

Rapid laser-induced ambient synthesis of highly crystalline Ag@Cu₂O nanowire networks for reconfigurable photoelectrochemical logic and hardware-encrypted communication

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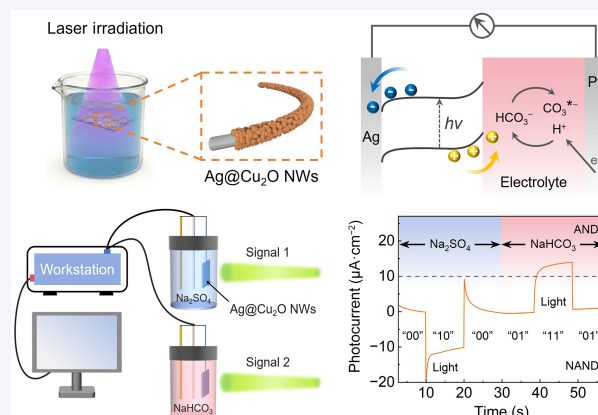
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ABSTRACT: Photoelectrochemical (PEC) photodetectors with switchable photocurrent polarity offer a promising route toward secured optical communication. However, achieving high-performance bipolar response typically demands complex heterostructure fabrication under stringent conditions. Here, we report the rapid, ambient laser-induced assembly of highly crystalline Ag@Cu₂O core-shell nanowire network driven by a ligand-to-metal charge transfer (LMCT) mechanism. Distinct from conventional thermal growth, this non-equilibrium photochemical strategy promotes kinetically controlled nucleation, establishing intimate semiconductor-metal interfaces with superior charge collection efficiency. PEC devices based on these networks operate in self-powered mode and display broad-spectrum photoresponse. Notably, the photocurrent polarity is reversibly switched not by structural redesign, but by simply tuning the redox potential of the electrolyte through controlled addition of NaHCO₃. This electrolyte-tuned bipolarity enables zero-bias, reconfigurable optical logic gates (AND, NAND, NOT) and a hardware-encrypted communication system based on the Alternate Mark Inversion (AMI) protocol, where the specific electrolyte composition serves as a physical key. Unauthorized interception yields invalid unipolar signals, ensuring physically secured data transmission. This work bridges high-quality materials synthesis, interfacial charge engineering, and functional optoelectronic applications in a single, scalable platform.

KEYWORDS: Ag@Cu₂O core-shell nanowires, laser-induced synthesis, bipolar photoresponse, ionic gating, in-sensor computing, hardware encryption



1 Introduction

Next-generation intelligent optoelectronic systems demand hardware capable of multi-dimensional signal processing beyond simple binary detection. Bipolar photoresponse devices have emerged as a pivotal platform for in-sensor computing and hardware-level information security, as the polarity of the

photocurrent serves as an additional degree of freedom for encoding logic states and encrypting data transmission [1–4]. Although reversible polarity switching has been achieved in solid-state devices such as gate-modulated field-effect phototransistors [5, 6], photoelectrochemical (PEC) photodetectors are particularly attractive because their semiconductor/electrolyte interface is reconfigurable [7–10]. By leveraging the dynamic semiconductor/liquid boundary, PEC systems offer tunable interfacial energetics where interfacial band alignment and electric fields can be dynamically modulated, providing intrinsic capabilities for polarity reconfiguration distinct from rigid solid-state junctions [11–14].

To date, bipolar photoresponse in PEC platforms has been predominantly realized through complex heterostructures, where competing built-in fields at distinct interfaces drive opposing carrier

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trajectories [15–17]. Prominent examples include $\text{Cu@CuO}_x\text{-a-Ga}_2\text{O}_3$ core-shell architectures that exhibit wavelength-dependent polarity reversal [18], $\text{ZnO@Sb}_2\text{Se}_3$ core-shell heterojunctions showing sign switching between ultraviolet (UV) and visible-near infrared (NIR) excitation [19], and plasmonic-metal-assisted nitride nanowire heterostructures in which the photocurrent direction can be reconfigured by balancing carrier transport across internal junctions versus the electrolyte interface [20]. However, integrating dissimilar materials imposes stringent requirements on lattice matching and interfacial band alignment. Realizing such architectures typically necessitates high-temperature or vacuum-based deposition, processes that are not only energy-intensive but also prone to introducing interfacial defects that compromise charge collection efficiency [21–23]. Therefore, achieving reversible switching of photocurrent polarity in a single-semiconductor material system remains a significant challenge. Copper oxide (Cu_2O), due to its excellent visible light harvesting capability and inherent sensitivity to interfacial band structure tuning, is a promising candidate material for achieving this goal [24–27]. However, current Cu_2O based optoelectronic devices typically suffer from low hole mobility and severe carrier recombination [28, 29]. Consequently, effectively addressing carrier transport and recombination issues while maintaining the tunability of the Cu_2O interface is crucial for fully realizing its potential in optoelectronics.

Herein, we demonstrate the precise assembly of high-crystallinity $\text{Ag@Cu}_2\text{O}$ core-shell nanowire network ($\text{Ag@Cu}_2\text{O}$ NWs) via a laser-directed photochemical strategy in an ambient aqueous environment. In this architecture, Ag nanowires (AgNWs) play a synergistic role: They serve as a highly conductive backbone to efficiently collect charges, thereby mitigating carrier recombination in Cu_2O , and act as a physical template for localized shell growth [30, 31]; simultaneously, they function as plasmonic antennas, enhancing near-field light absorption via the localized surface plasmon resonance (LSPR) effect [32, 33]. Unlike conventional solvothermal methods governed by slow thermodynamic equilibrium, our approach exploits nanosecond pulsed laser irradiation to trigger a non-equilibrium ligand-to-metal charge transfer (LMCT) mechanism [34–36]. This kinetically controlled process promotes selective heterogeneous nucleation while effectively suppressing bulk precipitation, thereby ensuring the formation of a dense Cu_2O shell with superior crystallinity and robust interfacial contact with the Ag core [37, 38]. This establishes a pristine structural foundation for efficient carrier regulation.

Leveraging this high-quality architecture, the $\text{Ag@Cu}_2\text{O}$ NWs network functions as a self-powered photodetector with broadband spectral sensitivity. Crucially, we demonstrate that the photocurrent polarity is not intrinsic but dynamically reconfigurable. Unlike previous studies that relied on complex solid-state heterojunctions to achieve bipolarity, our single-semiconductor (Cu_2O) architecture can reversibly alter the direction of charge carrier transport solely through ionic gating controlled by external bias voltages or the redox potential of the electrolyte. This liquid-gated interface offers a versatile mechanism to manipulate the interfacial band bending direction, distinct from fixed solid-state junctions. Exploiting this tunable bipolarity, we realize a suite of reconfigurable zero-bias optical logic gates (AND, NAND, NOT). Furthermore, extending beyond elementary computation, we construct a hardware-encrypted communication system based on the Alternate Mark Inversion (AMI) protocol. In this system, the specific electrolyte configuration acts as a physical security key, creating a dynamic

barrier where unauthorized signal interception yields invalid unipolar data. This establishes a paradigm for secure information transmission anchored in the device's fundamental physicochemical properties.

2 Results and discussion

Figure 1(a) schematically illustrates the site-selective assembly of the $\text{Ag@Cu}_2\text{O}$ NWs network. Initially, a pristine AgNWs percolation network was constructed on a sapphire substrate via spray-coating. Upon immersion in a copper acetate precursor solution and irradiation with a nanosecond pulsed laser, a rapid, light-directed growth process was initiated. Unlike bulk solution reactions, the high-energy laser pulses trigger a localized LMCT mechanism specifically at the solid-liquid interface. In this non-equilibrium process, photo-excited electrons from carboxylate ligands efficiently reduce Cu^{2+} to Cu^+ , leading to the preferential heterogeneous nucleation of Cu_2O nanocrystals along the AgNWs backbone. Within minutes, these nanocrystals densely coalesce to form a continuous, uniform shell wrapping the Ag core [39]. Detailed reaction steps are provided in the Electronic Supplementary Material (ESM). Modulating the reaction time allows for precise control over the reaction kinetics and resulting product morphology, as revealed by scanning electron microscopy (SEM, Fig. 1(b)). The pristine AgNWs exhibit a smooth surface with an average diameter of ~ 60 nm. After 5 min of irradiation, sparse Cu_2O nanoparticles (Cu_2O NPs) were deposited on the AgNWs surface. Extending the irradiation to 10 min significantly increased the surface coverage and particle size. By 15 min, a dense and uniform layer of Cu_2O NPs forms on the AgNWs network, with an average particle size of approximately 50 nm. These nanoparticles displayed well-defined polyhedral geometries, indicative of high crystallinity. Corresponding energy-dispersive X-ray spectroscopy (EDS) mapping (Fig. 1(c)) verified the spatial distribution of Ag and Cu, confirming the successful construction of the $\text{Ag@Cu}_2\text{O}$ core-shell architecture. Furthermore, by adjusting the precursor concentration and liquid level, the effective laser energy incident on the AgNWs surface can be systematically optimized, thereby enabling effective control over the coverage of the Cu_2O shell (Figs. S1 and S2 in the ESM).

To systematically characterize the properties of the $\text{Ag@Cu}_2\text{O}$ NWs network prepared by the photochemical method, multiple experimental techniques were employed. The phase composition and crystallinity of the $\text{Ag@Cu}_2\text{O}$ NWs were investigated via X-ray diffraction (XRD) (Fig. 2(a)). The diffraction pattern of the $\text{Ag@Cu}_2\text{O}$ NWs network shows characteristic peaks of both Ag and Cu_2O , with no detectable impurity peaks from other copper compounds, confirming the high phase purity of the product obtained via the photochemical method. Notably, the sample irradiated for 15 min displays sharp diffraction peaks with full width at half maximum (FWHM) values of 0.20° and 0.12° for the Cu_2O (111) and (200) planes, respectively. The crystalline quality was further evaluated by X-ray rocking curve (ω -scan) measurements (Fig. 2(b)), which yielded FWHM values of 2.28° and 0.72° for the (111) and (200) peaks, respectively. These narrow linewidths indicate the formation of highly crystalline Cu_2O NPs, demonstrating the efficacy of the rapid photochemical synthesis. To highlight the advantage of our approach, Table S1 in the ESM compares the FWHM of the Cu_2O (111) plane from this work with those reported in the literature. The Raman spectrum of the

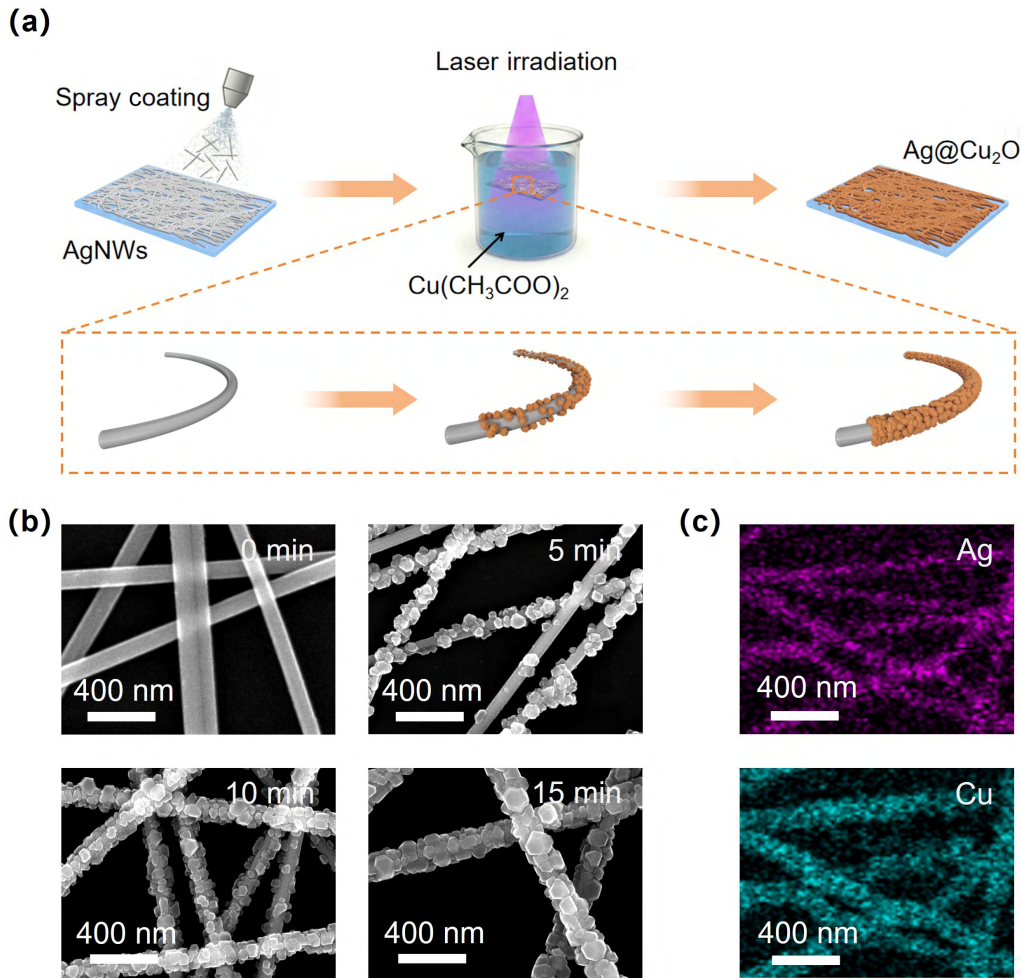


Figure 1 Laser-induced assembly of $\text{Ag}@\text{Cu}_2\text{O}$ NWs network. (a) Schematic of the laser-directed site-selective assembly of $\text{Ag}@\text{Cu}_2\text{O}$ NWs network. (b) SEM images of $\text{Ag}@\text{Cu}_2\text{O}$ NWs network at irradiation times of 0, 5, 10, and 15 min. (c) EDS elemental mapping images of Ag and Cu.

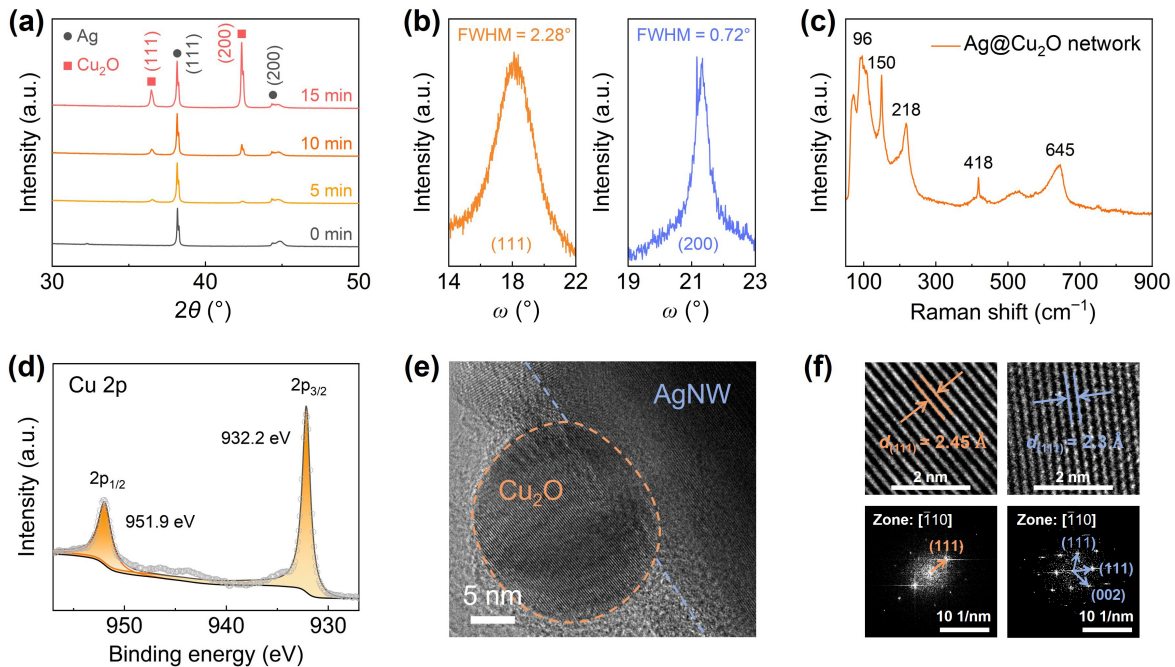


Figure 2 Structural characterization of $\text{Ag}@\text{Cu}_2\text{O}$ NWs network. (a) XRD spectra of AgNWs and $\text{Ag}@\text{Cu}_2\text{O}$ NWs network with different irradiation time. (b) Rocking (ω -scan) curves of Cu₂O (111)/(200) with 15 min irradiation. (c) Raman spectrum (488 nm excitation) of $\text{Ag}@\text{Cu}_2\text{O}$ NWs network. (d) Cu 2p XPS spectrum of $\text{Ag}@\text{Cu}_2\text{O}$ NWs network. (e) TEM image of $\text{Ag}@\text{Cu}_2\text{O}$ NW. (f) HRTEM images of the Cu₂O NP and AgNW.

Ag@Cu₂O NWs (Fig. 2(c)) exclusively exhibits peaks characteristic of Cu₂O, further validating the successful growth of the shell layer [40, 41].

To verify the surface chemical states, X-ray photoelectron spectroscopy (XPS) was performed (Fig. S3 in the ESM and Fig. 2(d)). The Cu 2p spectrum displays two distinct peaks at 932.2 and 951.9 eV, corresponding to the Cu 2p_{3/2} and Cu 2p_{1/2} states of Cu⁺, respectively. The absence of characteristic Cu²⁺ satellite peaks (typical of CuO) confirms the high phase purity of the Cu₂O shell [42, 43]. Ultraviolet–visible (UV–vis) absorption spectra (Fig. S4 in the ESM) revealed distinct absorption edges for AgNWs, Cu₂O NPs, and Ag@Cu₂O NWs network. AgNWs display two characteristic peaks arising from different LSPR modes [30, 32]. Cu₂O NPs exhibit broad absorption (400–600 nm) with a calculated bandgap of 2.2 eV (Fig. S5 in the ESM). To precisely determine the band positions of the Cu₂O shell, valence band X-ray photoelectron spectroscopy (VB-XPS) and Kelvin probe force microscopy (KPFM) measurements were further conducted (see Fig. S6 in the ESM). The VB-XPS spectrum shows that the energy difference between the Fermi level (E_F) and the valence band top (E_V) is 0.15 eV. KPFM measurements determined the surface work function (ϕ) to be 4.97 eV. Combining these values with the optical bandgap of 2.2 eV, it was calculated that E_V and the bottom of the conduction band (E_C) are located 5.12 and 2.92 eV below the vacuum energy level, respectively. Notably, the small $E_F - E_V$ energy gap (0.15 eV) clearly confirms that the synthesized Cu₂O exhibits strong p-type characteristics, which can be attributed to intrinsic copper vacancies generated during rapid LMCT photochemical processes at room temperature. The Ag@Cu₂O NWs retain the Cu₂O absorption profile but show a redshifted Ag LSPR signal; this shift is attributed to the increased local dielectric constant induced by the Cu₂O coating [44]. Figure 2(e) and Fig. S7 in the ESM

present transmission electron microscopy (TEM) images of the Ag@Cu₂O nanowire, revealing a well-defined core–shell structure. The high-resolution TEM (HRTEM) image in Fig. 2(f) displays distinct lattice fringes, where the measured interplanar spacings of 0.245 and 0.23 nm correspond to the (111) planes of Cu₂O and Ag, respectively. Furthermore, the sharp diffraction spots in the fast Fourier transform pattern viewed along the $[\bar{1}10]$ zone axis confirm the single-crystalline nature of the Cu₂O NPs.

Figure 3(a) schematically illustrates the photoelectrochemical measurement system used to evaluate the photodetection performance of the Ag@Cu₂O NWs network. The measurements were conducted in a standard three-electrode cell employing a saturated calomel electrode (SCE) as the reference and a Pt wire as the counter electrode. To investigate the influence of Cu₂O growth time on device performance, photocurrent measurements were conducted on Ag@Cu₂O NWs photoelectrochemical photodetectors (PEC-PDs) with different Cu₂O growth durations (5, 10, and 15 min) under 0 V bias (vs. SCE) and 550 nm illumination at 20 mW·cm⁻². The results are shown in Fig. 3(b). The photocurrent increased progressively with the reaction time, indicating the excellent self-powered characteristics of the device. The observed cathodic photocurrent is consistent with the typical carrier transport behavior of p-type Cu₂O, where photogenerated electrons are driven toward the semiconductor/electrolyte interface to participate in reduction reactions. Responsivity (R), a key figure of merit for photodetectors, is defined as $R = I_{ph}/(P \times S)$, where P is the incident optical power density and S is the effective illuminated area of the photoanode (0.3 cm² in this study) [45]. The responsivity of devices with different growth times is compared in Fig. S8 in the ESM. The enhancement in responsivity with prolonged reaction time is attributed to the increased Cu₂O content and improved crystalline quality. The spectral response of the optimized device

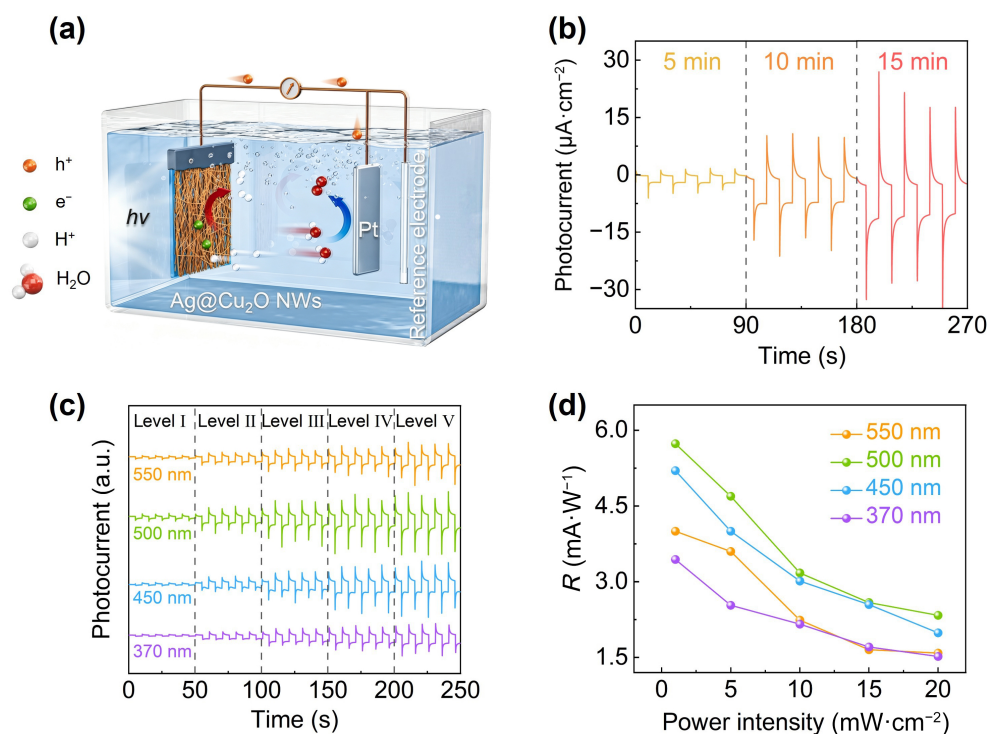


Figure 3 Photoelectrochemical performance of the Ag@Cu₂O NWs PEC-PDs. (a) Schematic of the three-electrode PEC cell (working electrode: Ag@Cu₂O NWs PEC-PDs; counter electrode: Pt; reference electrode: SCE; electrolyte: 0.5 M Na₂SO₄). (b) $I-t$ curves at 0 V (VS. SCE) under 550 nm illumination for samples grown 5/10/15 min. (c) Photoresponse and (d) responsivity of Ag@Cu₂O NWs PEC-PDs at 370/450/500/550 nm under different light intensities (1–20 mW·cm⁻²).

(15 min growth) was evaluated under light-emitting diode (LED) illumination at wavelengths of 370, 450, 500, and 550 nm. The optical power density was systematically varied across five levels (1, 5, 10, 15, and 20 $\text{mW}\cdot\text{cm}^{-2}$). As illustrated in Fig. 3(c), the photocurrent (I_{ph}) of the Ag@Cu₂O NWs photoanode exhibits a monotonic increase with rising incident power density across all tested wavelengths. Figure 3(d) displays the variation of responsivity with power density for different wavelengths. At Level I (1 $\text{mW}\cdot\text{cm}^{-2}$), the R values were 3.44, 5.20, 5.73, and 4.00 $\text{mA}\cdot\text{W}^{-1}$ for 370, 450, 500, and 550 nm illumination, respectively, indicating a good response across both UV and visible regions. The highest responsivity occurred at 500 nm, which can be attributed to the proximity of this photon energy to the direct bandgap transition threshold of Cu₂O, resulting in a higher absorption coefficient and more efficient generation of electron-hole pairs. In addition, the LSPR of AgNWs significantly enhances their photoresponsivity. The near-field electric field distribution of Ag@Cu₂O NW was simulated using the Wave Optics Module in COMSOL multiphysics, as shown in Fig. S9 in the ESM. The Ag core effectively acts as an optical antenna; under 500 nm illumination, it induces a significant LSPR effect, leading to a substantial concentration and enhancement of the near-field electric field within the surrounding Cu₂O shell. In stark contrast, under the same conditions, the electric field intensity within pure Cu₂O NPs is notably weaker. This LSPR-induced near-field enhancement significantly amplifies the light absorption cross-section, thereby promoting the efficient generation and separation of photogenerated carriers within the Cu₂O shell. Notably, the Cu₂O shell coating on the AgNWs is only about 60 nm thick, and the network occupies less than one third of the substrate area. Nevertheless, the device exhibits a responsivity of $-5.73 \text{ mA}\cdot\text{W}^{-1}$, comparable to some reported Cu₂O-based photodetectors that employ dense thin films, nanorod arrays, or even heterojunction architectures [46–48]. This result demonstrates that a pure-Cu₂O, PEC-type self-powered detector based on a nanowire network can

simultaneously ensure high visible-light transmittance and maintain effective photoresponse.

To achieve bipolar photoresponse in the Ag@Cu₂O NWs PEC-PDs, we propose two modulation strategies: external bias regulation, and electrolyte composition tuning. First, the effect of bias voltage was investigated, as shown in Fig. 4(a). When the bias voltage is scanned from -0.2 to $+0.2$ V (vs. SCE), the dark current density increases due to enhanced ion migration. Notably, a distinct photocurrent polarity inversion occurred when the applied bias exceeded $+0.1$ V (vs. SCE). Complementarily, polarity switching was achieved by tailoring the electrolyte composition via the introduction of NaHCO₃ into the 0.5 M Na₂SO₄ solution. As displayed in Fig. 4(b), the initial photocurrent of $-10 \mu\text{A}\cdot\text{cm}^{-2}$ gradually diminished with increasing NaHCO₃ concentrations, reaching a transition point near $10 \text{ mg}\cdot\text{mL}^{-1}$. A full polarity reversal is observed at $20 \text{ mg}\cdot\text{mL}^{-1}$, and the photocurrent further enhances to $>10 \mu\text{A}\cdot\text{cm}^{-2}$ at $40 \text{ mg}\cdot\text{mL}^{-1}$. To verify the interfacial energetic changes, open-circuit potential (OCP) measurements were conducted (Fig. 4(c)). The OCP drops from ~ 0.04 V (vs. SCE) to nearly 0 V at a NaHCO₃ concentration of $10 \text{ mg}\cdot\text{mL}^{-1}$, and shifts to negative values at higher concentrations. This negative shift stems from the modulation of the electrolyte's effective redox potential, which realigns the interfacial energetics and reverses the band bending direction, mirroring the observed photocurrent reversal [16, 49].

The carrier dynamics were analyzed based on the energy band structure to elucidate the bipolar characteristics. In the initial state, downward band bending occurs at the interface, establishing a built-in electric field directed from the electrolyte toward the Cu₂O. Under illumination, this field drives photogenerated electrons to the surface to participate in reduction reactions, while holes migrate toward the bulk and are collected by the external circuit, resulting in a negative photocurrent. However, when the applied positive bias is sufficient to offset the initial built-in potential, the direction of interfacial band bending reverses. This phenomenon stems from

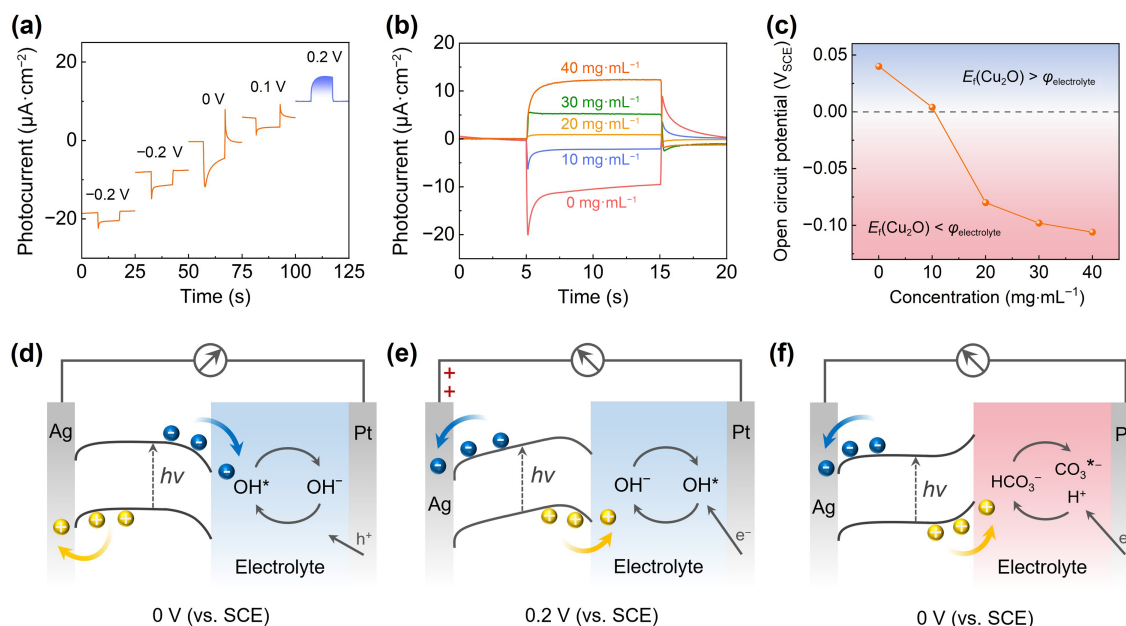


Figure 4 Mechanism for achieving tunable bipolar optical response through bias and electrolyte regulation. (a) I - t curve of Ag@Cu₂O NWs PEC-PDs under bias from -0.2 to 0.2 V (vs. SCE). (b) I - t curves of Ag@Cu₂O NWs PEC-PDs in $0.5 \text{ M Na}_2\text{SO}_4$ with increasing NaHCO₃ concentrations (0 – $40 \text{ mg}\cdot\text{mL}^{-1}$). (c) Variation of OCP as a function of NaHCO₃ concentration for the Ag@Cu₂O NWs PEC-PDs. (d) and (e) Band diagrams and charge transfer for Ag@Cu₂O NWs PEC-PDs at 0 and 0.2 V (vs. SCE), respectively. (f) Schematic illustration of the corresponding band alignment and carrier-transfer direction for Ag@Cu₂O NWs PEC-PDs after NaHCO₃ addition.

the modulation of the band alignment at the semiconductor/electrolyte interface by the external bias. This alteration redirects carrier transport: Photogenerated holes are driven to the interface to react with OH^- , while electrons flow to the counter electrode, generating a positive photocurrent. Schematic illustrations of these band configurations are presented in Figs. 4(d) and 4(e). The composition of the electrolyte in a PEC system plays a critical role in modulating the electrochemical processes at the photoelectrode [49–54]. Adding NaHCO_3 modulates the redox potential of the electrolyte to achieve polarity switching without external bias. Specifically, thermodynamic analysis indicates that the standard redox potential of the $\text{CO}_3^{*+}/\text{HCO}_3^-$ couple is approximately 1.78 V (relative to normal hydrogen electrode, NHE) [55, 56]. By comparison, the standard redox potential of the H^+/H_2 couple at pH 7 is -0.414 V (vs. NHE). As shown in Fig. 4(f) and the unified band diagram (Fig. S10 in the ESM), the Fermi level of the strongly p-type Cu_2O we studied lies between the redox potentials of these two electrolytes. In pure Na_2SO_4 , the effective redox potential of the electrolyte lies above the Cu_2O Fermi level (more negative relative to NHE), thereby inducing a downward bending of the band structure and forming a built-in electric field directed toward the Cu_2O bulk phase. However, upon the addition of NaHCO_3 , the introduction of the $\text{CO}_3^{*+}/\text{HCO}_3^-$ couple shifts the effective redox potential significantly toward more positive values (vs. NHE). When this effective potential drops below the Cu_2O Fermi level, a new electrochemical equilibrium is established through the injection of electrons from the Cu_2O bulk into the electrolyte interface. This charge redistribution creates a new positive space charge region, causing the energy band to bend upward (Fig. 4(f)). Consequently, the direction of the built-in electric field reverses, effectively sweeping photogenerated holes toward the surface to drive the bicarbonate oxidation reaction ($\text{HCO}_3^- + \text{h}^+ \rightarrow \text{CO}_3^{*+} + \text{H}^+$), thereby generating the observed positive photocurrent.

To exclude potential interference from pH variations, control experiments were performed by adjusting the pH of the Na_2SO_4 electrolyte (range 5–10) using H_2SO_4 and NaOH (Fig. S11 in the ESM). Relative to neutral conditions, acidic environments yielded enhanced photocurrents, attributed to accelerated hydrogen evolution reaction (HER) kinetics driven by the high proton concentration [12, 57]. Conversely, alkaline conditions suppressed the photocurrent, likely due to sluggish HER kinetics that induce interfacial electron accumulation and subsequent surface recombination [58–62]. Crucially, no photocurrent polarity inversion was detected even under strongly alkaline conditions. This result confirms that the NaHCO_3 induced polarity switching originates from the specific modulation of interfacial band alignment and the built-in electric field, rather than from bulk pH changes. In addition to the highly tunable bipolarity, the long-term stability and reproducibility of the device are also crucial for practical logic and communication applications. As shown in Fig. S12 in the ESM, the $\text{Ag@Cu}_2\text{O}$ NWs PEC-PDs maintained a stable cathodic photocurrent in Na_2SO_4 electrolyte and a stable anodic photocurrent in electrolyte containing NaHCO_3 under illumination for over 1800 s (> 100 cycles), with no significant signal decay observed. Furthermore, post-measurement SEM characterization confirmed that the highly crystalline, dense Cu_2O shell assembled via our LMCT strategy effectively prevents photocorrosion, maintaining an intact core-shell morphology even after testing.

Leveraging the polarity-tunable photoresponse of the $\text{Ag@Cu}_2\text{O}$ NWs PEC-PDs, we developed reprogrammable multifunctional

optical logic gates [15, 63]. To implement these operations, a dual-channel photoelectrochemical system was constructed (Fig. 5(a)). In this setup, two photoanodes were connected in parallel to a single electrochemical workstation (0 V vs. SCE), with one immersed in 0.5 M Na_2SO_4 and the other in 0.5 M Na_2SO_4 containing 40 $\text{mg}\cdot\text{mL}^{-1}$ NaHCO_3 . Based on this platform, two distinct signal inputs were defined: Input A represents the illumination state (Logic “1” = 550 nm, 20 $\text{mW}\cdot\text{cm}^{-2}$; Logic “0” = Dark), while Input B denotes the electrolyte composition (Logic “1” = 0.5 M Na_2SO_4 with 40 $\text{mg}\cdot\text{mL}^{-1}$ NaHCO_3 ; Logic “0” = pure 0.5 M Na_2SO_4). Given that the device exhibits photocurrents of opposing polarities depending on the electrolyte and remains silent in the dark, the Boolean output was determined by benchmarking the photocurrent magnitude against a threshold of 10 $\mu\text{A}\cdot\text{cm}^{-2}$. This specific threshold provides sufficient margin to ensure that the system can tolerate minor fluctuations in light intensity. Furthermore, as the detection criteria are defined at the software level, the threshold can be dynamically recalibrated to maintain logical accuracy under changing environmental conditions. Such a configuration enabled the realization of AND, NAND, and NOT logic functions (Fig. 5(b)). Specifically, the AND gate (Boolean expression: $Y = A \cdot B$) was achieved by defining the output as “1” only when the photocurrent exceeds 10 $\mu\text{A}\cdot\text{cm}^{-2}$. As shown in the truth table (Fig. 5(c)), a logic “1” output occurs exclusively under the “11” input condition (simultaneous light and NaHCO_3 presence), where the anodic photocurrent is maximized. Conversely, the NAND gate ($Y = \overline{A \cdot B}$) was realized by inverting the output criterion—assigning logic “1” when the photocurrent is below the threshold. Consequently, the output is “0” only for the “11” input state, while all other combinations yield “1” (Fig. 5(d)). Notably, switching between AND and NAND logic requires only a software-level adjustment of the threshold criterion, without altering the hardware architecture. Additionally, a NOT gate ($Y = \overline{A}$) was implemented by fixing the electrolyte environment to the NaHCO_3 condition (Input B = “1”) and using illumination as the sole variable input. By maintaining the output criterion that logic “1” corresponds to a current below 10 $\mu\text{A}\cdot\text{cm}^{-2}$, the device outputs “1” in the dark (Input “0”) and “0” under illumination (Input “1”), successfully replicating the inverter function (Fig. 5(e)). In conclusion, multiple Boolean logic operations were integrated into a single $\text{Ag@Cu}_2\text{O}$ NWs PEC-PDs via dual-input modulation of light and electrolyte composition. This opto-electrolytic gating strategy provides a novel paradigm for photoelectrochemical logic devices and expands potential applications in photochemical synapses and intelligent optoelectronic systems [64].

Conventional optical communication relying on single-band intensity modulation faces inherent security vulnerabilities, as the signal patterns are easily intercepted [1, 65]. To overcome this limitation, we constructed a dual-channel photoelectrochemical system that implements the AMI coding protocol for physical-layer encryption. The AMI protocol employs a ternary encoding scheme, where logic “0” corresponds to a zero-current state (dark), and logic “1” is represented by strictly alternating positive and negative pulses. Physically, this bipolar modulation is achieved by alternating the optical irradiation between NaHCO_3 and Na_2SO_4 electrolytes. Figure 5(f) schematically illustrates the AMI encoding process for the letter “N” (Code: 0+00−+−0). The final bipolar waveform is synthesized from two parallel unipolar signal streams: Signal 1 (00001010, transmitted via Na_2SO_4) and Signal 2 (01000100, transmitted via NaHCO_3). At the receiver end, the algebraic summation of photocurrents from the $\text{Ag@Cu}_2\text{O}$ NWs PEC-PDs

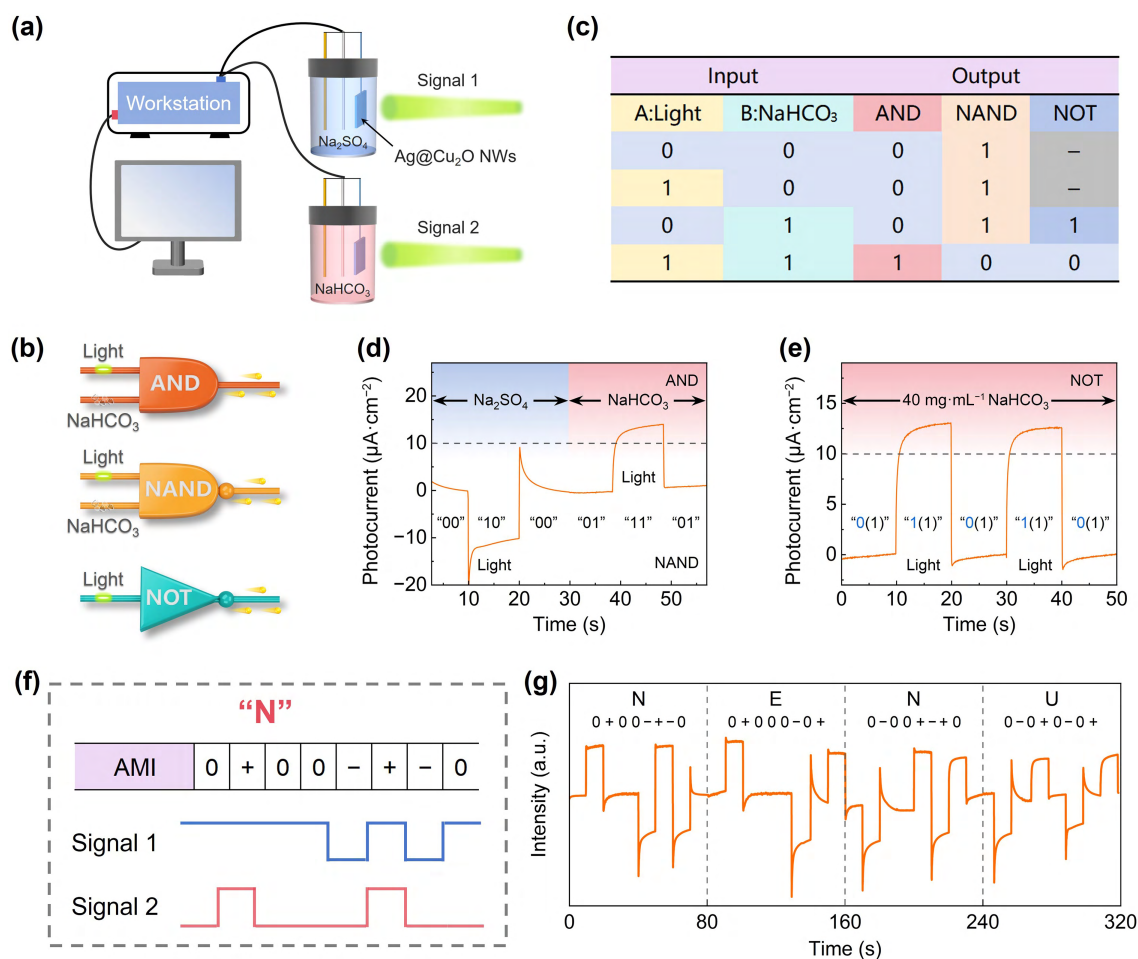


Figure 5 Reconfigurable optical logic gates and hardware-encoded communication system. (a) Schematic demonstration of logic-gate operation enabled by dual inputs of illumination and electrolyte composition. (b) Schematic diagrams of the optical switching logic gates, including AND, NAND, and NOT. (c) Truth table of AND, NAND, and NOT logic gates. (d) I - t outputs for AND and NAND logic operations under different illumination and electrolyte conditions. (e) I - t output for the NOT logic operation. (f) Schematic illustration of the AMI encoding process for the letter “N”, demonstrating two parallel unipolar signal streams: Signal 1 (Na₂SO₄ channel) and Signal 2 (NaHCO₃ channel). (g) The bipolar photocurrent response curves of the Ag@Cu₂O NWs PEC-PDs under parallel signal transmission with combined electrolytes to transmit the information “NENU”.

reconstructs the original coded sequence. To validate the fidelity of this electrolyte-gated communication, the AMI string “NENU” was transmitted using the dual-channel system. As shown in Fig. 5(g), the measured photoresponse exhibits a distinct bipolar waveform where logic “1” states strictly adhere to the polarity alternation rule, while “0” states correspond to dark intervals with negligible current, ensuring a high signal to noise ratio. The security of this system is intrinsically anchored to the specific electrolyte configuration, which functions as a physical security key. For an unauthorized interceptor utilizing a conventional single-electrolyte detector (e.g., pure Na₂SO₄), the captured optical sequence yields a monotonic unipolar photocurrent train. This violation of the fundamental AMI polarity alternation rule immediately flags the signal as invalid or intercepted, thereby preventing data decryption [66]. It is worth noting that Cu₂O’s inherent sensitivity to extreme chemical environments, such as strong acids, can be uniquely leveraged as a built-in anti-tampering mechanism suitable for high-security communication scenarios. Exposure to such environments leads to rapid corrosion of the Cu₂O shell, triggering irreversible device degradation and information destruction (Fig. S13(a) in the ESM). However, this “self-destruct” property also limits the long-term stability of the device in complex real-world environments. To

address this critical issue, we introduced a passivation strategy by transferring a graphene layer onto Ag@Cu₂O NWs; thanks to the protective effect of graphene on the Cu₂O shell, the passivated device exhibits exceptional corrosion resistance, maintaining a high and stable photocurrent for over 1000 s even in a strongly acidic environment (pH = 4) (Fig. S13(b) in the ESM). Raman spectroscopy confirms the successful loading of graphene. SEM images (Fig. S14 in the ESM) clearly show that the graphene layer tightly envelops the nanowires, effectively protecting the underlying Cu₂O NPs from acid etching. Consequently, this design enables Ag@Cu₂O NWs PEC-PDs to serve not only as a stable platform for long-term optical communication in harsh environments but also as tamper-resistant hardware keys to achieve high-level security.

3 Conclusions

In summary, we have demonstrated the laser-directed assembly of high-crystallinity Ag@Cu₂O NWs network via a non-equilibrium LMCT mechanism. This kinetically controlled strategy overcomes thermodynamic limitations to ensure superior interfacial quality, enabling a self-powered PEC photodetector with reversible polarity switching. By leveraging ionic gating (electrolyte redox tuning) and

external bias regulation, we achieved dynamic reconfiguration of the interfacial band alignment and carrier transport direction. This tunable bipolarity facilitated the realization of zero-bias optical logic gates (AND, NAND, NOT). Furthermore, we constructed a hardware-encrypted communication system based on the AMI protocol, establishing a “physical-layer security” paradigm where the specific electrolyte configuration serves as an uncloneable security key. This work bridges precision nanomaterial synthesis, interfacial energetic engineering, and secure optical communication, offering a scalable route for next-generation intelligent optoelectronics.

4 Experimental

4.1 Materials

AgNWs colloidal solution was purchased from Nanjing XFNANO Materials Tech Co. Ltd. $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$, Na_2SO_4 , and NaHCO_3 were purchased from Beijing Institute of Chemical Reagents Co., Ltd. All the materials were used as received, without any further purification.

4.2 Preparation of Ag@Cu₂O NWs network

The AgNWs network was fabricated by spray-coating AgNWs colloidal solution in water ($0.15 \text{ mg} \cdot \text{mL}^{-1}$) onto a sapphire substrate. The spray nozzle of the spray-coating setup was placed ca. 15 cm away from the sapphire substrate. In this process the sapphire substrate was supported on a hot plate which provided a constant temperature of 180°C . A $\text{Cu}(\text{OAc})_2$ aqueous solution with a concentration of $1 \text{ mg} \cdot \text{mL}^{-1}$ was prepared as the precursor for Cu_2O growth. Silver pad contact was coated on one end of AgNWs network to establish external contact for photoelectrochemical testing. The sapphire substrate coated with the AgNWs network was immersed into the $\text{Cu}(\text{OAc})_2$ aqueous solution at room temperature (25°C) and maintained at a distance of 1–4 mm from the solution surface. A fluorine-krypton (KrF) excimer nanosecond pulsed laser with a wavelength of 248 nm was used as the light source. The output energy of the pulsed laser was set to 120 mJ, with a pulse frequency of 10 Hz, and the beam was directed perpendicularly onto the AgNWs via a mirror. Simultaneously, the solution was stirred to ensure a more uniform reaction process. The reaction was conducted for 5 to 15 min to obtain Ag@Cu₂O NWs network with different Cu₂O nanoparticle coating ratios.

4.3 Materials characterization and photoelectrochemical measurements

The morphology of the samples was characterized by scanning electron microscopy (Hitachi S-4800). Transmission spectra were measured by a Jasco V-770 spectrometer with an integrating sphere. Structural characterizations were accomplished by XRD using a Rigaku D/max-2500 set-up. Raman spectra were studied using a Horiba HR evolution spectrophotometer system equipped with a 488 nm excitation source. XPS investigations and valence band edge spectrum studies were carried out with Thermo Scientific Escalab 250 Xi. Time-dependent current and open-circuit potential responses, along with electrochemical impedance spectra, were measured using an electrochemical workstation of Shanghai Chenhua Instrument Co., Ltd. A three-electrode configuration was employed with a saturated calomel reference electrode, Pt counter electrode, and $0.5 \text{ M Na}_2\text{SO}_4$ electrolyte. Photoresponse measurements utilized UV (254 nm) and visible-light (450 nm,

550 nm) LEDs as excitation sources. During the operation, it was ensured that the working electrode and platinum counter electrode faced the light sources. Incident light intensity was modulated via a precision potentiometer, while pulse width was controlled using the GCI-73M precision electronic timer from Daheng New Era Technology Co., Ltd. A Newport 1916-C optical power meter was used to measure the incident light intensities.

Electronic Supplementary Material: Supplementary material (detailed synthesis mechanisms of Cu_2O , parameter optimization, structural and optical characterization (including XPS, HRTEM, KPFM, and Raman spectroscopy), local electric field simulations of Ag@Cu₂O NWs, thermodynamic band alignment, comprehensive photoelectrochemical stability and pH-dependence tests, tests on the protective effect of graphene passivation layers on devices, and a comparison table with the literature) is available in the online version of this article at <https://doi.org/10.26599/NR.2026.94908844>.

Data availability

All data needed to support the conclusions in the paper are presented in the manuscript and the Electronic Supplementary Material. Additional data related to this paper may be requested from the corresponding author upon request.

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Declaration of competing interest

All the contributing authors report no conflict of interests in this work.

Author contribution statement

J. S. Y.: Conceptualization, data curation, investigation, writing original draft. H. B. W.: Funding acquisition, writing review and editing. Z. S. J.: Investigation. Z. M.: Investigation. M. L. L.: Investigation. K. X. L.: Formal analysis. L. Y.: Funding acquisition, supervision, writing review and editing. P. L.: Resources. J. G. M.: Conceptualization, funding acquisition, project administration, supervision, writing review and editing. H. Y. X.: Supervision. Y. C. L.: Supervision. All the authors have approved the final manuscript.

Use of AI statement

None.

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