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Multicolor Inks of Black Phosphorus for Midwave-Infrared Optoelectronics

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Black phosphorus (bP) based ink with a bulk bandgap of 0.33 eV ($\lambda = 3.7 \mu m$) has recently been shown to be promising for large-area, high performance mid-wave infrared (MWIR) optoelectronics. However, the development of multicolor bP inks expanding across the MWIR wavelength range has been challenging. Here a multicolor ink process based on bP with spectral emission tuned from 0.28 eV ($\lambda = 4.4 \,\mu$ m) to 0.8 eV ($\lambda = 1.5 \,\mu$ m) is demonstrated. Specifically, through the reduction of bP particle size distribution (i.e., lateral dimension and thickness), the optical bandgap systematically blueshifts, reaching up to 0.8 eV. Conversely, alloying bP with arsenic $(bP_{1-x}As_x)$ induces a redshift in the bandgap to 0.28 eV. The ink processed films are passivated with an infrared-transparent epoxy for stable infrared emission in ambient air. Utilizing these multicolor bP-based inks as an infrared light source, a gas sensing system is demonstrated that selectively detects gases, such as CO₂ and CH₄ whose absorption band varies around 4.3 and 3.3 µm, respectively. The presented ink formulation sets the stage for the advancement of multiplex MWIR optoelectronics, including spectrometers and spectral imaging using a low-cost material processing platform.

1. Introduction

The short-wave infrared (SWIR, $\lambda = 1-3 \mu m$) and mid-wave infrared (MWIR, $\lambda = 3-5 \mu m$) regions offer enriched optical information with distinct advantages in detecting thermal emission, material discrimination, and IR absorption in gases and biomolecules. While bandgap modulation has been achieved

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in III-V and II-VI heteroepitaxial semiconductors, such as $InAs_{1-x}Sb_x$ on GaSb and $Hg_{1-x}Cd_{x}Te$ on $CdTe_{x}^{[1,2]}$ their device performances have been constrained by high Auger recombination rates, which fundamentally increases with the reduction of the bandgap.^[3,4] Furthermore, they suffer from high fabrication processing costs, which has limited their broad adoption in consumer electronics and other applications. Recently, van der Waals (vdW) layered black phosphorus (bP) has been demonstrated to outperform conventional optoelectronic devices in MWIR range, owing to its unusually low Auger recombination rate compared to materials of the similar bandgap.^[5-8] Notably, scalable MWIR light-emitting devices and photodetectors have been realized using an ink solution based on bP, with a bandgap at 0.33 eV $(\lambda = 3.7 \ \mu m)$.^[9] The layered crystal structure results in self-terminated surfaces with a low density of dangling bonds, which is less detrimental to surface carrier losses.

As a result, ink-based bP films, consisting of stacked bP particles exhibit high optoelectronic performance, with photoluminescence (PL) quantum yield at the same magnitude as the single-crystal flakes.^[9]

Multicolor emitters (and detectors) in SWIR and MWIR are essential for most imaging, sensing, and spectroscopy applications. Although the scalable ink process has been extensively studied

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Figure 1. Process overview for multicolor SW–MWIR 2D inks. a) Schematic of ink process for bP and $bP_{1-x}As_x$. b) Schematic illustration of concept for bandgap tuning by alloying and size control to shrink and increase the bandgap, respectively. c) Photographic images of as-synthesized ink and spin-coated ink films.

for bP and other layered materials,^[9,10] the bandgap tunability over SWIR to MWIR has not been demonstrated. While bandgap engineering in small-scale bP flakes has been explored through lattice straining^[7,11,12] and high vertical electric field,^[13,14] such approaches are incompatible with ink processed films. Thus, the development of bP inks with tuned spectral emission is required. Here, we present an ink formulation for achieving multicolor wavelengths from 1.5 to 4.4 µm based on bP and its arsenic compounds. The controlled reduction of bP particle size distribution in the ink leads to an increased optical bandgap, up to 0.8 eV $(\lambda = 1.5 \ \mu m)$ due to quantum confinement effects, as validated by PL and absorption spectra. Additionally, bP05As05 alloy-based ink is employed to approach a narrower bandgap down to 0.28 eV $(\lambda = 4.4 \,\mu\text{m})$. Although the air stability of smaller bP particles is relatively lower than that of bulk bP,^[15] passivation with infraredtransparent epoxy enhances its stability in a scalable manner. Taking advantage of the solution processing, this low-cost technique is compatible with variable substrates unlike epitaxial films that require lattice matching. Finally, we demonstrate a gas sensing system using the ink films as SW-MWIR light sources, efficiently detecting multiple gases, including CO₂ and CH₄, at their absorption bands around 4.3 and 3.3 µm, respectively. This work provides valuable insights for exploring multiplex light sources and detectors, operable across the SWIR to MWIR spectrum using a simple ink processing.

2. Results and Discussion

Figure 1a illustrates the step-by-step procedure for ink formation. Commercially available bP bulk sources were mechanically crushed to obtain sub-millimeter-sized bP powder. This powder was then sonicated in a solvent using a probe sonicator to produce fine particles, with N-methyl-2-pyrrolidone (NMP) selected as the solvent due to its higher effectiveness in exfoliation of bP flakes compared to other organic solvents.^[16,17] The sonication time was varied to control particle size and thickness distributions (details in the Experimental Section). After sonication, a centrifugation step was employed to separate particles based on size and thickness, with the solvent later replaced with toluene because of the lower boiling point of the toluene (111 °C) compared to the NMP (204 °C), which helps to form a uniform film at later spin-coating or drop-casting process. The oleylamine was added as a binder and moderately sonicated to create a uniform dispersion that we call bP ink. The prepared bP ink was spincoated or drop-casted onto target substrates of quartz or 50 nm SiO₂/Si.^[9,18] Since the bulk bP inherently possesses a bandgap of 0.33 eV, we optimized the particle size to further control its bandgap by adjusting sonication and centrifugation conditions. Figure 1b conceptually illustrates the bandgap modulation of bP ink, showing that reducing bP particle size/thickness leads to an increased bandgap due to quantum confinement effects. In addition, $bP_{0.5}As_{0.5}$ alloy ink was employed to achieve a narrower bandgap in MWIR region (≈0.28 eV).^[19-21] Similarly with pure bP, the same ink preparation process was performed on a commercially available bP_{0.5}As_{0.5} source as well. As a result, these ink solutions and deposited thin films were obtained, as shown in Figure 1c.

To optimize the ink process, sonication and centrifugation conditions were systematically varied. **Table 1** summarizes the sonication/centrifugation parameters used here: Sample bP-A, B, C; and bPAs-A. **Figure 2**a,b displays histograms of particle's lateral dimension and thickness, respectively, illustrating how

 Table 1. List of ink samples with different sonication times and centrifugation conditions.

Ink sample	Material	Sonication time [min]	Centrifugation [rpm]
bPAs-A	bP _{0.5} As _{0.5}	10	One-step (8000)
bP-A	Pure bP	10	One-step (8000)
bP-B	Pure bP	60	Two-steps (2000 \rightarrow 8000)
bP-C	Pure bP	180	Two-steps (2000 \rightarrow 8000)

the sonication time and centrifugation steps affect particle size and thickness distributions. The sonication time was changed between 10 and 180 min, and increased from Sample bP-A to C (Table 1). Along with the sonication time, the samples were centrifuged differently. Sample bP-A was processed with onestep centrifugation, where the vdW solution was centrifuged at the speed of 8000 rpm (4014 rcf) to form a bP sediment; while the Sample bP-B and C were processed via two-steps centrifugation including pre-centrifugation at 2000 rpm (251 rcf) to remove large particles, followed by main sedimentation at 8000 rpm. As shown in the bottom of Figure 2a, the lateral dimension distributes over a wide range of 100-2600 nm with an average lateral dimension of \approx 760 nm, through a short time sonication and onestep centrifugation (Sample bP-A). When sonicated longer and sedimented with two-steps, the lateral dimension distribution becomes distinct with an average lateral dimension of \approx 340 nm (Sample bP-C, top of Figure 2a). Sample B revealed intermediate distribution gradually changing from Sample A to C. Similar results were obtained for the thickness distribution as shown in Figure 2b. The average lateral dimension and thickness are plotted as a function of sonication time, as shown in Figure 2c,d, respectively. Here we assume the particle's lateral dimension and thickness, *d* and *L*, evolute proportionally to the following equation: $(P \times t)^{-m}$, where *P*, *t*, and *m* is sonication power, time, and power law exponent, respectively.^[22] The experimental results of bP were fitted with this equation to obtain the power exponent of m = 0.23 and 0.56 for lateral dimension and thickness, respectively, indicating the ease of exfoliating each layer rather than the lateral isolation. This is consistent with the fact that interlayer vdW force is weaker than the intralayer covalent bonding. The lateral dimension/thickness distribution measurements were conducted for Sample bPAs-A, exhibiting similar results as Sample bP-A.

To assess the crystalline quality of bP and bPAs inks, Raman spectra and transmission electron microscopy (TEM) images were measured. Figure 3a shows Raman spectra for various ink samples together with exfoliated flakes of bP and bP05As05 as references, demonstrating that the crystalline quality is preserved even after ink formation processes. For bP samples, typically, specific Raman peaks were found at $\approx\!\!360,\,430,\,and\,\,470$ $\rm cm^{-1}$ corresponding to $A_{\alpha}^1,$ $B_{\rm 2g},$ and A_{α}^2 peaks, respectively. The peak width increases with sonication time, probably due to the coexistence of different bP thicknesses;^[23,24] while the effects of process-induced defects, especially at the particle edges, cannot be excluded.^[25,26] Alongside bP, bPAs ink film also indicates the preserved crystalline quality compared to the reference flake, without Raman quenching. Specifically, A_{g}^{1} , B_{2g} , and A_{g}^{2} peaks were confirmed at 220-250 cm⁻¹ which is consistent with previous reports on bPAs at similar concentrations.^[19] Figure 3b shows a Raman mapping of the main peak of bP Raman spectrum (A_{α}^2) , indicating a pin-hole free film with uniform crystalline quality over a millimeter scale. We note that the film



Figure 2. Optimization of sonication and centrifuge process. a,b) Histograms of bP particle's lateral dimension and thickness, respectively, for different ink processes. c,d) Time evolutions of average lateral dimension (L) and thickness (d), respectively. The bP and bP_{0.5}As_{0.5} sources were sonicated with different times, followed by the one-step centrifugation at 8000 rpm. Solid lines are fitting curves for the results of bP.

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Figure 3. Crystallographic characterizations of ink samples. a) Typical Raman spectra for different ink samples: bP Film A, B, and C; and bP_{0.5}As_{0.5} Film. Raman spectra from mechanically exfoliated bP and bP_{0.5}As_{0.5} flakes are also shown, as references. b) Raman mapping of main peak intensity for bP spectrum (A_g^2) . c,d) TEM image of bP ink sample with multi and single particles, respectively. Inset in (c) shows a diffraction pattern (scale bar: 10 nm⁻¹). e) High-resolution TEM image at the folded edge of a single bP particle in (d).

consistency deteriorates when no binder is added in bP ink, due to a formation of coffee ring resulting in discontinuity and pinholes.^[9,16] In addition to the Raman spectroscopy, we performed high-resolution plan-view TEM for the bP solution processed with the longest sonication time, Sample bP-C. Here note that the bP solution was prepared without adding oleylamine to prevent degraded TEM image resolutions caused by olevlamine residues. Figure 3c,d shows low magnification TEM images of multilayer stacked and single bP particles, respectively. As indicated in the diffraction pattern (inset in Figure 3c), each bP particle in the random stack has a different crystal orientation. Figure 3e shows a high-resolution TEM image obtained from the single bP particle (Figure 3d). The lattice constant was determined to be 5.4 Å at the folded edge, which is consistent with the interlayer distance along [010] plane in the previous reports.^[27] Similarly, the bP crystal structure was confirmed in the different bP particles, as shown in Figure S1 (Supporting Information). This sustained crystalline quality is attributed to the vdW crystal structure.^[9]

To verify the modulation of optical bandgap as conceptualized in Figure 1b, we investigated PL and absorption characteristics. **Figure 4a** shows typical PL spectra from Sample bP-A, B, C; and bPAs-A. Compared to the peak position of bP flake reference at 0.33 eV ($\lambda = 3.7 \mu m$, Figure S2, Supporting Information), bP-A, B, and C show a blueshift to 0.35, 0.40, and 0.48 eV, respectively. As well as peak shift, a long tail was observed in the larger bandgap regime, ranging up to 0.8 eV ($\lambda = 1.5 \mu m$) for Sample bP-C. This broad emission is owing to the thickness distribution that results in the optical bandgap change (Figure 2).^[28] The transition from free carrier to excitonic system takes place at ≈ 10 layers, where the thickness is smaller than bP's exciton Bohr radius of ≈ 5 nm.^[28-30] In addition to the quantum confinement, the optical bandgap can be modified by the nonlocal effect of dielectric screening, which alters electron-hole interaction.^[31,32] The increased ratio of thinner bP particles leads to the emission at higher energy. The external quantum efficiency (EQE) was calculated for different ink samples (see details in the Experimental Section). The PL EQE was determined to be 0.14%, 0.12%, and 0.10% for bP-A, bP-B, and bP-C, respectively, which is comparable to previously reported bP ink/flakes (EQE = 0.04%-0.2%) and conventional III-V/II-VI materials (EQE = 0.1%-0.9%).^[8,9] Along with the optical bandgap change, the PL spectrum shape is also attributed to the nonradiative recombination processes such as the Auger recombination. The ratio of the Auger lifetime to the radiative lifetime exponentially increases with the bandgap so that PL quantum yield can change with the optical bandgap.^[33,34] The nonradiative recombination rate can increase at the edge, whose effect is predominant when the flake size is at sub hundred-nm order, as confirmed in 2D transition-metal dichalcogenides.^[25,26] Moreover, carrier diffusion can be complicated under the coexistence of different bandgap bP particles. In contrast to the reduction of particle size, bP0.5As0.5 alloy indicates the redshift down to 0.28 eV (4.4 µm), which agrees with previously reported results.^[19-21] The absorption spectra for samples bP-A, B, C, and bPAs-A, calculated from reflection and transmission (see Figure S3, Supporting Information), are presented in Figure 4b. The band edge monotonically increases from bP-A to

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Figure 4. Optical characterizations of ink films. a) Multicolored PL spectra, and b) normalized absorption spectrum from bP and bP_{0.5}As_{0.5} ink films. c) Time-resolved PL measurement from bP ink (Film bP-C) with passivation. The samples were measured in the laboratory ambient. The IR-transparent epoxy was used to passivate the ink film.

B to C, while a smaller band edge was confirmed for bPAs-A, consistent with the results of PL spectroscopy. Although the stability of smaller bP particles (Sample bP-C) is relatively lower than that of larger bP particles,^[9] passivation with infrared-transparent epoxy enhances its stability under a low thermal budget. To prevent a chemical reaction with oxygen and water vapor in air ambient, we passivated bP-C sample by using an infrared transparent epoxy. The epoxy was cured at 150 °C for 1 h after spin coated on the sample in the glove box. Figure 4c shows timeresolved PL emission from Sample bP-C (the passivation structure of the ink film and the measurement setup are described in Figure S4, Supporting Information). Without passivation, the PL quenched in a few minutes, however, a stable emission was confirmed over hours when passivated. The fluctuation of PL intensity was mainly due to the mechanical drift of the optical setup. A storage lifetime was also investigated in an ambient condition with a relative humidity of $40\% \pm 5\%$. Figure S5 (Supporting Information) shows PL spectra of bP-B and bP-C after air exposure for 1 day and 10 days. No significant change was observed for bP-B, while a slight reduction of PL intensity was found in bP-C after 10 days. This is probably because of the degradation of thinner bP particles, which is relatively more unstable than bulk bP (>50 nm).^[28,35] The epoxy passivation is scalable, and its thermal budget is relatively lower than the oxide passivation via atomic layer depositions that operated at 150-200 °C, commonly used for a passivation layer for bP flakes.^[35,36] This approach is compatible with a variety of substrates, making it suitable for scalable applications.

With discrete multicolor emissions at SW- and MW-IR ranging 1.5–4.4 µm, multiple gas sensing can be realized. Figure 5a displays the absorption band of different gas molecules, overlaying PL emission from multicolor ink films. As a proof of concept, we demonstrated a gas sensing system using bP ink films as light sources (Figure 5b). The ink films were optically illuminated by a 638 nm laser diode. The IR emission passed through a gas chamber enclosed by KBr optical windows, with two holes in the side walls as gas inlet and outlet. To selectively detect different gases, Sample bP-A and bPAs-A were utilized for the detection of CH₄ and CO₂, respectively. Figure 5c shows broad PL emission from Sample bPAs-A with CO₂ gas at different concentrations from 0.1% to 100%. Fingerprints of CO_2 gas are confirmed with sharp light absorption at around 0.29 and 0.46 eV, corresponding to 4.3 and 2.7 µm in wavelength. Similarly, light absorption at around 3.3 μ m was confirmed for CH₄ gas (Figure 5d). Finally, we have demonstrated the time-resolved gas detection measurements using these passivated films. The IR emission was counted by a commercially available InSb photodetector. In sync with the light sources, optical bandpass filters were designed to be switchable to another one. Figure 5e, f indicates a stable gas detection over time. Stable gas detections were realized owing to the epoxy passivation down to the concentration of 0.1% for CO₂. The present gas sensing system was able to detect other gas molecules such as C2H4

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Figure 5. Gas detection systems using ink film as a mid-IR source. a) Schematic of concept for the gas detection with using multicolor ink films. b) Schematic illustration of gas sensing measurement setup. c,d) The PL spectra from Sample bPAs-A and bP-A films with light absorption by CO_2 and CH_4 gases, respectively. A commercial InSb detector was used to e,f) Time-resolved gas detection measurements for CO_2 and CH_4 gases with changing gas concentration, 0.1%, 1%, 10%, and 100%.

and C_3H_8 , as shown in Figure S6 (Supporting Information). The detection sensitivity at ppb or ppm level has been achieved in similar optical gas sensing systems using light absorption.^[37] The performance limit of our gas detection system can be further improved by using an optimized gas chamber with multiple reflecting mirrors to enhance the optical path. The efficiency of MWIR emission from bP is limited by the Auger recombination at the generation rates commensurate with the light-emitting devices' practical use.^[28,34] Even without extensive optimization, present bP-based ink films already exhibit a quantum efficiency compet-

itive with state-of-the-art technologies. Further improvement is feasible, particularly through the utilization of the Purcell effect within an optimized optical cavity structure. Notably, PL and electroluminescence efficiency was improved by one to two orders of magnitudes in \approx 40 nm bP flake through the use of an optical cavity compatible with ink films.^[8,28] Achieving efficient Purcell enhancement requires precise control of the ink film thickness (<100 nm).^[8] It is beneficial to utilize multicolor bP-based ink to advance the development of vertical *p*–*n* heterojunction devices for wavelength-selective light-emitting diodes (LEDs) and

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photodetectors. Our recent works have demonstrated that bP ink film can be optically excited by a commercially available visible LED, functioning effectively as a phosphor.^[9] Consequently, further efforts are encouraged to develop multiplex light sources by integrating multicolor inks and micro LEDs on a chip.

3. Conclusion

We have developed a multicolor bP-based ink process for high performance short-wave to mid-wave IR optoelectronics. By controlling particle size distribution and alloying with arsenic, we achieved systematic blue- and redshifts in the bandgap, spanning wavelengths from SWIR ($1.5 \mu m$) to MWIR ($4.4 \mu m$). Notably, the crystalline and optical qualities of the inks remain intact postprocessing, even with their enhanced surface-to-volume ratio. The inks, when passivated with IR-transparent epoxy, exhibit robust IR emissions without noticeable degradation. Demonstrating a gas sensing system using these bP-based inks as phosphors, we highlight the potential of this process in advancing integrated multiplex devices like LEDs and photodetectors.

4. Experimental Section

Ink Procedures: Bulk sources of bP (Rasa Industries, Smart Elements) and bP05As05 were mechanically crushed into fine powders with submillimeter dimensions, using either a mortar and pestle or ball milling. These powder samples were ultrasonicated in N-methyl-2-pyrrolidone (NMP) using a 150 W probe sonicator (Cole Parmer). To mitigate degradation from oxygen or water present in NMP, nitrogen gas was bubbled throughout the solution. Also, the sonication power and duty cycle were set to 50% and 20%, respectively, to suppress the excess heating during the operation. The sonication time varied from 10 min to 3 h, resulting in the lateral dimension and thickness distributions. After the probe sonication, the solutions were processed in centrifugation to separate the particle size. A one-step centrifugation at 8000 rpm (4014 rcf) for 10-60 min, yielded larger particles. For the segregation of smaller particles, a two-step centrifugation process was implemented. The first phase involved lowspeed centrifugation at 2000 rpm (251 rcf) for 10 min to precipitate larger particles, followed by the collection of the supernatant. The subsequent stage required centrifugation at 8000 rpm for 30 min, culminating in the gathering of fine particle sediments. Although NMP is suitable for liquid phase exfoliation of bP and $bP_{0.5}As_{0.5}$, it has a relatively high boiling point (204 °C) and its residue results in strong light absorption including MWIR wavelength. Thus, the solvent was replaced with toluene, whose boiling point is lower (111 °C), through the following process. A 2.5 mL of toluene was introduced to the 0.5 mL of condensed vdW solutions previously in NMP. A moderate sonication was performed in the bath sonicator to disperse vdW particles in toluene, followed by centrifugation at 8000 rpm for 30 min. The sediment (0.5 mL) was collected again and put in a new vial with another 2.5 mL toluene. To enhance the homogeneity of the resulting ink film, we introduced 150 µL of oleylamine (Sigma Aldrich) as a binding agent. By sonicating for 1 min in the bath sonicator, the vdW flakes were uniformly dispersed in the solution. These vdW inks were spin-coated on the target substrates of SiO₂/Si or quartz, at a constant speed of 300 rpm for 3 min. The toluene solution was naturally vaporized at ambient conditions. An infrared-transparent epoxy (EPO-TEK 377, Epoxy Technology) was utilized to encapsulate the sample. The epoxy was spin-coated on the sample and then cured at 150 °C for 1 h. The spin-coat and curing process were conducted inside the glove box.

Material Characterization: The lateral dimensions and the thicknesses of the flakes were measured using atomic force microscopy (AFM, Bruker Dimension Icon with ScanAsyst). To identify isolated particles without stacking each other, the ink solution was diluted by adding toluene. Raman spectra and mapping were measured by a Raman microscopic system (Horiba Labram HR Evolution Confocal Raman Microscope) with a 532 nm line of a Nd:YAG laser as the excitation source, employing the lowest excitation power that provided a perceptible signal-to-noise ratio. TEM characterization was carried out at the National Center for Electron Microscopy at Lawrence Berkeley National Laboratory using FEI TitanX 60-300 and an FEI ThemIS 60-300 microscope operated at 300 kV. The bP solution was prepared without adding oleylamine to prevent unexpectedly degraded TEM image resolutions. The calibrated PL and absorption measurements were performed using a Fourier transform infrared spectrometer (iS50, Thermo Fisher) equipped with a liquid-N2-cooled HgCdTe detector, as described in the aforementioned study.^[7] The excitation source for photoluminescence measurements included a laser diode ($\lambda = 638$ nm, Thorlabs) and a laser diode controller (LDC500, Thorlabs). The measured PL spectra were calibrated according to the instrument response function (IRF) of the detector (Figure S7, Supporting Information). To extract the EQE for PL results, light absorption in bP samples and light collection efficiency in the PL setup were considered.^[7,28] The incident excitation laser power was measured on the sample. The absorption of the 638 nm laser in the ink films was measured to be 80%.[9]

Gas Sensing: The PL spectra with gas absorption were measured by the infrared PL setup as described above, equipped with a 3 in. length gas chamber. The gas chamber is a cylindrical tube enclosed with a KBr optical window. The gas inlet and outlet lines were connected to the chamber. The gas flow rates were controlled by a mass flow controller, mixing nitrogen and target gases (CO_2 , CH_4 , C_2H_4 , and C_3H_8) to obtain specific gas concentrations. The total flow rate was fixed at 50 sccm. The time-resolved gas absorption measurements were performed using InSb photodiode (Teledyne Judson Technologies).

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.

Author Contributions

J.I. and K.N.H. contributed equally to this work. J.K., N.H., and A.J. conceived the idea for the project and designed the experiments. J.K. and N.H. synthesized ink solutions. J.K, N.H., and S.W. performed optical characterizations. J.K., N.H., R.Y., and M.S. performed TEM measurements. J.K., N.H., and A.J. analyzed the data. J.K., N.H., and A.J. wrote the manuscript. All authors discussed the results and commented on the manuscript.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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