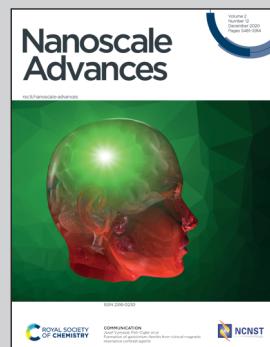


Showcasing research from the Smart 3D Printing Team at Korea Electrotechnology Research Institute (KERI), Republic of Korea.

3D-printed Cu₂O photoelectrodes for photoelectrochemical water splitting

Cuprous oxide (Cu₂O) 3D photoelectrode comprised of pyramid arrays was realized by a sequential process including extrusion-based 3D printing and electrodeposition. The Cu current-collecting layer and the p-n homojunction Cu₂O photocatalyst layer were deposited onto the printed graphene structures. The performance for PEC water splitting was enhanced by increasing the total light absorption area of the photoelectrode via controlling the electrode topography.

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3D-printed Cu₂O photoelectrodes for photoelectrochemical water splitting†

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Photoelectrochemical (PEC) water splitting is an alternative to fossil fuel combustion involving the generation of renewable hydrogen without environmental pollution or greenhouse gas emissions. Cuprous oxide (Cu₂O) is a promising semiconducting material for the simple reduction of hydrogen from water, in which the conduction band edge is slightly negative compared to the water reduction potential. However, the solar-to-hydrogen conversion efficiency of Cu₂O is lower than the theoretical value due to a short carrier-diffusion length under the effective light absorption depth. Thus, increasing light absorption in the electrode–electrolyte interfacial layer of a Cu₂O photoelectrode can enhance PEC performance. In this study, a Cu₂O 3D photoelectrode comprised of pyramid arrays was fabricated using a two-step method involving direct-ink-writing of graphene structures. This was followed by the electrodeposition of a Cu current-collecting layer and a p–n homojunction Cu₂O photocatalyst layer onto the printed structures. The performance for PEC water splitting was enhanced by increasing the total light absorption area (A_a) of the photoelectrode via controlling the electrode topography. The 3D photoelectrode ($A_a = 3.2 \text{ cm}^2$) printed on the substrate area of 1.0 cm^2 exhibited a photocurrent (I_{ph}) of -3.01 mA at 0.02 V (vs. RHE), which is approximately three times higher than that of a planar photoelectrode with an $A_a = 1.0 \text{ cm}^2$ ($I_{ph} = -0.91 \text{ mA}$). Our 3D printing strategy provides a flexible approach for the design and the fabrication of highly efficient PEC photoelectrodes.

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1. Introduction

Unlike fossil fuels, hydrogen is a clean fuel that, when consumed in a fuel cell, produces only water, electricity, and heat.¹ Hydrogen can be produced by several methods, such as natural gas reforming, biological processes, and electrolysis.^{2,3} Currently, most hydrogen is generated worldwide by natural gas steam-reforming, which is an important technology that employs high temperatures (700–1000 °C) and high pressures (300–2500 kPa) to produce hydrogen from natural gas.^{4,5}

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Although this method is efficient, excessive fossil fuel and electricity energy consumption in the process can lead to environmental pollution and greenhouse gas emissions.⁶

Hydrogen generation from the separation of water into oxygen and hydrogen by electrolysis using renewable resources of electricity can solve these issues.^{1–3,7,8} The photoelectrochemical (PEC) water splitting process is the most promising method of producing renewable hydrogen without greenhouse gas emissions. In the PEC water splitting process, hydrogen is produced using sunlight and specialized semiconductors in a water-based electrolyte. The semiconducting materials convert solar energy directly to chemical energy in the form of hydrogen; the minority charge carriers (electrons and holes for p-type and n-type semiconductors, respectively) generated through light absorption by the semiconductor are driven into the solution by the electric field at the junction, where they drive redox reactions such as the hydrogen evolution reaction (HER) on the cathode or the oxygen evolution reaction (OER) on the anode.^{9–12}

Cuprous oxide (Cu₂O), an attractive photocathode material, is an intrinsic p-type semiconductor with a direct band gap of 2.0–2.2 eV. The conduction band (ECB = -1.4 eV) of Cu₂O is slightly negative compared to the water reduction potential required to reduce hydrogen from water.^{13–15} Under air mass



(AM) 1.5 conditions (1.5 atmospheric thickness), Cu_2O has a theoretical photocurrent density (I_{ph}) of 14.7 mA cm^{-2} and a solar-to-hydrogen conversion efficiency of 18%.^{16,17} However, the conversion efficiency of Cu_2O is lower than its theoretical value due to the short diffusion length (20–100 nm) of the minority carriers in the Cu_2O photoelectrode at an effective light absorption depth ($\sim 10 \mu\text{m}$).^{17–20} Therefore, to improve the performance of hydrogen generation during the PEC water splitting process, one effective approach is to increase the total dose of light absorption in the electrode–electrolyte interfacial layer by using a three-dimensional (3D) geometrical photoelectrode.^{17,21–27}

3D printing, also known as additive manufacturing, is a promising method for creating complex 3D objects with large surface-to-volume ratios. As such, it has been used for various electronic applications that require functional components with large surface areas.^{28–31} Recently, research groups have fabricated PEC 3D electrodes using a selective laser sintering (SLS) 3D printing approach, which uses high energy to sinter metallic powders. First, 3D metallic collectors were produced using the SLS method. Catalytically active layers (IrO_2 or TiO_2) were deposited on the 3D-printed collectors by thermal processing or electrodeposition.^{32,33} However, in SLS, it is difficult to reduce the sizes of the printed structures to a micron scale or to use light-weight and flexible polymeric substrates that can be damaged by heat.

In this study, we successfully fabricated the first Cu_2O 3D photoelectrode with a large surface-to-volume ratio for PEC water splitting using an extrusion-based 3D printing approach with functional ink at room temperature. Our approach consisted of two steps: (i) direct-ink-writing of graphene 3D structures and (ii) successive electrodeposition of Cu (current collecting layer) and p–n homojunction Cu_2O (photocatalyst layer) onto the printed graphene structures. The relatively large light absorption area (A_a) of the 3D photoelectrode increases the activation sites for carrier generation under chopped-light illumination, resulting in a larger photocurrent. The 3D pyramid-shaped photoelectrode ($A_a = 3.2 \text{ cm}^2$) printed on the substrate area of 1.0 cm^2 exhibits I_{ph} values of -3.01 mA at 0.02 V (vs. RHE), which is approximately three times higher than that of a planar photoelectrode with an $A_a = 1.0 \text{ cm}^2$ ($I_{\text{ph}} = -0.91 \text{ mA}$).

2. Experimental

Preparation of graphene ink

The graphene ink was prepared by mixing graphene microflakes (0.5 g; Graphene Supermarket) and ethyl cellulose (0.2 g, Sigma-Aldrich, assay 47.5–49.5%) in a mixed solvent composed of toluene (0.65 g, Sigma-Aldrich, $\leq 99.9\%$) and xylene (0.65 g, Sigma-Aldrich, $\leq 98.5\%$) with a mixer (ARE-310; THINXY Cor.). The rheological properties of the ink were characterized using a rheometer (MCR102, Anton Paar) with a parallel-plate geometry configuration. A stress sweep at a constant frequency of 1 Hz was also performed to record variations in the storage (G') and loss (G'') moduli of the ink as a function of sweep stress.

3D printing of graphene pyramids

Extrusion-based 3D printing of the graphene pyramids was conducted using a fluid dispenser (Ultimus V, EFD Inc.). The ink was packed into a syringe (3 mL barrel, EFD Inc.) and extruded through a micronozzle (nozzle inner diameter (ID) = $100 \mu\text{m}$) under an applied pressure ($P_a = 50 \text{ psi}$). The micronozzle position was accurately controlled using three-axis stepping motors. The nozzle motion corresponding to the printed paths was determined using parameterized G-code scripts converted from the designed 3D model. The printing process was observed *in situ* using an optical monitoring system consisting of an optical lens ($10\times$) and a charge-coupled device camera. Cu foil (thickness: $\sim 20 \mu\text{m}$) was used as the substrate. For electrodeposition of Cu and Cu_2O layers, an insulation tape was attached to expose a substrate area of 1.0 cm^2 and graphene pyramids were printed on the exposed area.

Electrodeposition of Cu and Cu_2O layers

A Cu current collecting layer was deposited on the graphene surface at -0.4 V (vs. Ag/AgCl) in an electrolyte composed of $0.5 \text{ M CuSO}_4 \cdot 5\text{H}_2\text{O}$ and $0.8 \text{ M H}_2\text{SO}_4$ for 30 min. The deposition temperature was maintained at 25°C . The p-type Cu_2O (photocatalyst layer) was deposited on the surface of the graphene/Cu at -0.3 V (vs. Ag/AgCl) in electrolyte ($0.4 \text{ M CuSO}_4 \cdot 5\text{H}_2\text{O}$ and 3.0 M sodium lactate) at a pH of 12 for 30 min (deposition temperature: 60°C). The n-type Cu_2O layer for the p–n homojunction was deposited on the surface of the graphene/Cu/p-type Cu_2O at 0.02 V (vs. Ag/AgCl) in electrolyte (0.02 M copper acetate and 0.08 M acetic acid) at a pH of 4.9 for 10 min (deposition temperature: 70°C). The pH of the plating bath was adjusted by adding NaOH. Electrodeposition was performed using a potentiostat (COMPACTSTAT, IVIUM TECHNOLOGIES). The platinum plate was used as the counter electrode and the deposition temperature was maintained using a circulating chiller (DHJF-2005, Zhengzhou Greatwall Scientific Industrial and Trade Co., Ltd).

Characterization of photoelectrodes

Morphological changes to the surface of the photoelectrodes during each fabrication step were analyzed using a field-emission scanning electron microscopy (FE-SEM, S4800, Hitachi). The crystalline structure was characterized using an X-ray diffractometer (XRD, Rigaku, D/MAX-2500/PC). The electrode resistance was determined from current–voltage sweep curves obtained using a two-probe system (Keithley 2612A instrument). The PEC performance and Mott–Schottky (M–S) plots of the photoelectrodes with a Cu/p-type Cu_2O layer and a Cu/p–n homojunction Cu_2O layer were measured in a 0.5 M NaSO_4 electrolyte with a three-electrode configuration consisting of an Ag/AgCl electrode (reference), a platinum plate (counter), and a photoelectrode (working). The photoelectrodes were illuminated using an AM 1.5 solar simulator (Sun 2000, Xe lamp, Abet Technologies). The light intensity was calibrated to 100 mW cm^{-2} using a calibrated silicon detector. Photocurrent transients as a function of the applied potential were recorded by

chopped-light illumination (20 s dark and 20 s light). M-S plots were obtained at a fixed frequency of 10³ Hz. All potentials were converted to reference with the reversible hydrogen electrode (RHE). In addition, a 150 W Xe lamp equipped with a monochromator was used as the monochromatic excitation light source to carry out the incident photon-to-electron conversion efficiency (IPCE) measurement. UV-vis absorption spectra of the photoelectrode were recorded using a spectrophotometer (Cary 5000, Agilent Technologies).

3. Results and discussion

Fig. 1a illustrates the fabrication of the 3D photoelectrode, comprising pyramid arrays, by a sequential process including extrusion-based 3D printing and electrodeposition, *i.e.*, consisting of (i) direct-ink-writing of graphene 3D pyramids and (ii) electrodeposition of Cu and p-n homojunction Cu₂O on the printed pyramids. The extrusion-based 3D printing approach requires ink with specific rheological (exhibiting transitions between solid-like and fluid-like behaviors with respect to the applied shear stress) and viscoelastic properties to facilitate the extrusion of the ink through a nozzle under applied pressure.^{34–36}

The layer-by-layer printed pyramids with a base length (L_b) of 490 μm and a height (h_p) of 365 μm were obtained by successive horizontal and vertical movements of the nozzle (ID = 100 μm). The nozzle was filled with the graphene ink (25 wt% graphene flake and 10 wt% ethyl cellulose (EC) dispersed in a 65 wt% organic solvent mixed with toluene and xylene in the same proportions) and moved by applying a pressure of 50 psi (Video S1 in ESI†). Graphene flakes (average size: ~7 μm) in the ink served as the conducting and supporting components. The EC acted both as a rheological modifier for continuous ink dispensing and as a binder for maintaining the shape of the printed graphene object during printing (Video S2 in ESI†). The PEC function on the printed structures was assigned by the

following simple electrodeposition process: the Cu (layer thickness (T) = 20 μm) current collecting layer and the p-n homojunction Cu₂O (T = 5 μm) photocatalyst layer were deposited on the printed pyramids (see FE-SEM image in Fig. 1a for a cross-section of the pyramid electrode). During electrodeposition, the EC also acted as a dissolution inhibitor of the printed graphene object due to its hydrophobic property.

Fig. 1b shows the graphene ink viscosity as a function of the shear rate. The ink had a viscosity (η) of 1.79×10^5 mPa s (at a shear rate of 1 s^{-1}) and exhibited clear shear thinning behavior. The storage (G') and loss (G'') moduli of the ink are shown in Fig. 1c. The ink exhibited rheological properties with transitions (shear yield stress = 350 Pa) between solid-like ($G' > G''$) and fluid-like ($G' < G''$) behaviors with respect to the applied shear stress. In an extrusion-based 3D printing approach, such rheological properties ensured a continuous supply of the ink through the micronozzle and maintained the shape of the printed structure, enabling the fabrication of 3D graphene structures.^{34–36}

First, we demonstrated a 3D photoelectrode with a p-type Cu₂O photocatalyst layer, which was fabricated by printing 400 graphene pyramids (L_b = 450 μm and h_p = 390 μm) followed by successive electrodeposition of Cu and p-type Cu₂O layers (Fig. 2). After Cu electrodeposition onto the printed graphene pyramids (i), an area containing dominantly agglomerates of Cu grains and some crystalline structures was observed (ii). The crystallinity of the printed graphene and deposited Cu was confirmed by XRD analyses (Fig. S1 in ESI†). The p-type Cu₂O (iii) deposited at -0.3 V (vs. Ag/AgCl) in electrolyte (0.4 M CuSO₄·5H₂O and 3.0 M sodium lactate) at a pH of 12 exhibited an octahedral morphology because of the increased concentration of hydroxyl ions, which promoted the growth of the (110) and (111) faces to the (100) face.³⁷ The XRD patterns of the p-type Cu₂O layer confirmed the presence of the (111), (200), (211), (220), and (310) planes. The change in the resistance of the 3D photoelectrode with respect to the fabrication progress is

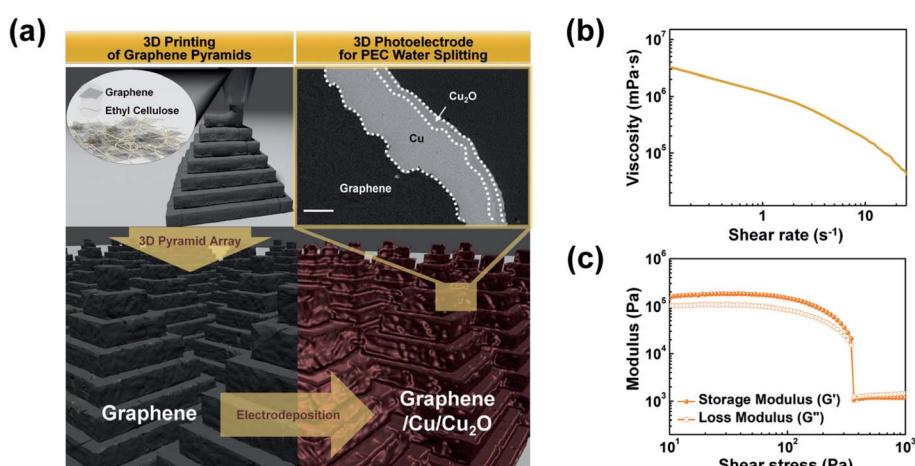


Fig. 1 (a) Schematic illustration of the fabrication process of 3D-printed photoelectrodes for water splitting *via* two successive steps: 3D printing of a pyramid array using graphene ink and functionalization via electrodeposition (Cu and Cu₂O layers). Scale bar is 20 μm . (b) Viscosity vs. shear rate and (c) storage (G') and loss (G'') moduli vs. ink shear stress. During the printing process, the graphene ink transitions from a solid-like fluid to a liquid-like fluid as a function of the shear stress.



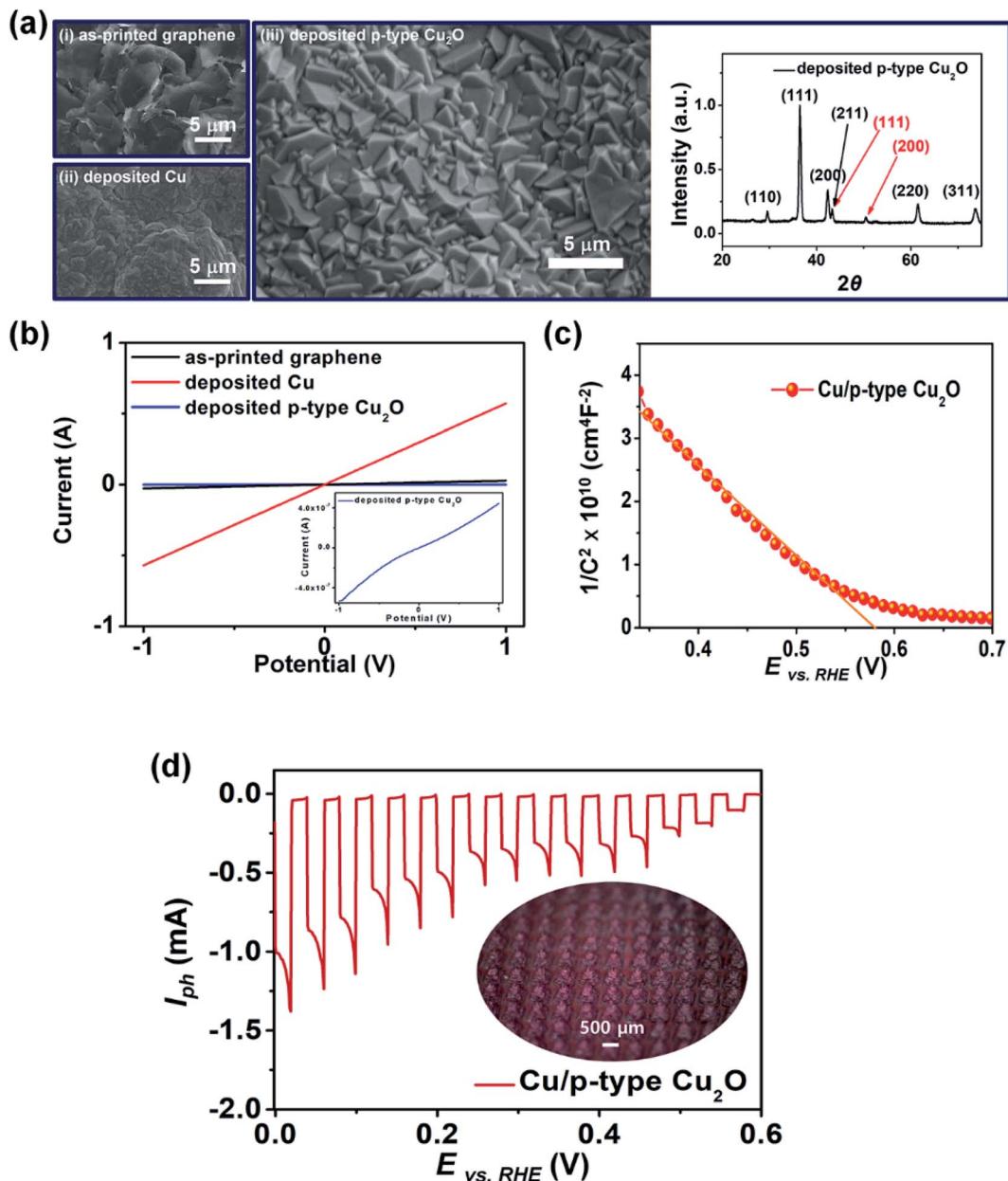


Fig. 2 (a) FE-SEM images showing the morphological changes on the surface of the 3D pyramid electrode in each step: (i) as-printed graphene, (ii) deposited Cu layer, and (iii) deposited p-type Cu₂O layer. XRD patterns of the deposited Cu/p-type Cu₂O layer on the 3D graphene pyramids (red: Cu, black: Cu₂O). (b) I – V characteristics of the 3D photoelectrode with respect to the fabrication progress. The inset graph shows an ohmic contact between the Cu and Cu₂O after the deposition of p-type Cu₂O on the Cu layer. (c) M–S plot of the Cu/p-type Cu₂O layer deposited on the 3D graphene pyramids ($V_{fb} = 0.58$ V vs. RHE). (d) Chopped-light PEC performance of the 3D photoelectrode as a function of the applied potential (vs. RHE). Inset is an optical image of the 3D photoelectrode composed of 400 pyramids.

shown in Fig. 2b. After Cu electrodeposition (current efficiency of electrodeposition: 80.07%, Fig. S2 in ESI†), the resistance decreased to 1.58Ω , which is similar to that of typical Cu foil (20 μm thickness) (Fig. S3 in ESI†). This indicates that the electrodeposited Cu layer is a suitable current collecting layer for the 3D photoelectrode. The I – V curve of the 3D electrode exhibited an ohmic contact between the Cu layer and the p-type Cu₂O layer due to the high work function of Cu (inset of Fig. 2b).³⁸ This led to an accelerated transfer of electrons (and holes) under the electric field, improving the PEC performance of the

photoelectrode.³⁹ Fig. 2c shows an M–S plot of the fabricated 3D electrode. The negative slope of the linear fit implies that the deposited Cu₂O layer is a p-type semiconductor with a flat band potential (V_{fb}) of 0.58 V vs. a reversible hydrogen electrode (RHE).^{40,41} Fig. 2d shows the PEC performance (photocurrent, I_{ph}) of the 3D photoelectrode as a function of the applied potential (vs. RHE) under chopped-light illumination. As the applied potential increased, the I_{ph} value, which was generated by the chemical reduction of protons and induced photoelectrons, also increased. The spike in I_{ph} observed in the



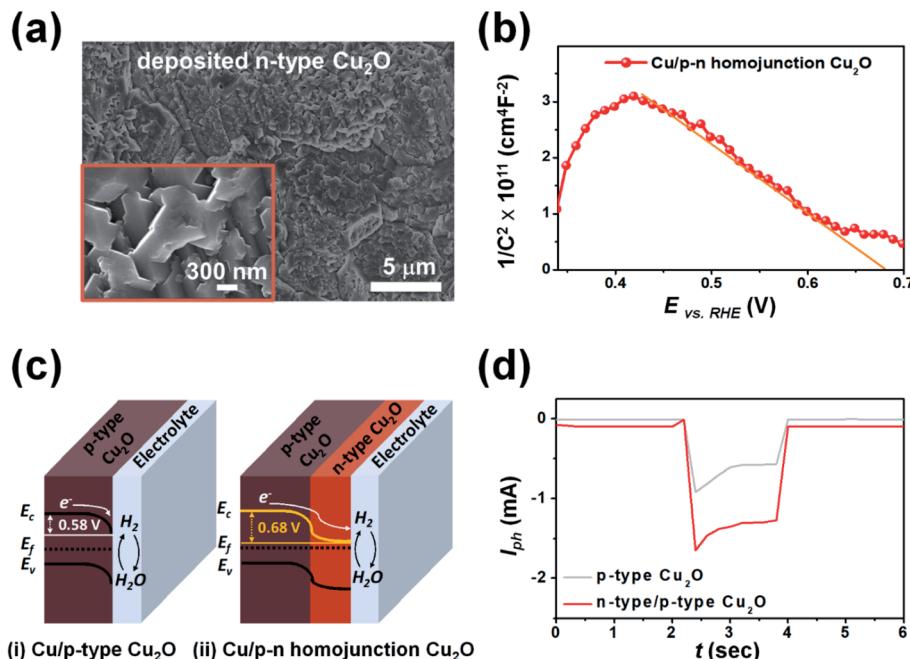


Fig. 3 (a) FE-SEM image showing the surface morphology of the n-type Cu₂O deposited on the Cu/p-type Cu₂O layer of the 3D pyramid photoelectrode. (b) M-S plot of the p-n homojunction Cu₂O 3D photoelectrode ($V_{\text{fb}} = 0.68 \text{ V}$ vs. RHE). (c) Schematic band diagram of (i) Cu/p-type Cu₂O ($V_{\text{fb}} = 0.58 \text{ V}$) and (ii) Cu/p-n homojunction Cu₂O ($V_{\text{fb}} = 0.68 \text{ V}$) at equilibrium under dark conditions. (d) Chopped-light PEC performance of the 3D photoelectrode with two different types of photocatalyst layers as a function of time at an applied potential of 0.2 V (vs. RHE).

illumination cycle was attributed to pre-adsorbed water molecules on the surface of the 3D photoelectrode.^{41,42}

To enhance the PEC performance of the 3D pyramid photoelectrode, we adjusted the band gap of the photocatalyst layer by additional deposition of n-type Cu₂O, which was achieved by controlling the operating conditions such as the applied potential, solution temperature and pH, electrolyte composition, and additives. Fig. 3a is an FE-SEM image of the n-type Cu₂O formed on the surface of the graphene/Cu/p-type Cu₂O at an applied potential of 0.02 V (vs. Ag/AgCl) in the electrolyte (0.02 M copper acetate and 0.08 M acetic acid) at a pH of 4.9 for 10 min (deposition temperature: 70 °C). The low concentration of hydroxide ions (OH⁻) under acidic conditions induced multiple oxygen vacancies in the deposited Cu₂O layer, resulting in the deposition of n-type Cu₂O.^{43,44} The morphology of the n-type Cu₂O layer exhibited laterally grown polycrystals, in which the crystal growth in the (100) direction was more dominant than in other directions such as (110) and (111). This was due to the dissolution of the thermodynamically unstable Cu₂O surface in the acidic solution.^{45,46}

Fig. 3b shows an M-S plot of the fabricated 3D photoelectrode consisting of Cu (current collecting layer) and a p-n homojunction Cu₂O (photocatalyst layer). The multi-linear region is described by two capacitors in series; one corresponding to an n-type Cu₂O/electrolyte interface and the other to a p-type Cu₂O/n-type Cu₂O interface.^{40,41} The linear fit indicates that the V_{fb} of the p-n homojunction Cu₂O was 0.68 V vs. RHE. The V_{fb} value was larger than that of the p-type Cu₂O due to band-bending formed by upward band-bending of n-type Cu₂O and downward band-bending of p-type Cu₂O in the

depletion region of the p-n junction.⁴⁷ The p-n homojunction Cu₂O resulted in greater splitting of quasi-fermi levels under chopped light illumination, generating a larger I_{ph} than that of p-type Cu₂O alone (Fig. 3c).⁴¹ Fig. 3d shows the PEC performance of the 3D photoelectrode with a p-n homojunction Cu₂O and p-type Cu₂O as the photocatalyst layer at an applied potential of 0.2 V (vs. RHE) under chopped light illumination (2 s dark and 2 s light). The maximum I_{ph} of the p-n homojunction Cu₂O (1.65 mA) is 1.8 times larger than that of the p-type Cu₂O ($I_{\text{ph}} = 0.92 \text{ mA}$). The I_{ph} of the p-n homojunction Cu₂O under dark conditions is slightly larger than that of the p-type Cu₂O due to enhanced generation of minority carriers in the depletion region of the p-n junction.^{40,48}

We also studied the variations in PEC performance of the p-n homojunction Cu₂O photoelectrode due to different shapes, i.e., planar or 3D pyramid, with respect to the total light absorption area (A_a) of the electrode. The 3D photoelectrode consisted of 400 pyramids, each with a fixed L_b of 490 μm, which were printed in close contact without gaps (Fig. 4a). As h_p increased to 390, 525, and 650 μm, the A_a values were calculated to increase to 2.45, 2.81, and 3.20 cm², respectively. As shown in Fig. 4b, increased A_a led to larger I_{ph} values from the photoelectrode under chopped light illumination. The photocurrent density, the UV-vis absorption spectra, and the IPCE of the p-n homojunction Cu₂O electrodes with planar and 3D pyramid shapes exhibited similar value due to same photoelectrode configuration (Fig. S4 and S5 in ESI†). Thus, these results were attributed to an increased number of activation sites for photocurrent generation. The I_{ph} of a planar electrode with an A_a of 1 cm² was 0.91 mA, while the 3D pyramid photoelectrode



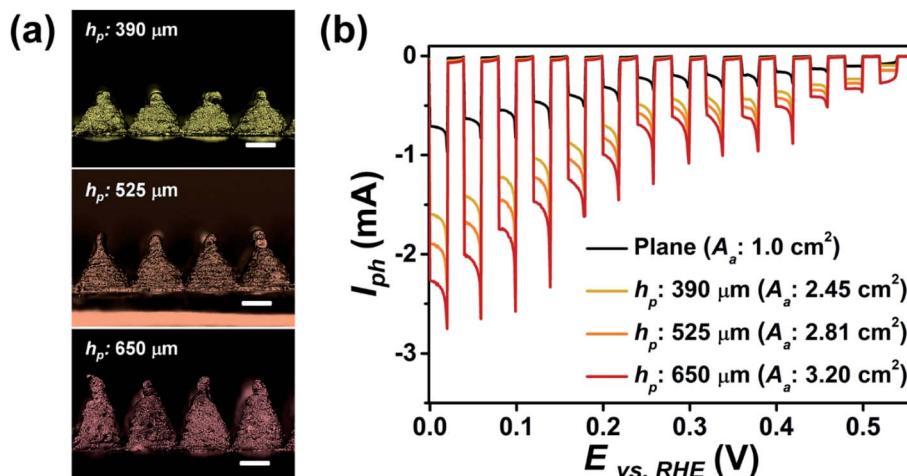


Fig. 4 (a) Optical images of the fabricated 3D photoelectrodes composed of 400 pyramids. The total light absorption area (A_a) of the 3D photoelectrodes is modulated by adjusting h_p to 390, 525, and 650 μm (fixed L_b : 490 μm). The scale bar is 250 μm . (b) Chopped-light PEC performance of the p-n homojunction Cu_2O electrodes with planar and 3D pyramid shapes with respect to the total light absorption area (A_a).

exhibited 2.35, 2.70, and 3.01 mA at 0.02 V (vs. RHE), as h_p increased. These results show that PEC performance can be enhanced through the use of specially designed 3D photoelectrodes.

4. Conclusions

We demonstrated the fabrication process for a novel Cu_2O 3D photoelectrode with a large total light absorption area (A_a) for PEC water splitting. The fabrication process is a two-step method consisting of direct-ink-writing of graphene pyramid arrays and electrodeposition of a Cu current collecting layer and a p-n homojunction Cu_2O photocatalyst layer onto the printed pyramids. The rheological properties of the 3D-printable graphene ink enabled continuous ink extrusion without clogging the nozzle while also retaining the shape of the printed graphene structures. The PEC performance of the 3D photoelectrode was enhanced through two fabrication factors: (i) by adjusting the band gap of the photocatalyst layer using simple electrodeposition and (ii) by increasing the A_a value of the photoelectrode. The deposited p-n homojunction Cu_2O resulted in enhanced splitting of quasi-fermi levels under chopped light illumination, inducing greater carrier generation. Increasing the A_a value of the photoelectrode contributed to increased activation sites for carrier generation. As A_a increased, the 3D pyramid photoelectrode with the p-n homojunction Cu_2O layer exhibited I_{ph} values of 2.35, 2.70, and 3.01 mA at 0.02 V (vs. RHE) under chopped light illumination of 100 mW. We believe that this method is an effective approach for fabricating diversely shaped 3D photoelectrodes that exhibit high PEC performances. As such, this study is an important advance in PEC water splitting research.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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