

# $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> Nanorod Array–Cu<sub>2</sub>O Microsphere *p*–*n* Junctions for Self-Powered Spectrum-Distinguishable Photodetectors

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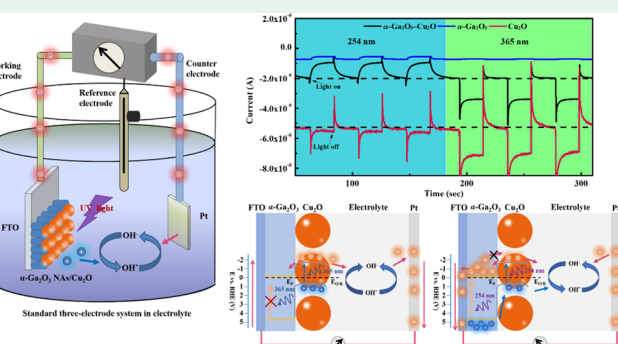
**ABSTRACT:** Most of the photodetectors can measure all of the light illumination with a wavelength below the absorption edge of the detector materials, while they cannot distinguish the different waveband. Herein, a self-powered spectrum-distinguishable photoelectrochemical (PEC) type photodetector based on an  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> nanorod array (NA)/Cu<sub>2</sub>O microsphere (MS) *p*–*n* junction was reported. Under the combined action of the built-in electric field of the *p*–*n* junction and the semiconductor/electrolyte junction, the photodetector exhibits an opposite direction of the photocurrent to the illumination of 254 and 365 nm UV light under the applied bias of 0 V, which can be used to distinguish the different wavelengths of light. The photodetector shows a responsivity of 0.42 mA/W under 254 nm UV light and 0.57 mA/W upon 365 nm, respectively. Our results provide an idea for distinguishing the different illumination wavebands through a photodetector constructed by the heterojunction with two different band gap materials.

**KEYWORDS:** *p*–*n* junction, Ga<sub>2</sub>O<sub>3</sub>/Cu<sub>2</sub>O, solid/liquid junction, spectrum-distinguishable, self-powered

## INTRODUCTION

In the applications of environmental detection, implantable biological detector, and space detection, the demand for a high-performance photodetector is gradually increasing.<sup>1–12</sup> Conventional photodetectors cannot work independently and require additional power supply, which limits the convenience and applicability of them in various environments.<sup>13–20</sup> The self-powered photodetector based on photovoltaic effect can realize the conversion of light to electricity.<sup>21–25</sup> Thus, they can work by incident light instead of using batteries, which is more portable and environmentally friendly.<sup>26–31</sup> Photoconductive detectors are generally inferior to self-powered photodetectors in terms of response speed because of surface effects.<sup>32</sup> Considering the different interface properties of the heterojunction, the self-powered photodetectors can be divided into *p*–*n* junction type,<sup>33,34</sup> Schottky junction type,<sup>35,36</sup> photoelectrochemical (PEC) type,<sup>37,38</sup> etc. Because of the advantages of simple preparation process, low production cost, and good responsivity, the solid/liquid junction base PEC type photodetector composed of semiconductor and electrolyte has a good application prospect in varieties of harsh environments.<sup>39,40</sup>

Under the action of the interfacial space electric field of semiconductor/electrolyte, the PEC self-powered photodetector can effectively and rapidly separate photogenerated carriers and avoid their recombination.<sup>41</sup> Nowadays, most of the PEC type self-powered photodetectors that have been reported can measure all of the light with a wavelength below the absorption edge of the detector materials, while they cannot distinguish the wavelengths of different illumination.<sup>42,43</sup> Herein, we constructed a PEC type self-powered photodetector based on an *n*-type and a *p*-type semiconductor with different light absorption ranges for the application of spectrum-distinguishment. Varieties of metal oxide semiconductors including ZnO,<sup>44</sup> TiO<sub>2</sub>,<sup>45</sup> SnO<sub>2</sub>,<sup>46</sup> and Ga<sub>2</sub>O<sub>3</sub><sup>47–49</sup> have been widely used in the field of photoelectric detection because of their suitable band gap and excellent photoelectric performance.  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub>, with a band gap of about 5.3 eV, is a direct band gap III–VI wide band gap semiconductor, which is a *n*-type semiconductor due to self-compensation effect.<sup>50</sup> Meanwhile, the vertical nanorod structure is conducive to the rapid



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transmission and separation of photogenerated carriers. The large specific surface area of nanorod arrays ensures a sufficient contact area between  $\text{Ga}_2\text{O}_3$  and electrolyte solutions.

$\text{Cu}_2\text{O}$  with a band gap of 2.0 eV is widely used in the field of photoelectric detection because of its simple and nontoxic synthesis method.<sup>51</sup> As we know, in the case of Cu vacancies and excess oxygen,  $\text{Cu}_2\text{O}$  is usually a *p*-type semiconductor.<sup>52</sup> When the *n*-type semiconductor  $\alpha\text{-Ga}_2\text{O}_3$  combined with  $\text{Cu}_2\text{O}$ ,  $\alpha\text{-Ga}_2\text{O}_3$  NA/ $\text{Cu}_2\text{O}$  MS *p*–*n* junctions were obtained, which can effectively promote the separation of photoinduced carriers and broaden the range of light detection.<sup>53</sup> In addition, under the action of the *p*–*n* junction and solid/liquid junction, the spectrum-distinguishable feature of the detector can be realized.

In this work, we report a self-powered spectrum-distinguishable photodetector based on  $\alpha\text{-Ga}_2\text{O}_3$  NA/ $\text{Cu}_2\text{O}$  microsphere (MS) *p*–*n* junctions.  $\alpha\text{-Ga}_2\text{O}_3$  NAs were obtained by a hydrothermal method and post annealing treatment, and then  $\alpha\text{-Ga}_2\text{O}_3$  NAs/ $\text{Cu}_2\text{O}$  MS *p*–*n* junctions were constructed through a chemical bath deposition (CBD) process. The  $\alpha\text{-Ga}_2\text{O}_3$  NA/ $\text{Cu}_2\text{O}$  MS *p*–*n* junction photodetector shows a spectrum-distinguishable feature with an opposite photocurrent response upon the illumination of 254 and 365 nm ultraviolet light without bias, which is a promising candidate of distinguishable UV band self-powered photodetectors.

## EXPERIMENTAL SECTION

Copper dinitrate [ $\text{Cu}(\text{NO}_3)_2$ ], Tris(2-hydroxyethyl)Amine ( $\text{C}_6\text{H}_{15}\text{NO}_3$ , 98%), and Hydrazine hydrate ( $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ , 80%) were got from Shanghai Macklin Biochemical Co., Ltd. Gallium nitrate hydrate [ $\text{Ga}(\text{NO}_3)_3\cdot x\text{H}_2\text{O}$ , 99.99%] was obtained from Alfa Aesar Co., Ltd. The fluorine-doped tin oxide layer on the surface of the commercial FTO substrate (Shanghai Daheng Optics and Fine Mechanics Co., Ltd.) was used as the seed crystal layer for the growth of nanorods.

After hydrothermal reaction and post annealing treatment, the  $\alpha\text{-Ga}_2\text{O}_3$  NAs were obtained. The FTO glass was treated with acetone, anhydrous ethanol and deionized water in turn before use. A layer of  $\text{SnO}_2$  on the surface of the FTO was used as a seed layer for the growth of  $\text{GaOOH}$  NAs. The  $\text{Ga}(\text{NO}_3)_3$  with a concentration of 0.39 M/L was used as a precursor solution. Subsequently, the FTO glass was placed in the lining of the hydrothermal kettle containing the precursor solution. After heating at 150 °C for 12 h, the  $\text{GaOOH}$  NAs was obtained. Finally, the dried  $\text{GaOOH}$  NAs were annealed at 400 °C for 4 h to obtain  $\alpha\text{-Ga}_2\text{O}_3$  NAs.

The  $\text{Cu}_2\text{O}$  MSs was synthesized on the  $\alpha\text{-Ga}_2\text{O}_3$  NAs by chemical bath deposition (CBD). 0.05 M (0.4832 g)  $\text{Cu}(\text{NO}_3)_2$  and 1.5 M (10.194 mL) Tris(2-Hydroxyethyl)Amine were evenly distributed in a certain amount of DI water after stirring. Here the TEA was used as a complexing agent. Then keep the substrate with  $\alpha\text{-Ga}_2\text{O}_3$  NAs vertically in the solution by using electrode holder. The 0.1 M (242.54  $\mu\text{L}$ ) hydrazine hydrate ( $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ ) that we added is as a reducing agent. After 2 h of growth, the  $\alpha\text{-Ga}_2\text{O}_3$  NA/ $\text{Cu}_2\text{O}$  MS *p*–*n* junctions were obtained.

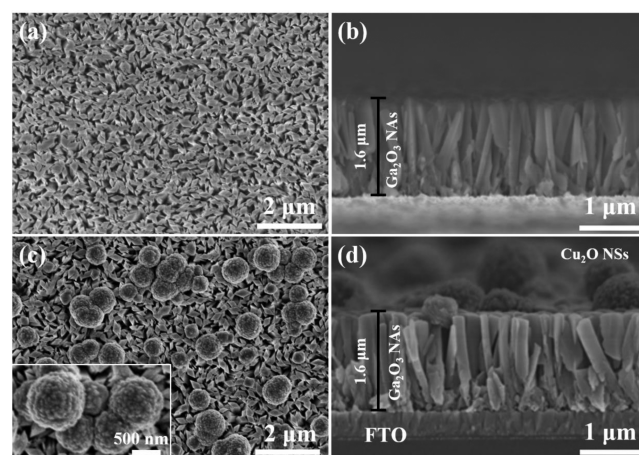
The structure, composition and other basic characterization of the materials were analyzed by the field-emission scanning electron microscopy (FESEM, Hitachi S-4800) and Bruker D8 Advance X-ray diffractometer (XRD). The energy level distribution and optical band gap of the materials were tested by UV–vis spectrophotometer (Hitachi U-3900) and X-ray photoelectron spectroscopy (Thermo Scientific K-Alpha XPS).

The photoresponse performance of the spectrum-distinguishable photodetector was tested by electrochemical system (CHI660E). The effective working area of the  $\alpha\text{-Ga}_2\text{O}_3$  NA/ $\text{Cu}_2\text{O}$  MS based UV detector is about 1  $\text{cm}^2$ . A 0.5 M aqueous solution of  $\text{Na}_2\text{SO}_4$  was used as the electrolyte, and the counter electrode here is a Pt sheet.

The intensities of the ultraviolet lamp (300 W xenon lamp, PLS SXE300) were gradually increased from 300 to 2500  $\mu\text{W}/\text{cm}^2$ .

## RESULTS AND DISCUSSION

The top-view of the  $\text{Ga}_2\text{O}_3$  NAs is shown in Figure 1a, and Figure 1b represents the cross-sectional FESEM image of



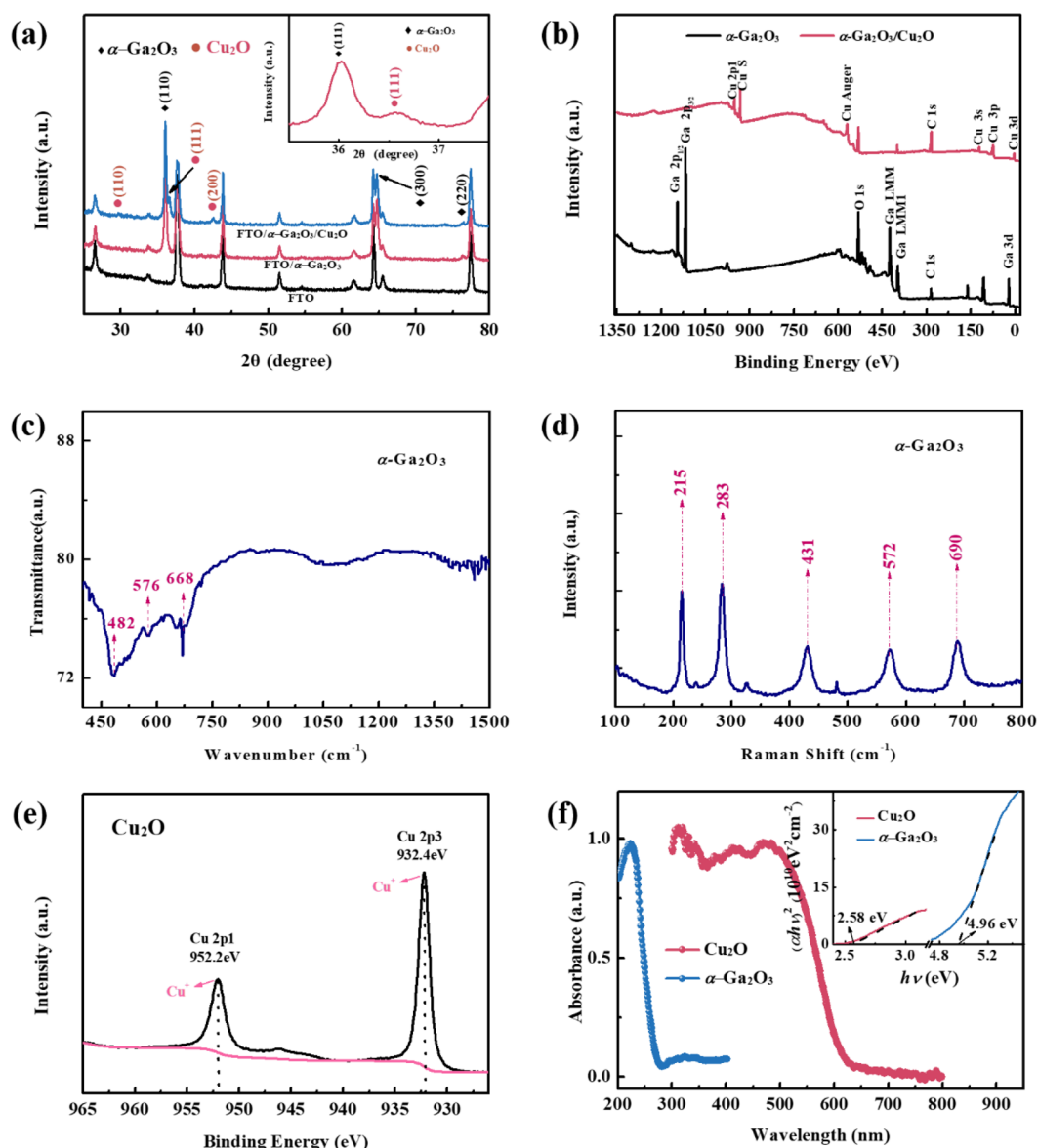
**Figure 1.** (a) Top-view FESEM image and (b) cross-sectional FESEM image of  $\text{Ga}_2\text{O}_3$  NAs. (c) Top-view FESEM image and (d) cross-sectional FESEM image of  $\text{Ga}_2\text{O}_3$  NAs/ $\text{Cu}_2\text{O}$  MSs, the inset is an enlarged view.

$\text{Ga}_2\text{O}_3$  NAs. It can be seen in Figure 1a that a uniform array of  $\text{Ga}_2\text{O}_3$  nanorods grows vertically on FTO glass. The average diameter of the hexagonal-prism-like  $\text{Ga}_2\text{O}_3$  nanorods ranges from 80 to 200 nm (Figure 1a) and a mean length of about 1.6  $\mu\text{m}$  (Figure 1b). The  $\text{Cu}_2\text{O}$  MSs disperse on the  $\text{Ga}_2\text{O}_3$  NAs after CBD process with an average diameter of about 1  $\mu\text{m}$ , which can be seen in Figure 1c, d.

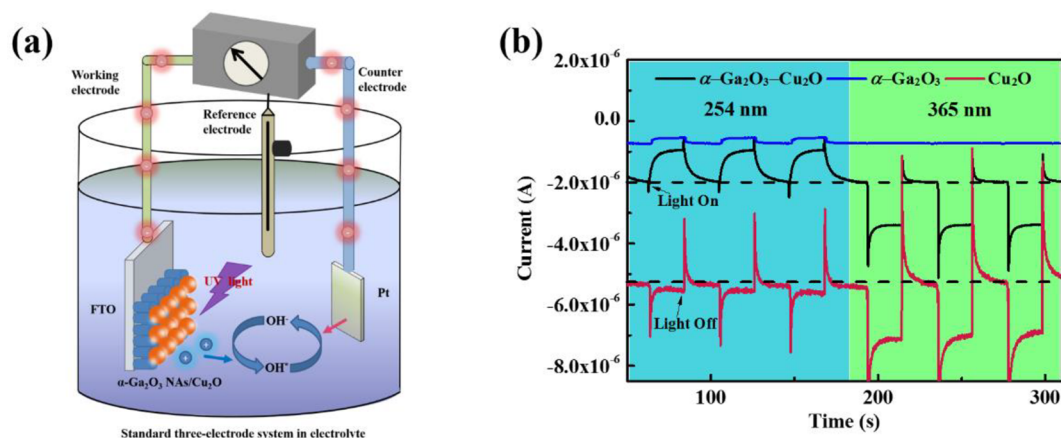
The XRD patterns of the FTO glass,  $\text{Ga}_2\text{O}_3$  NAs and  $\text{Ga}_2\text{O}_3$  NAs/ $\text{Cu}_2\text{O}$  MSs are represented in Figure 2a. The diffraction peak of FTO glass is due to the presence of the  $\text{SnO}_2$  layer. In addition, the (110), (300) and (220) crystal planes of  $\alpha$  phase  $\text{Ga}_2\text{O}_3$  can be observed by the three diffraction peaks at 36.0, 64.7, and 76.4°. After the process of chemical bath method, the existence of  $\text{Cu}_2\text{O}$  MSs can be observed from the three added peaks situated at 29.5, 36.4, and 42.2°, which can be indexed to (110), (111), and (200) planes of  $\text{Cu}_2\text{O}$ . Significant diffraction peaks of Cu and CuO were not observed, indicating that  $\text{Cu}(\text{NO}_3)_2$  was completely reduced in the CBD process. And no additional diffraction peaks of possible impurities were detected.

To further study the chemical states of each element in  $\alpha\text{-Ga}_2\text{O}_3$  NAs/ $\text{Cu}_2\text{O}$  MSs, the XPS test was performed. As presented in Figure 2b that the peaks at 21.7, 397.3, 424.1, 1117.7, and 1144.8 eV could be attributed to Ga 3d, Ga LMM1, Ga LMM, and Ga 2p, respectively. Characteristic peaks of C 1s, Cu 2p, Cu 3p, Cu 3s, Cu 3d, Cu S, and Cu Auger are also observed in Figure 2b. Figure 2e shows the core energy level of Cu 2p, from which the oxidation state of Cu element in  $\text{Cu}_2\text{O}$  MSs can be further determined. In addition, the binding energies of Cu 2p 3/2 and Cu 2p 1/2 can also be determined by peaks located at 932.4 and 952.2 eV.<sup>54</sup>

Figure 2c presents the IR spectra of the  $\alpha\text{-Ga}_2\text{O}_3$  NAs, which has a R3c symmetrical corundum structure, and its crystal structure can be described by  $\text{GaO}_6$  octahedron. Therefore, the broadband peak centered at 668  $\text{cm}^{-1}$  can be interpreted as the

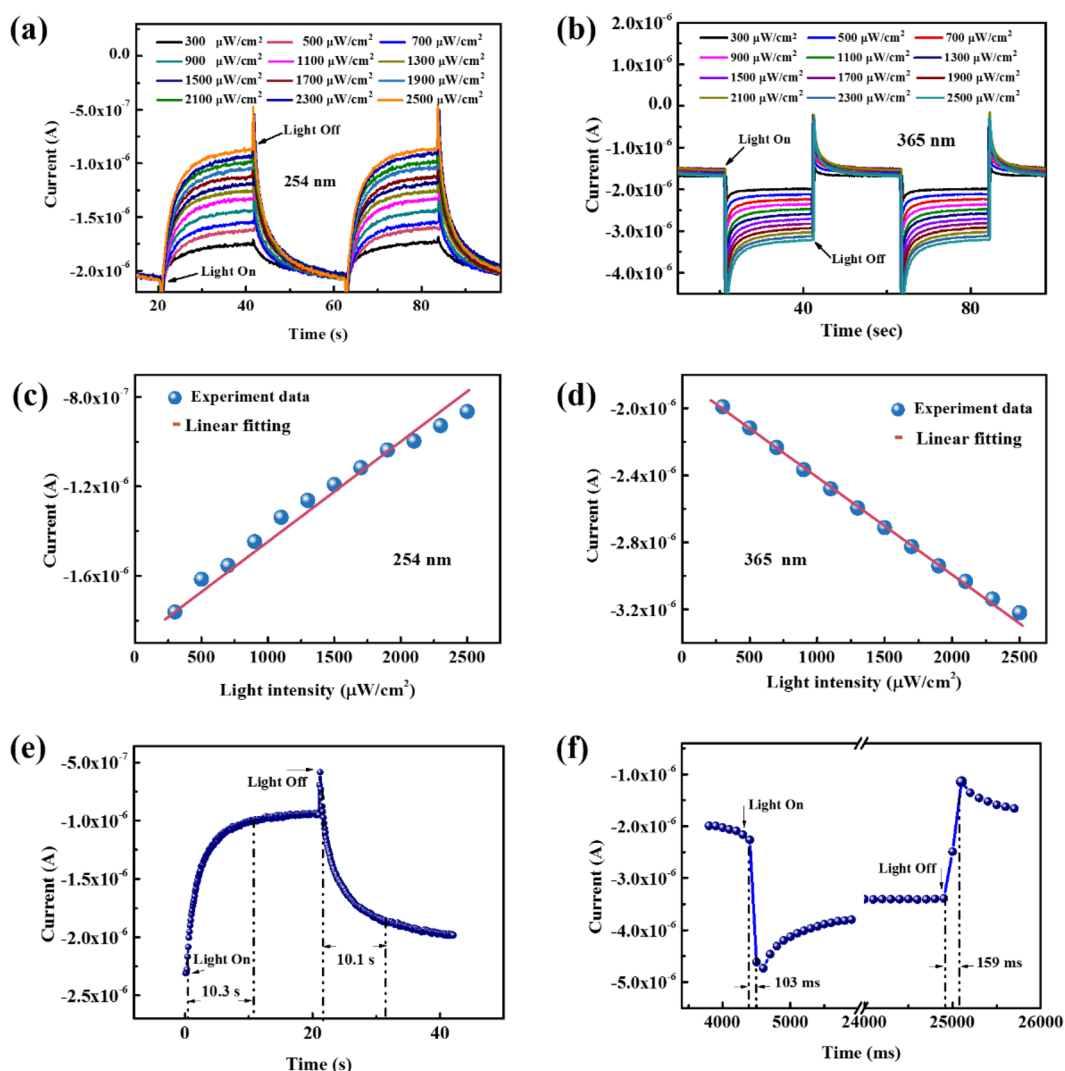


**Figure 2.** (a) XRD patterns of the FTO, FTO/Ga<sub>2</sub>O<sub>3</sub> NAs, and FTO/Ga<sub>2</sub>O<sub>3</sub> NAs/Cu<sub>2</sub>O MSs. (b, e) the XPS spectra of Ga<sub>2</sub>O<sub>3</sub> NAs/Cu<sub>2</sub>O MSs. (c) Infrared spectrum and (d) Raman spectrum of  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> NAs. (f) UV-vis absorption spectra of the Ga<sub>2</sub>O<sub>3</sub> and Cu<sub>2</sub>O MSs, insert is the plot of  $(\alpha h\nu)^2$  versus the energy of light ( $h\nu$ ).



**Figure 3.** (a) Typical PEC system built for evaluating the photoresponse behaviors of the  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> NA/Cu<sub>2</sub>O MS  $p$ - $n$  junctions based photodetector. (b) Transient current upon 254 and 365 nm UV light on/off cycles for the photodetector at zero bias.





**Figure 4.** (a, b) Photoresponse of the device upon 254 and 365 nm UV light with various intensities. (c, d) Relationship between the light intensity and photocurrent. (e, f) Magnified rise and decay edges of the current response.

Ga–O vibration of the  $\text{GaO}_6$  octahedral lattice in  $\alpha\text{-Ga}_2\text{O}_3$  NAs in the IR. In the Raman spectrum of  $\alpha\text{-Ga}_2\text{O}_3$  NAs (Figure 2d), the frequency peak range is related to different vibration modes. The high-frequency peak exceeding  $600\text{ cm}^{-1}$  is derived from the symmetric stretching vibration of  $\nu_1$  of  $\text{GaO}_4$ ; in the range of Raman shifts of 300 and  $600\text{ cm}^{-1}$ , the peak corresponds to the symmetric stretching vibration of the  $\text{GaO}_6$  octahedron. The low-frequency peak below  $200\text{ cm}^{-1}$  is caused by the O–Ga–O bending vibration of the  $\text{GaO}_6$  octahedron. The Raman spectrum and IR of  $\alpha\text{-Ga}_2\text{O}_3$  NAs indicates the high crystal quality of  $\alpha\text{-Ga}_2\text{O}_3$  NAs, which is consistent with the XRD patterns.

The UV–visible absorbance spectra of  $\alpha\text{-Ga}_2\text{O}_3$  NAs and  $\text{Cu}_2\text{O}$  MSs are displayed in Figure 2f. To avoid interference from FTO glass, we tested the UV–vis absorbance of  $\alpha\text{-Ga}_2\text{O}_3$  by  $\alpha\text{-Ga}_2\text{O}_3$  nanorods powder loaded on a glass slide. It can be seen that the pure  $\alpha\text{-Ga}_2\text{O}_3$  is a good solar-blind photo-detection material,<sup>55</sup> whereas the  $\text{Cu}_2\text{O}$  shows a broader light absorption range.<sup>56</sup> The optical band gaps of  $\alpha\text{-Ga}_2\text{O}_3$  NAs and  $\text{Cu}_2\text{O}$  MSs were calculated by using the equation  $((\alpha h\nu)^2 = A(h\nu - E_g))$ , which is shown in the inset of Figure 2f. The optical band gap of  $\alpha\text{-Ga}_2\text{O}_3$  NAs is estimated to be  $\sim 4.96\text{ eV}$  and that of  $\text{Cu}_2\text{O}$  MSs is  $\sim 2.58\text{ eV}$ . Consequently, strong

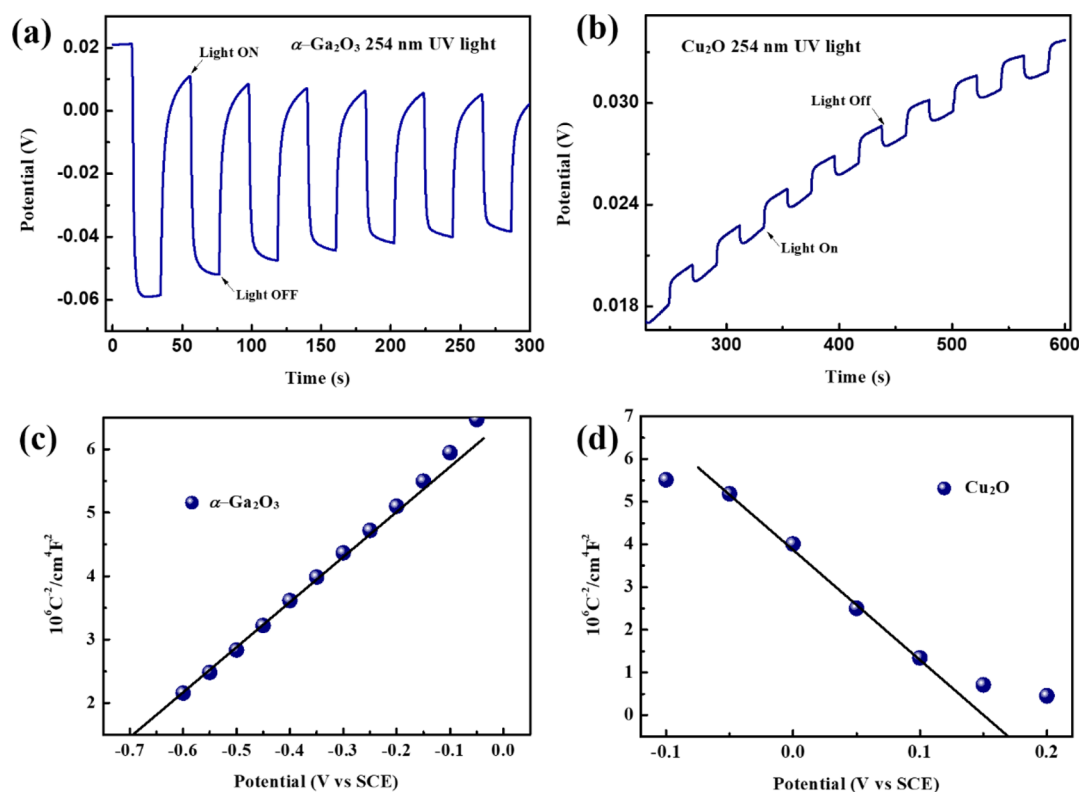
visible light absorption of  $\text{Cu}_2\text{O}$  MSs expands the light detection range of  $\alpha\text{-Ga}_2\text{O}_3$  NAs and the remarkable light band distinguishing performance of such a structure is expected.

Figure 3a shows a standard three-electrode system based on an electrochemical system for testing the typical photoresponse characteristics of the detector. The  $\alpha\text{-Ga}_2\text{O}_3$  NA/ $\text{Cu}_2\text{O}$  MS  $p$ – $n$  junctions and platinum sheet were used as the working electrode and counter electrode, respectively. In addition, saturated calomel was used as the reference electrode to ensure the stability of the system. As a control, pure  $\alpha\text{-Ga}_2\text{O}_3$  NAs and  $\text{Cu}_2\text{O}$  MSs were also tested as working electrodes under the same conditions.

It can be seen in Figure 3b that the photoresponse performance of the detector under the illumination of different wavelengths and various intensities can be tested by switching on and off the UV lamp periodically. In dark, the  $\alpha\text{-Ga}_2\text{O}_3$  NA/ $\text{Cu}_2\text{O}$  MS  $p$ – $n$  junction exhibits a negative dark current of about  $-2.00\text{ }\mu\text{A}$  without bias voltage. A typical steady-state current of  $-0.90\text{ }\mu\text{A}$  was generated when the  $\alpha\text{-Ga}_2\text{O}_3$  NA/ $\text{Cu}_2\text{O}$  MS  $p$ – $n$  junction was upon 254 nm UV light. The  $\Delta I$  ( $I_{\text{ph}} - I_{\text{dark}}$ ) is calculated to be  $1.10\text{ }\mu\text{A}$ . The detector shows a considerable stability after several cycles.<sup>57,58</sup> It is noteworthy that when the illumination switches to 365 nm ultraviolet light,

**Table 1.** Comparison of the Key Parameters of the  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> NA/Cu<sub>2</sub>O MS  $p$ - $n$  Junction Self-Powered Photodetectors and Other Previously Reported Devices

materials	device type	illumination (nm)	responsivity ( $\mu\text{A/W}$ )	response time	ref.
2D Bi <sub>2</sub> S <sub>3</sub>	PEC	300–800	8.9 (365 nm)	0.1/0.1 s (400 nm)	38
Te nanosheet	PEC	350–475	1.85–2.15		43
BiQD <sub>s</sub>	PEC	200–600	19.3(350 nm)	0.1/0.2 s (350 nm)	53
ZnO/SnS	heterojunction	365	$3.64 \times 10^5$	49.1/51.8 s	57
ZnO/SnS	heterojunction	690	$1.55 \times 10^5$	0.4/0.2 s	57
$\alpha$ -Ga <sub>2</sub> O <sub>3</sub> /Cu <sub>2</sub> O	PEC	254	$4.2 \times 10^2$	10.3/10.1 s	this work
$\alpha$ -Ga <sub>2</sub> O <sub>3</sub> /Cu <sub>2</sub> O	PEC	365	$5.7 \times 10^2$	103/159 ms	this work

**Figure 5.** Open circuit potential transient upon chopping illumination of pure (a)  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> NAs, (b) Cu<sub>2</sub>O MSs; Mott–Schottky plots of pure (c)  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> NAs and (d) Cu<sub>2</sub>O MSs measured in an aqueous solution of Na<sub>2</sub>SO<sub>4</sub> (0.5 M).

the  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> NA/Cu<sub>2</sub>O MS  $p$ - $n$  junction exhibits an opposite direction of photoresponse current with a value of  $-3.40 \mu\text{A}$ . And the  $\Delta I$  ( $I_{\text{ph}} - I_{\text{dark}}$ ) is  $-1.40 \mu\text{A}$ . It means that this detector can distinguish the 254 and 365 nm ultraviolet light according to the positive and negative values of  $\Delta I$  ( $I_{\text{ph}} - I_{\text{dark}}$ ). For the purpose of comparison, photoresponse properties of pure  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> NAs and Cu<sub>2</sub>O MSs were also studied under the same irradiation conditions. As a comparison, Figure 3b shows the photocurrent of pure  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> NAs and pure Cu<sub>2</sub>O MSs. The initial dark current of pristine  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> NAs was  $-0.73 \mu\text{A}$  and the photocurrent was only  $-0.54 \mu\text{A}$ . Moreover, the pure  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> NAs almost has no response to 365 nm ultraviolet light. As for pure Cu<sub>2</sub>O MSs, they exhibit a preferable performance exposure to 365 nm ultraviolet light versus 254 nm ultraviolet light. In contrast to the pure  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> NAs and Cu<sub>2</sub>O MSs, the  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> NA/Cu<sub>2</sub>O MS  $p$ - $n$  junction exhibits a better responsivity and a light–dark current ratio.

The  $I$ - $t$  curves of  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> NA/Cu<sub>2</sub>O MS  $p$ - $n$  junction under different intensities of 254 and 365 nm UV irradiation are shown in Figure 4a, b. The photocurrent was enhanced with the increase of light intensity. Furthermore, as presented

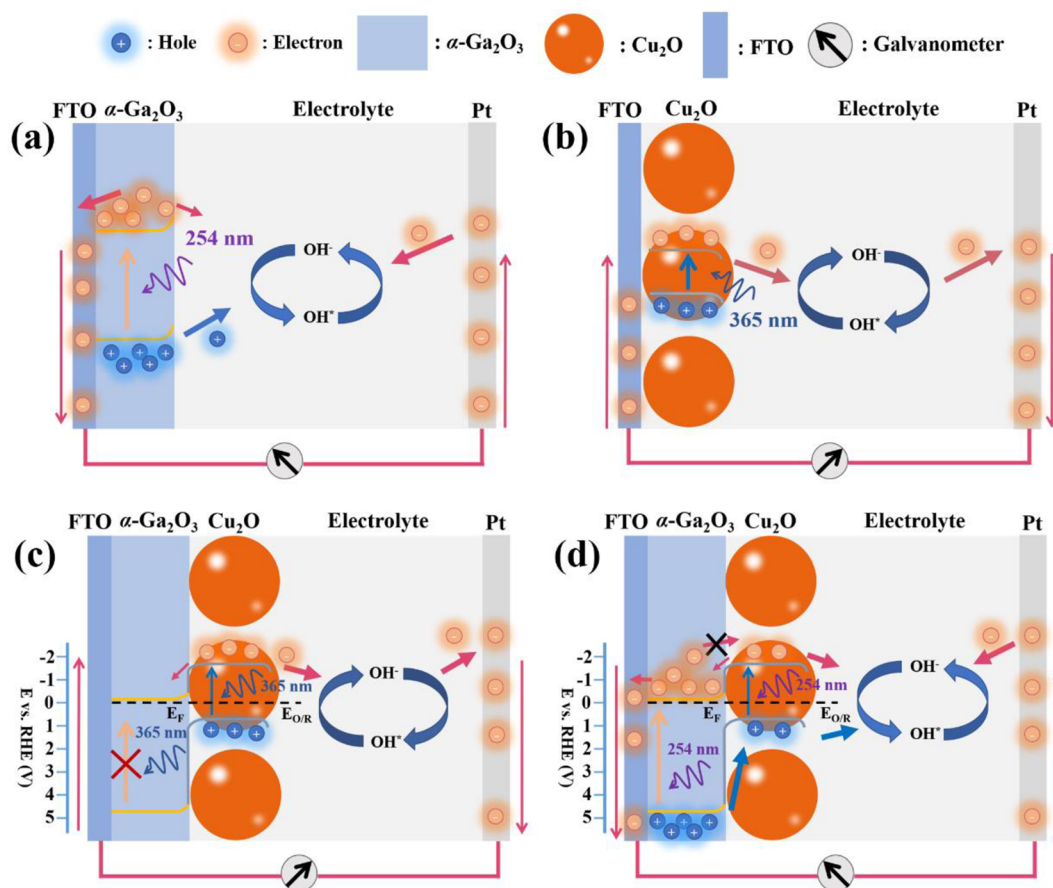
in Figure 4c, d, the photocurrent of  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> NA/Cu<sub>2</sub>O MS  $p$ - $n$  junction exhibits an obvious light intensity-dependent character with the increase of light intensity from 300 to 2500  $\mu\text{W}/\text{cm}^2$ .

Photoresponsivity is an important reference to assess the performance of a detector. The photocurrent generated by the unit effective area of the detector under a certain power of illumination is defined as  $R_{\lambda}$ , which can be calculated by this equation:<sup>59</sup>

$$\Delta I = I_{\text{ph}} - I_{\text{dark}} \quad (1)$$

$$R_{\lambda} = \Delta I / (PS) \quad (2)$$

where  $\Delta I$  is the change of current in the detector after illumination.  $P$  is the power density of ultraviolet lamp and  $S$  is the effective illumination area of the  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> NA/Cu<sub>2</sub>O MS  $p$ - $n$  junctions on FTO. When the power density of the UV lamp is  $2500 \mu\text{W}/\text{cm}^2$ , the  $R$  of  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> NA/Cu<sub>2</sub>O MS  $p$ - $n$  junction upon 254 nm UV light is  $0.42 \text{ mA/W}$ . And that is  $0.57 \text{ mA/W}$  for 365 nm UV light.



**Figure 6.** Schematic diagram of the self-powered  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> NA/Cu<sub>2</sub>O MS  $p$ - $n$  junction photodetectors.

The photoresponse time of the detector are respectively defined as the time required for the current to increase from 10 to 90% of the peak value, and vice versa.<sup>56</sup> As shown in Figure 4e, f, the rise time and decay time of  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> NA/Cu<sub>2</sub>O MS  $p$ - $n$  junction upon 254 nm UV light are about 10.3 and 10.1 s, respectively. And upon to 365 nm UV light these are 103 and 159 ms, exhibit the fast response speed. Besides  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> NA/Cu<sub>2</sub>O MS  $p$ - $n$  junction, some emerging new materials had been developed for novel photodetector. Such as few-layer BP nanosheets,<sup>40</sup> 2D InSe nanosheets,<sup>39</sup> 2D nonlayered Te nanosheets, ZnO NWs/shuttle-like SnS<sup>59</sup> and MoS<sub>2</sub>/graphene.<sup>37</sup> Table 1 compares the photoelectric performance of self-powered  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub>/Cu<sub>2</sub>O  $p$ - $n$  junction photodetector with the researches of others. Compared with the previous reports, our photodetector based on  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub>/Cu<sub>2</sub>O  $p$ - $n$  junction has good responsivity and the fastest response speed upon 365 nm UV light.

Figure 5a, b show the open circuit potential (OCP) curves of pure  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> NAs and Cu<sub>2</sub>O MSs upon chopped illumination of 254 nm ultraviolet light. The negative change of open-circuit potential upon illumination proves the upward energy band bending in the interfacial built-in electric field of  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> NAs/electrolyte (0.5 M Na<sub>2</sub>SO<sub>4</sub>). Thus, the  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> NAs is an  $n$ -type semiconductor.<sup>60</sup> Conversely, the positive OCP transient in Figure 5b indicates that the Cu<sub>2</sub>O MSs is an  $p$ -type semiconductor. Obviously, the  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub>/Cu<sub>2</sub>O heterojunction space charge region is formed after  $p$ -type Cu<sub>2</sub>O MSs loaded on the  $n$ -type  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> NAs. Mott-Schottky (MS) measurements were carried out to further verify the conduction type of the semiconductors and determine the

band structure. As shown in Figure 5c, d, the opposite directions of the slopes indicate the different conductivity types of  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> and Cu<sub>2</sub>O. The flat potential  $E_{fb}$  at the interface between semiconductor and solution can be calculated using the Mott-Schottky relation:<sup>61</sup>

$$1/C^2 = (2/e\epsilon\epsilon_0N)[(E - E_{fb}) - kT/e] \quad (3)$$

Where  $C$  is the capacitance of the semiconductor electrode per unit area,  $E_{fb}$  is the flat band potential,  $E$  is the electrode potential,  $\epsilon$  is the relative dielectric constant of the semiconductor (here the  $\epsilon$  of  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> is 10 and that of Cu<sub>2</sub>O is 7.6),<sup>62,63</sup>  $\epsilon_0$  is the vacuum dielectric constant,  $k$  is the Boltzmann constant, and  $T$  is the absolute temperature.  $e$  is the basic charge, at room temperature, and  $kT/e$  is about 0.026 V, which is negligible.

In the  $1/C^2$ - $E$  diagram, the straight-line extension of  $1/C^2$  intersects the potential  $E$  axis at  $E_{fb}$ . Thus, the flat band potential of the semiconductor electrode was obtained. As shown in Figure 5c, d, the  $E_{fb}$  of the  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> NAs is  $-0.70$  V (vs SCE) and that of Cu<sub>2</sub>O MSs locates at  $0.17$  (vs SCE). The  $E_{fb}$  is usually switched to the normal hydrogen electrode (NHE) scale using the Nernst equation for subsequent calculations.<sup>64</sup>

$$E_{NHE} = E \text{ (vs SCE)} + 0.0591pH + 0.244 \quad (4)$$

The  $E_{fb}$  of the  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> NAs locates at  $-0.0423$  V (RHE) and that of Cu<sub>2</sub>O MSs locates at  $0.8277$  (RHE). According to the change of semiconductor Fermi energy level before and after contact with solution, the energy band bending of solid/liquid

junction space electric field can be calculated by using equation:  $V_{sc} = E_{OCP} - E_{fb}$ .<sup>60</sup> The band bending across the solid/liquid junction of  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> NAs is calculated to be 0.72 V and that of Cu<sub>2</sub>O MSs is -0.12 V. It can be considered that the flat band potential  $E_{fb}$  is approximately the bottom of the conduction band for *n*-type semiconductor, or the top of the valence band for the *p*-type semiconductor.<sup>60</sup> Combined with the optical band gap of  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> (4.96 eV) and Cu<sub>2</sub>O (2.58 eV) we have measured, the electronic energy band diagram of the heterojunction can be given easily.

Figure 6 shows the mechanism of spectrum-distinguishable photodetector based on  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> NA/Cu<sub>2</sub>O MS *p*-*n* junction operated without bias. When the semiconductor (solid) in contact with the electrolyte (liquid), the condition for the semiconductor/solution system to reach an equilibrium is that the Fermi level ( $E_f$ ) of the semiconductor at the interface equal to the Redox couple level ( $E_{O/R}$ ) of the solution.<sup>65</sup> The band structure diagram of  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> NA/Cu<sub>2</sub>O MS *p*-*n* junction under the scale of normal hydrogen electrode (NHE) is shown in Figure 6, and the band positions of  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> and Cu<sub>2</sub>O were given. As shown in Figure 6a, because of the influence of the redox couple in the solution, the carrier distribution of the pure  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> NAs changed, forming a space charge region and an upward energy band bending. Photoinduced electrons excited in pure  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> would transfer to FTO driven by the space-charge region of  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub>/electrolyte junction under 254 nm UV light. Several photoinduced electrons also diffuse to the electrolyte because of the large specific surface area of nanorods.<sup>66</sup> In the meantime, photon-induced holes also transport into the electrolyte and trap the electrons of OH<sup>-</sup> ( $h^+ + OH^- = OH^*$ ) at the solid/liquid interface. The positive OH\* was then reduced at the counter electrode ( $e^- + OH^* = OH^-$ ) to form a current loop. In addition, no significant photocurrent was observed upon 365 nm ultraviolet light due to the large band gap of pure  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub>. Conversely, the direction of built-in electric field at Cu<sub>2</sub>O/electrolyte interface is opposite to that of  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub>/electrolyte due to the different types of conduction. Under the illumination of 254 or 365 nm ultraviolet light, photoinduced electrons in the conduction band of the pure Cu<sub>2</sub>O transfer to electrolyte and then oxidized at the counter electrode, which forms the photocurrent in opposite direction compared with pure  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> NAs. Different photogenerated electrons transport directions upon illumination in pure  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> NAs and Cu<sub>2</sub>O MSs lead to different photoresponse currents, which corresponds to the result in Figure 3b.

As for the  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> NA/Cu<sub>2</sub>O MS *p*-*n* junction upon to 254 nm UV light (Figure 3b), the device exhibits enhanced photoresponsivity than the pure  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> NAs. It can be attributed to two factors as follows (Figure 6d): (1) The as-formed built-in electric field in  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub>/Cu<sub>2</sub>O heterojunction junctions effectively block the diffusion of the photoinduced electrons from  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> to the electrolyte; (2) a number of carriers would be generated in Cu<sub>2</sub>O MSs, and then the photoinduced electrons would migrate from Cu<sub>2</sub>O toward to  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> driven by the  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub>/Cu<sub>2</sub>O *p*-*n* junctions. As a result, it would collect more electrons at the FTO, and produce an enhanced photocurrent. However, when the illumination turns to 365 nm UV light, the photoinduced carriers only can be produced in the Cu<sub>2</sub>O MSs because of the only deep UV absorption of  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> NAs (Figure 6c). Noteworthily, the surface of Cu<sub>2</sub>O MSs is completely immersed in electrolyte except the bottom, leading to a larger area of Cu<sub>2</sub>O/electrolyte

junction than  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub>/Cu<sub>2</sub>O *p*-*n* junction. Therefore, although the photogenerated electrons in Cu<sub>2</sub>O MSs can transport to both  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> NAs and electrolyte, most of the photogenerated electrons will transfer to the electrolyte. As a result, it shows the same directions of photocurrent as pure Cu<sub>2</sub>O MSs (Figure 3b). These factors contribute to the difference in the photocurrent of the  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> NA/Cu<sub>2</sub>O MS *p*-*n* junction upon 254 and 365 nm ultraviolet light. Thus, it can be seen, under the interaction of the space charge region of the  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> NA/Cu<sub>2</sub>O MS *p*-*n* junction and the semiconductor/electrolyte junction, that the photodetector based on  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> NA/Cu<sub>2</sub>O MS *p*-*n* junction exhibits a reverse photocurrent upon 254 and 365 nm UV light without bias. It provides an idea for distinguishing the different illumination wavebands by a photodetector constructed by the heterojunction with two different band gap materials.

## CONCLUSIONS

In a word, a self-powered spectrum-distinguishable detector based on  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> NA/Cu<sub>2</sub>O MS *p*-*n* junctions has been constructed successfully. Under the irradiation of 254 and 365 nm UV light, the different photoinduced electrons transport directions in the device lead to different photoresponse currents, which can be used to distinguish the wavelengths of these two kinds of illumination.  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> NA/Cu<sub>2</sub>O MS *p*-*n* junction photodetector have a responsivity of 0.57 mA/W (0.42 mA/W) upon exposure to 365 (254) nm ultraviolet light. The detector also has a fast-operated speed with a rise time of 103 ms upon exposure to 365 nm ultraviolet light. The  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> NA/Cu<sub>2</sub>O MS *p*-*n* junction-based PEC type self-powered photodetector we constructed is an interesting candidate for the application of spectrum-distinguishment.

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### Notes

The authors declare no competing financial interest.

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