It has been reported that the passivation of trap states of perovskite using O2,21,23,46 Lewis base (e.g. pyridine and thiophene),46,47 methylammonium bromide48 and sodium ions49 that acted as trapping sites for the charge carriers, mediate non-radiative recombination.46 Photo-induced formation of emissive sub-band gap defect states quenches the band-to-band radiative emission in an inert environment, while the presence of O2 was found to inhibit such PL quenching effects.44 This is also in line with the recent results on the optoelectronic properties of perovskite single crystals modulated by the environmental atmosphere.23 As a result, non-radiative recombination is increased when CPBI is exposed to pure N2 gas and only a small fraction of the photogenerated carriers can survive and contribute to the photocurrent, reflected in the photocurrent measurement in an inert environment (Fig. 3e; Fig. S10a, ESI†) shows the corresponding sensor response of Fig. 3e). Based on the PL and photo-chemoresistive response of the CPBI devices under exposure to an inert and oxidizing environment, here, it is suggested that the trap states play a dominant role in the gas sensing behaviour of CPBI devices. In such perovskites, trap states are usually localized at the surface and grain boundary, where the bulk crystalline symmetry is broken.50,51 Therefore, it is inferred that the grain boundaries and interface play a key role in the chemical sensing process.52

Here, the following chemical sensing mechanism is proposed based on aforementioned analysis for the CPBI devices (Fig. 4). The CPBI is firstly photo-excited and generates electrons and holes under simulated sunlight as shown in Fig. 4a. The electrons located in conduction band of CPBI are rapidly collected across the TiO2 hole-blocking layer on the FTO substrate, while the holes are directly transferred to the top Au contact (Fig. 1b). During the charge-transfer process, recombination between the electrons and holes happens mainly at the trap states within the CPBI film and only the remaining photo-excited charges can be successfully collected contributing to the measured photocurrent. In the inert N2 atmosphere, the non-radiative recombination among the photo-excited charges is more significant due to the large amount of trap states available within CPBI (Fig. 4a). As a result, the PL intensity is weak and the photocurrent in the out circuit is relatively small (Fig. 3e). In the presence of O2, the PL intensity and the photocurrent are significantly enhanced due to the passivation of the trap states by the O2 molecules (Fig. 4b). As a result, a higher fraction of photo-excited charges can be collected and contribute to the photocurrent (Fig. 3e). A similar sensor response mechanism is hypothesized for the other gas molecules.

As the O2 is a good passivating molecule (Fig. 3a–d), it competes with the tested VOCs and NO2 for the passivation of the trap states within CPBI. As a result, the sensor response to the various reducing or oxidizing gas molecules is weaker in the presence of O2 (Fig. 2c), while in an inert atmosphere, the higher concentration of available trap states results in a significant enhancement of the photocurrent under the exposure to reacting gas molecules (Fig. 4d). It would suggest that some time-resolved techniques like a transient terahertz time-domain spectroscopy, a transient capacitance technique, and transient-absorption spectroscopy might be useful to obtain some useful information about the trap density and the passivation. By virtue of the operation under an inert N2 atmosphere, it is expected that the present device might be useful for the selective detection of O2 and oil and gas extraction and refinement plants with very low or zero moisture concentrations.

Conclusions

Here, we have demonstrated the use of a CPBI perovskite as a promising light-activated self-powered photo-chemoresistive sensor at room temperature. Rapid measurement of a range of environmental and medically relevant gas molecules was achieved at room-temperature down to trace concentrations of 1 ppm with very fast response and recovery times of ca. 100–150 s. Furthermore, the 0.9 V potential generated by the CPBI under simulated sun light illumination was sufficient to self-power the devices without the need of an external power source and bias. In situ measurements of the CPBI PL and photo-chemoresistive response under alternate exposure to oxidizing molecules and an inert atmosphere indicated that the passivation of the CPBI trap
states by the physisorption of the analyte gas molecules plays a major role in the sensing mechanism. We believe that these new insights provide guiding principles for the design of inorganic perovskite materials for self-powered room-temperature chemical sensing applications.

**Experimental section**

Fabrication of CPBI devices

Firstly, the preetched FTO glass (Pilkington, 7 Ω cm⁻¹) was cleaned with 2% Hellmanex, acetone and 2-propanol sequentially and then transferred to a UVO cleaner for 20 min of UVO cleaning. A compact TiO₂ layer was then deposited by spray-pyrolysis using a solution of titanium diisopropoxide bis(acetylacetonate) in isopropanol. Before CPBI film coating, the compact-TiO₂ coated FTO glass was UVO cleaned again for 20 min. The precursor of CPBI was prepared by dissolving 0.75 M CsI (Alfa Aesar) and 0.75 M PbBr₂ (Alfa Aesar) in dimethyl sulfoxide (Sigma-Aldrich). The CPBI film was deposited on compact-TiO₂ coated FTO glass by a gas quenching technique with a spin-coating condition set at 3000 rpm for 30s. After the spin started for 5 s, a N₂ gas stream was blew from the N₂ gun towards the surface at a distance of 5 cm for 5 s with a gage pressure of 4.5 bar. After the spin stopped, the device was put on a hotplate and annealed at 150 °C for 15 min.

Gas sensing measurement

The sensor measurements were performed as follows. For any gas sensing measurements, the carrying gas was either pure N₂ or simulated air with a volume ratio of N₂ to O₂ at 4 (N₂ and O₂, BOC gas). The gas flow rate was controlled by mass flow controllers (Bronkhorst), but the total gas flow rate kept at 0.5 L min⁻¹. During the chemical sensing measurement, the carrying gas was flown on first, and then the light was switched on. After the device was stabilized, any VOCs or NO₂ gas (ethanol, 9.91 ppm in N₂, Coregas; acetone, 10.1 ppm in N₂, Coregas; methanol, 10 ppm in N₂, BOC gas; ETBZ, 10 ppm in N₂, BOC gas; PROP, 10 ppm in N₂, BOC gas, and NO₂, 10 ppm in N₂, BOC gas) was diluted to a desired concentration before purging into the chamber and the total gas flow rate was still kept at 0.5 L min⁻¹. The temperature of the hotplate in a chamber (Linkam HFS600E) was controlled by a temperature controller and the sample was illuminated through a quartz window by a solar simulator (42.3 mW cm⁻², NewSpec, LCS-100) with an AM 1.5 filter glass. For the gas sensing measurements, two probes were separately placed on top of the bare FTO and the CPBI film under a short-circuit condition (applied voltage was zero) and the dynamic response of the gas sensor was recorded by an electrochemical workstation (CHI 660E, USA). In order to remove the effect of humidity, the devices would be firstly heated to 100 °C for 2–3 minutes to remove the moisture on its surface, then cooled down to 35 °C for the following chemical sensing measurement. All the operations were conducted in a sealed chamber with a hot plate (Linkam HFS600E) to precisely control the working temperature. Meanwhile, all gases flown into the chamber are dry gases for the chemical sensing measurements. The standard errors were calculated based on 5 different devices with 1–3 times of measurements.

**Characterization**

The morphology was investigated by using a Zeiss Ultraplus (FESEM) at 3 kV. Time-resolved photoluminescence decay measurements were performed using a Horiba LabRAM Evolution system with a time-correlated single photon counting (TCSPC) system (DeltaPro-DD, Horiba). A 508 nm diode laser (DD-510L, Horiba) with a pulse duration of 110 ps, fluence of ~10 μJ cm⁻² per pulse, and a repetition rate of 312.5 kHz was used for excitation. Both the incident light and the reflected light went through a 50× objective lens (LEICA PL FLUOTAR L 50×/0.55), which resulted in a spot size of ~3.6 μm. The samples were kept in N₂ or air environment during the measurements. For the analysis of the time-resolved PL decay, the two-exponential model in the commercial Decay Analysis software was used to fit the experimental results in order to extract the lifetimes. The crystallinity was characterized by X-ray diffraction using a Bruker system (XRD, D 2 Phaser, USA) equipped with Cu Kα radiation of average wavelength 1.54059 Å. The absorbance spectra were measured using a PerkinElmer (Lambda 1050 UV/vis/NIR) spectrophotometer and a 150 mm integrating sphere.

**Conflicts of interest**

There are no conflicts to declare.

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