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Ultraviolet Sensors Based on Two-Dimensional Zinc Oxide Structures

Naif H. Al-Hardan, Muhammad Azmi Abdul Hamid, Roslinda Shamsudin and Norinsan Kamil Othman

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Abstract

In this chapter, we review the application of zinc oxide (ZnO) in ultraviolet (UV) sensing and emphasise on the two-dimensional (2D) ZnO structures. The synthesis of 2D ZnO structures, the morphologies, and the photoluminescence emission will be reviewed and highlighted. The performance of the UV sensors based on 2D ZnO structures is explored. The lack in the study of the 2D ZnO UV sensors might be due to the difficulties of controlling the growth of the 2D ZnO compared to the one-dimensional (1D) ZnO structures.

Keywords: two dimensional (2D), zinc oxide (ZnO), nanostructures, photoluminescence spectroscopy, ultraviolet (UV) sensors

1. Introduction

In the past few decades, zinc oxide (ZnO) has garnered attention due to its unique characterisations that been found to be useful in a variety of applications, such as rubber manufacturing, the ceramic industry, food additives, and pigments [1]. Furthermore, ZnO as a bio safe compound is found to be useful in applications linked to human life, such as in cosmetic, medical, and dental products [1, 2]. It has become one of the most promising compounds that can be employed in advance technology applications, and it demonstrates outstanding performance in various application fields, such as sensors for different analytics including those for hydrogen, oxygen, Volatile organic compounds (VOCs) [3–5], urea, cholesterol, and glucose [6–9].

In addition, ZnO also been employed as a photodetector in the ultraviolet (UV) region of the electromagnetic spectra [10–12] as well as in light emitting diodes (LEDs) [13], UV lasers [14], thin films transparent transistors (TFTs) [15], memory devices [16], and transparent conducting oxides for consumer devices [17]. The subject related to the applications of ZnO was boosted with the advantage of the easy synthesis process compared to the other competitive compounds, such as gallium nitride (GaN) and silicon carbide (SiC). Moreover, ZnO can be synthesised through different processes, and films were grown on different low-cost substrates, such as ordinary papers [18], polymers [19, 20], slide glasses [15], and silicon wafers [10]. Furthermore, high-quality ZnO can be prepared using simple methods with repeatable characteristics, including methods such as radio frequency (RF) magnetron sputtering [21], low temperature hydrothermal processes [22, 23], thermal evaporation [24, 25], sol-gel [26], electrodeposition [27], and chemical vapour deposition (CVD) [28]. Another advantage of ZnO is that it is easily synthesised into different structures in the nanoscale range (nanostructures). Those nanostructures have found potential applications in different areas, such as gas sensors, biosensors, UV sensors, UV lasers, and LEDs. The ZnO nanostructure forms are favourable over the thin film form, especially in nano-size device applications. Furthermore, it demonstrates a higher specific surface when compared with the thin film form [3, 7, 8, 10].

The ZnO nanostructures were classified dimensionally [29], such as one dimension (1D), which are typically nanowires, nanorods, and ribbons; two dimensions (2D), such as nanoplates, nanosheets, nanowalls, nanodisks; and three dimensions (3D), such as nanoballs, nanocoils, nanocones, nanopillars, and nanoflowers [30]. In the view of this chapter, we will focus on the 2D structures, as the remainder are out of the scope of this chapter.

The exceptional physical, optical, chemical and electronic properties of the 2D structures attracted the attention of many research groups globally. It was noted that these properties are due to the strong quantum confinement of electrons in 2D structures and the ultrahigh specific surface area [31].

Recently, 2D ZnO structures, such as nanosheets and nanoplates, have attracted attention due to their promising potential applications in different areas, ranging from catalysis to electronics [9, 31]. They also provide good opportunities to explore new physical and chemical applications of nanostructures with different dimensionalities [32].

In this chapter, we provide a comprehensive review of UV sensors based on the 2D ZnO structures. We focus on the synthetic process, crystallographic, morphology, optical characterisations, and the UV sensor device applications of these structures.
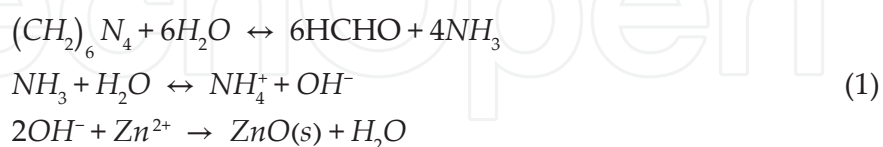
2. Synthesis methods of two-dimensional ZnO structures

Here, we summarised two of the most used methods in preparing 2D ZnO structures.

2.1. Solution-based chemical synthesis

In this process, the growth of ZnO is initiated with a thin film of ZnO seed layer coated on a substrate, typically a glass slide [33], silicon wafer [10], etc. This layer will control the

nucleation event. Several precursors were used to grow the ZnO nanostructure, such as zinc nitrate ($Zn(NO_3)_2$) with hexamethyltetramine ($C_6H_{12}N_4$–[HMT]) [34]. Alenezi et al. [35, 36] reported using zinc sulphate ($ZnSO_4$) with HMT to grow 2D ZnO nanostructures. In both cases, the precursors are dissolved in deionised water and the substrate with the seed layer is immersed in the solution. The vial containing the solution is kept inside an oven at temperature ranging from 50 to 95°C for several hours. Here, the Zn^{2+} species reacts with OH^- to form the $Zn(OH)_2$ intermediate complex, which decomposes to ZnO at high temperatures. This can be demonstrated in the following chemical reactions [37]:

$$(CH_2)_6N_4 + 6H_2O \leftrightarrow 6HCHO + 4NH_3$$
$$NH_3 + H_2O \leftrightarrow NH_4^+ + OH^- \quad\quad (1)$$
$$2OH^- + Zn^{2+} \rightarrow ZnO(s) + H_2O$$

In the case of using $ZnSO_4$, the nitride will change to sulphide [35].

The growth of 1D ZnO nanorods using $Zn(NO_3)_2$ with HMT was reported; however, it was demonstrated that adding of sodium citrate can produce plate-like ZnO crystals rather than rod-shaped particles [34]. The citrate is used, as it adsorbs strongly on mineral surfaces and significantly alters the mineral growth behaviour [38]. Using this method, Tian et al. [34] succeeded in growing 2D ZnO with plate (nanoplates) shapes. On the other hand, Alenezi et al. [35, 36] used $ZnSO_4$ to synthesise ZnO by employing a hydrothermal process. The ZnO structures were grown in 2D nanodisks. It was suggested that sulphate will behave as promoter agent that will hinder the nucleation on the (0001) direction and disrupt the growth processes in c-axis crystallographic directions. Interestingly, Ahmad et al. [9] succeed in growing 2D ZnO nanosheets using zinc nitrate with HMT; however, no clear explanations were introduced for the growth of the 2D ZnO nanosheets. However, this might be due to the silver seed layer that been coated over the silicon substrate prior to the growing process.

In conclusion, the ZnO nucleates and its growth takes place according to the inhabitant growth of ZnO crystals in the aqueous solution.

2.2. Electrodepositions

The electrochemical deposition method has been widely adapted for the growth of 2D ZnO structures. Several structures have been produced using this method, such as nanosheets [39], flake-like nanostructures [40], ZnO plate structures [27, 41], and ZnO nanowalls [42]. In this method, two or three electrodes are used; they are the working electrode, typically using conductive glass, such as indium tin oxide (ITO), and the second electrode is usually platinum (Pt), which serves as a counter electrode. The third electrode is the reference electrode, such as Ag/AgCl electrode. Zinc chloride ($ZnCl_2$) [27] or $Zn(NO_3)_2$ [42] is dissolved in deionised water, as the conductivity of the above solution is low; salts such as potassium chloride (KCl) [41] are to be added to increase the conductivity of the electrolyte. A potential is applied between the electrodes that depend on the cell configuration either for two-electrode or three-electrode cells. The cell is usually heated up to a temperature ranging between 70 and 85°C. The size of the 2D ZnO sheet-like structures was increased through adjusting the electrodeposition time [39]. The growth mechanism of the 2D ZnO nanostructures produced through the electrodeposition method might be summarised as follows. After the current is applied

to the cell, the free zinc ions (Zn^{2+}) in the solution move towards the cathode (substrate) and condense to Zn droplets on the substrate. These droplets agglomerate to the Zn spheres that form the core of the nanostructures. The Zn droplets react with the hydroxide to form ZnO on the substrate near the cathode. This can be summarised in the following reactions [40, 43]:

$$Zn^{2+} + 2OH^- \rightarrow Zn\,(OH)_2 \rightarrow ZnO + H_2O \qquad (2)$$
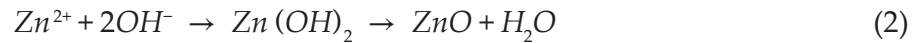
Furthermore, it was noticed that electronegative ions affect the shape of the prepared ZnO structures through the electrodeposition method. Ions, such as Cl^- or CH_3COO^- [41], are adsorbed (capping) preferentially on the positive polar face of the (0001) plane. This will limit the crystal growth along the c-axis and redirect the growth in the $(10\bar{1}0)$ plane, and as a result, a platelet-like ZnO is produced [41, 42, 44]. It is worth noting that the substrate type has a significant effect on the morphology of the prepared ZnO structures. According to Kim et al. [45], the 2D ZnO structures can be obtained using conductive glass substrates, such as indium-doped ZnO and indium tin oxide (ITO). This was supported by several published works [27, 39, 42].

2.3. Miscellaneous methods for preparing 2D ZnO

In addition to the above methods, several methods were used for the preparation of 2D ZnO. However, these methods are less popular. Here, we summarised some of them. The 2D ZnO nanostructures were synthesised through the sol-gel method. In this method, glycerol as an organic poly solvent is added to zinc acetate to synthesise ZnO polycrystalline nanostructures in the form of flakes (2D) [46]. A metal-organic chemical vapour (MOCVD) process was also used to prepare 2D ZnO nanowalls on GaN/Al_2O_3 substrates [47]. Physical vapour deposition (PVD) was used to synthesise ZnO nanosheets for dye solar cell applications [48] High-pressure pulsed laser deposition (PLD) method was also used for growing 2D ZnO nanowalls. In addition, it was found that the lattice parameter of the substrate used for the growth of 2D ZnO plays a crucial rule in the growing process. Using GaN as substrate, ZnO can be easily grown in 2D structures. Whereby using alumina (Al_2O_3) and silicon will result in the growing of nanorods [49]. Vapour-liquid-solid (VLS) mechanism using a gold catalyst was used to grow 2D ZnO nanowalls in this process, a high deposition temperature is used (~900–1100°C) [50–52].

The above processes are not used frequently in the synthesis of 2D ZnO as the solution-based chemical process (such as chemical bath deposition, hydrothermal and electrodeposition).

3. Two-dimensional (2D) ZnO characterisations

3.1. The crystal structural and the morphology of the 2D ZnO

At ambient pressure and temperature, ZnO crystals are typically formed in the wurtzite structure, as shown in **Figure 1**. **Figure 1** shows the hexagonal lattice that belongs to the space Group P63 mc and is characterised by two interconnecting sublattices of Zn and O, such that
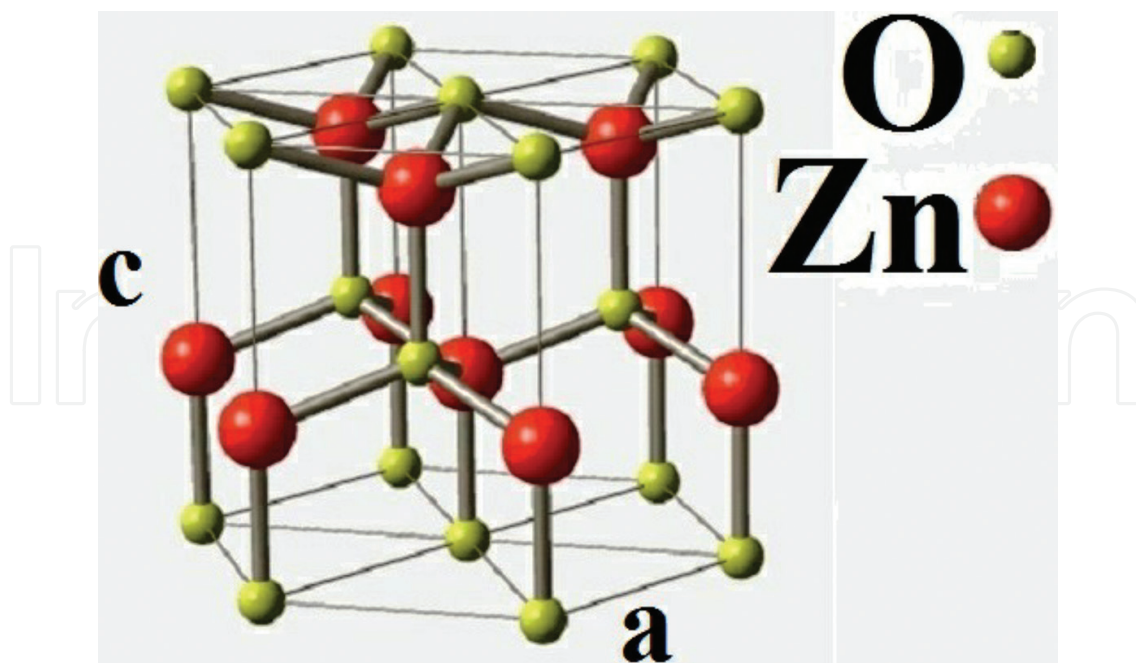
Figure 1. The hexagonal wurtzite structure of ZnO.

each Zn ion is surrounded by a tetrahedra of O ions and vice versa [53, 54]. The lattice parameters of the hexagonal unit cell are a = 3.2495 Å and c = 5.2069 Å, and the density is 5.605 gcm^{-3} [54].

The X-ray diffraction (XRD) pattern of the 2D ZnO films with different morphologies has been reported several times. The XRD patterns reveal the polycrystalline nature and can be indexed as hexagonal wurtzite structures of ZnO. Several published research studies showed the preferred orientation along the c-axis orientation of the (0001) plane [9, 27, 36, 39, 42, 55]. No significant difference in the XRD pattern was noticed for different morphologies of the prepared 2D ZnO. However, the morphology of 2D ZnO prepared through different methods reveals different shapes and diameters. It was found that controlling the experiment parameters results in significant changes in the morphology of the prepared 2D ZnO. Parameters such as substrate lattice mismatch between the substrate and the film will result in the modification of the ZnO structure [48]. The morphology of ZnO structures can be modified by adding salts, such as KCl and CH_3COONH, to the electrolyte in the electrodeposit method [41]. Furthermore, the variations in the electrochemical potential also gave rise to a variety of crystal morphologies [56]. **Figure 2** reveals different structures of 2D ZnO morphologies selected from published results and its corresponding X-ray diffraction patterns.

3.2. The optical properties of 2D ZnO

Photoluminescence (PL) analysis is the most widely applied technique to investigate optical properties of ZnO nanostructures [57, 58] because it can estimate the tightly bound excitons, the bandgap energy, and related defect transitions of ZnO. The photoluminescence measurements of ZnO structures have demonstrated highly efficient near-band-edge emission (NBE)
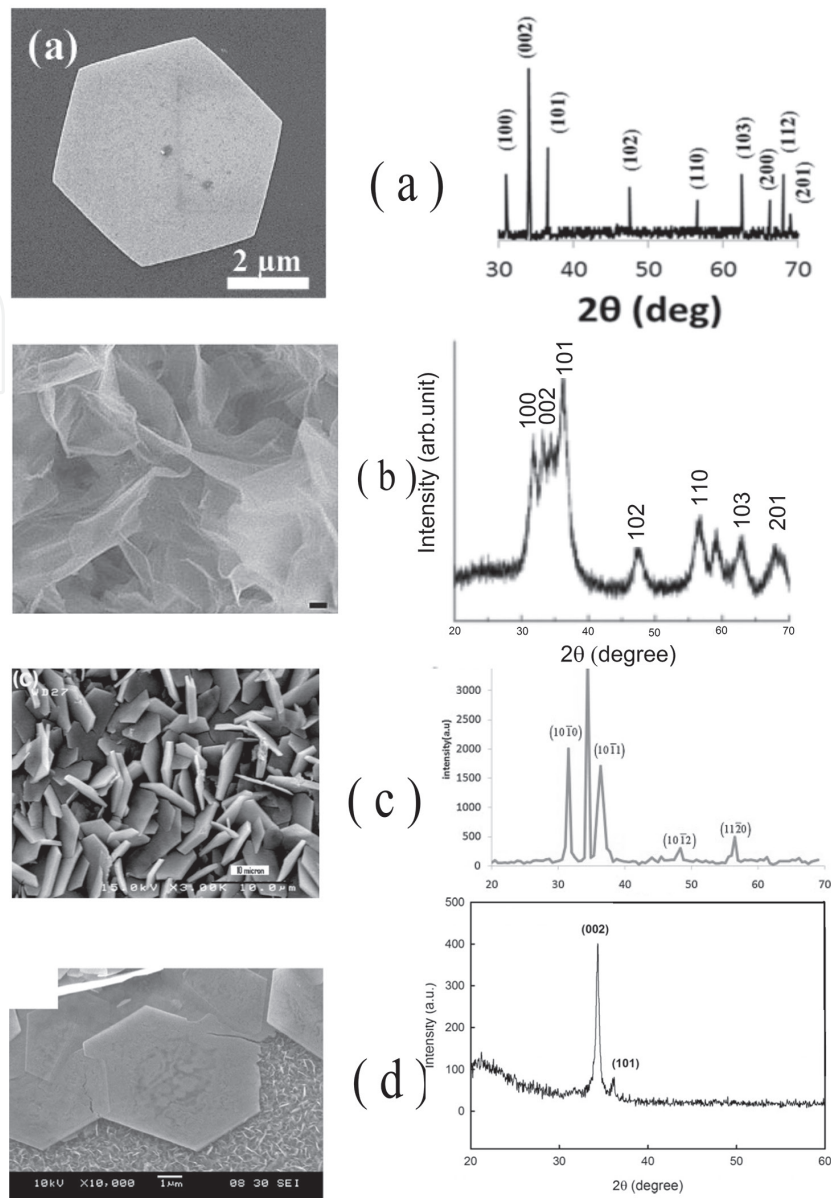
Figure 2. The electron scanning microscopy images of different 2D ZnO and their corresponding X-ray patterns. (a) Nanodisc ZnO prepared through hydrothermal (reprinted from [55] with permission from American Chemical Society (Copyright 2014)). (b) Nanowall ZnO prepared through high-pressure PLD (reprinted from [59] with permission from American Chemical Society Copyright 2009). (c) 2D ZnO nanosheets prepared through solvothermal process. (reprinted from [39] with Reprinted by permission from Macmillan Publishers Ltd: [Nature Communications] (39), copyright (2014), and (d) ZnO 2D plates prepared through electrodeposition using zinc chloride with potassium chloride (reprinted from [27]; with permission from Elsevier Copyright (2012)).

at the UV regions [58]. However, the hypothesis that strong UV emission means good crystal-line quality is not correct because ZnO nanostructures commonly exhibit a large number of defects with ionisation energies ranging from 0.03 to 3.14 eV [58]. It is a difficult task to cor-relate the PL emissions with optical transitions. Thus, the PL emissions from the ZnO defect energy levels are extremely complex and still not fully understood [27]. Nevertheless, 2D ZnO structures show the typical PL emission at room temperature that reveals the near-band-edge

UV emission at the range of 3.30–3.19 eV. This UV emission had been attributed to different origins; it may be attributed to either excitonic or defect-related emission [59]. It was also attributed to the near band-edge emission of ZnO (3.37 eV) [35].

The other familiar band of PL emission of the ZnO compound is located near the visible region (2.75–1.45) eV. This band was related to the surface defects; the source of these defects may be attributed to the oxygen vacancies or zinc interstitials [57, 60]. Furthermore, the strong dependence of the PL peak locations and intensities of ZnO nanostructures on the size and shape of the nanostructures was noted [35, 61]. Several 2D ZnO structures, such as 2D plate [27], nanodisk [35], and nanosheet [59] ZnO structures, show low intensity of the near edge UV emission, which was attributed to the surface states being nonradioactive centres due to their large surface-to-volume ratio [60] and higher intensity in the visible broadband. This was attributed to the wide surface area of the 2D structures that make the density of surface defects higher compared to the other ZnO structures, such as nanorods and nanowires [57, 60].

4. UV Sensors based on 2D ZnO structures

At room temperature, ZnO is a semiconductor compound with a wide energy band gap (Eg) of 3.37 eV [62]. This makes ZnO, a potential candidate, as a UV sensor, and it is favourable over several materials for this application, such as gallium nitride [63] and silicon carbide [64]. ZnO has a large exciton binding energy (60 meV) compared with gallium nitride (26 meV), which makes it more suitable for optoelectronic applications, especially at temperatures near and above room temperature [27]. In addition, ZnO had advantages over them, as it can be easily grown with high quality on low coast substrates. Several published papers show the application of ZnO for UV sensors. The metal-semiconductor-metal (MSM) and the Schottky photodiode configuration prove to be feasible for such applications [10, 27, 65, 66]. Different ZnO structures were studied for the UV applications, such as nanowires [67, 68], nanorods [69, 70] and nanobelts [71]; however, few results were published on 2D ZnO structures, and they focused on one type of device structure. The MSM type photoconductive UV based on 2D ZnO structures was explored by several groups [27, 39, 55]. Here, we review the application of 2D ZnO for UV sensors application.

The main parameters that show the performance of UV photosensors can be summarised as follows:

1. The photosensitivity; the ratio of the photocurrent (I_{ph}) to the dark current (I_d) [40]:

$$\text{Photosensitivity} = \frac{I_{ph}}{I_d} \tag{3}$$

2. The responsivity (A/W) [10, 55] can be defined as the ratio of net current ($I_{ph} - I_d$) to the incident UV light power (I_{inc}):

$$\text{Responsivity} = \frac{I_{ph} - I_d}{I_{inc}} \tag{4}$$

It is noteworthy that this parameter has spectral dependence.

3. One of the most important features of a photodetector is the speed of its response. The rise and fall of time, T_R and T_f, of a photodetector is defined as the time for the signal to rise or fall from 10 to 90% or 90 to 10% of the final value, respectively [72].

There have been few published reports on the synthesis of 2D ZnO nanostructures and their application for UV sensing. In these published reports, ions such as chloride or sulphate were used to control the growth of the 2D ZnO. In both cases, the ions are adsorbed on the (0001) plane of ZnO, and as a result, the growth of ZnO will be altered to 2D ZnO as mentioned previously [27, 55, 73]. Different experimental parameters were used to control the morphology of the produced 2D ZnO structures. The effect of the electrodeposition time period on the sheet size of 2D ZnO was explored by Ardakani et al. [74]. Initially, it was noticed that the dark current values increased with the sheet size of the prepared 2D ZnO. The current values increased from 0.5 to 2500 nA as the size of the sheet increased from 600 to 6000 nm. It was also found that the photosensitivity of the smaller sheet size is higher than the larger sheet size (decreased from 20000 to 188). However, it was noted the significant effect of the sheet size on the responsivity of the prepared 2D ZnO and the increase of the sheet size from 600 to 6000 nm will result in the enhancement of the UV photo responsivity from 0.522 to 18.04 A/W. This was attributed to the higher photocurrent in samples with larger sheets. Alenezi et al. [35] prepared 2D ZnO nanodisks through a hydrothermal process. Two types of UV sensors based on the prepared ZnO nanodisk were prepared, a single nanodisk and multiple-nanodisk UV sensors. It was noticed that the dark current of the sensors are 12 and 0.5 nA for the single and multiple nanodisk UV sensors, respectively. The lower dark current value of the multi-nanodisk was attributed to the presence of nanodisk-nanodisk junctions and surface-area extensions. The photosensitivity of the multiple-nanodisk sensor is approximately 1.5 times higher than that of the single nanodisk. However, the responsivity of the single nanodisk was 3300 A/W. The responsivity value obtained for the single nanodisk was among the highest values compared with the other published values for the ZnO nanostructures [75].

The timing characteristics of different ZnO structure photodetectors were published, and the results revealed different response times ranging from nanoseconds to minutes. While a correlation between different forms of ZnO and the response time is difficult to comprehend, it is important to realise that the response time is not only determined by the quality of the ZnO films [66] but also dependent on the electrode spacing of the photodetector [76], which can be expressed as [77]:

$$T_R = \frac{L^2}{\mu V_b} \tag{5}$$

where T_R is the rise time, L^2 is the distance between the contacts, μ is electron mobility, and V_b is the bias voltage.

The results from different structures of ZnO-based UV sensors are depicted in **Table 1**.

Synthesis method	Structure	Dark current	Photosensitivity @ λ	Responsivity @ λ	Response time	Recovery time	Reference
Electrodeposition	2D plate	0.7 mA	260@330 nm/3 V	0.74 A/W@330 nm/3 V	26 s	11 s	[27]
Hydrothermal	2D disk	12 nA	1058@365 nm/3 V	3300 A/W@365 nm/3 V	7 s	–	[55]
Hydrothermal	Network of 2D nanosheet and 1D nanorods	61 pA	1500@300 nm	–	133 s	199 s	[73]
Electrodeposition	2D nanosheet	0.5 nA	20,000@5 V	0.522 A/W@365 nm/5 V	4 s	26.5 s	[39]
High-pressure PLD	2D nanowalls	570 μA	0.66@365 nm/3 V	–	–	–	[59]
MOCVD	Thin films	–	–	~24 A/W@325 nm/3 V	~1 s	~45 s	[77]
Hydrothermal	1D nanorods	–	–	0.61 A/W@8 V	20 s	1050 s	[80]
Hydrothermal	1D nanorods	7.35 μA	3.11@370 nm/5 V	2 A/W@370 nm 5 V	72 s	110 s	[81]
Thermal evaporation	1D Nanowires	0.04 nA	1500@365 nm/5 V	–	120 ms	110 ms	[82]
Burner flame transport synthesis	Nano needle network	–	4500@365 nm/2.4 V	–	67 ms	30 ms	[83]
Vapour phase transport	1D ZnO nanowires	–	250,000	–	~1 ms	~1 ms	[84]

Table 1. Comparison of UV photo sensors performance with different ZnO structures.

5. UV detection mechanisms in 2D ZnO structures

The mechanism of UV photodetection was proposed earlier, which is based on the adsorption and desorption process of the oxygen molecules on the surface of the metal oxide semiconductors [27, 78]. According to this mechanism, it has been found that the photoresponse of ZnO consists of two components [66]: a fast response and a slow response. The fast response results from the reversible solid state process, such as intrinsic interband or excitonic transition, the slow one is governed by the surface-related oxygen adsorption and photodesorption process or by the bulk defect-related recombination process. It was found that the slow photoresponse component is the dominant process in the ZnO films [66]. Furthermore, this process was fitted with either a first- or second-order exponential function, which can be expressed as [58]:

$$Y = A_1 \exp\left(\frac{x}{\tau_1}\right) + A_2 \exp\left(\frac{x}{\tau_2}\right) + Y_o \tag{6}$$

where the constant, Y_o, represents the steady-state photocurrent in the photoresponse or the ultimate dark current in the photorelaxation process. The values of A_1 and A_2 are weighting factors that quantify the relative contribution of each mechanism (where $A_1 + A_2 = 1$) [79], where τ_1 and τ_2 represent the photoresponse and photorelaxation process. The shorter carrier lifetime, which means a faster process, is assigned to τ_1, whereas the slower time constant τ_2 is considered a slower process (slow decay), which suggests persistent photoconductivity [77].

Initially, oxygen molecules are adsorbed at the surface of ZnO to create charged ions by capturing free electrons from the ZnO [27, 55, 66, 78]:

$$O_2(\text{gas}) + e^- \rightarrow O_2^-(\text{adsorbed}) \tag{7}$$

This leads to the formation of a depletion region near the surface, resulting in a decrease of film conductivity. As the ZnO is illuminated with photon energy above the energy gap ($h\nu > E_g$), pairs of electron holes are photogenerated:

$$h\nu \rightarrow e^- + h^+ \tag{8}$$

The holes migrate to the surface of the film along the potential gradient (as a result of band bending) and recombine with trapped electrons previously captured by the oxygen molecules:

$$h^+ + O_2^- \rightarrow O_2(\text{gas}) \tag{9}$$

Hence, carrier concentration enhancement (due to photo generated electrons) is established on the surface of the ZnO structures, resulting in narrower depletion layers and an increase of the film conductivity.

Although the UV sensing mechanism of the 2D ZnO structures is basically the same as that of the other form of ZnO structures, due to their high specific surface area, the 2D ZnO photodetector shows higher sensitivity as can be noticed from **Table 1** [9, 55, 59]. In comparison with 1D ZnO structures, the growth of 2D ZnO nanostructures is much more difficult partially due to its hexagonal polar structure. It is known that the plane of (0001) has the highest surface energy; as a result, there is a fast growth along the c-axis direction with a preferred 1D ZnO growth [31, 84]. This might result in the lack of information on the UV sensors based on 2D ZnO structures.

6. Conclusion

In summary, we have reviewed the performance of UV sensors based on 2D ZnO structures. The performances are competitive with those of the 1D ZnO structures. The lack of the published results of the performance of 2D ZnO-based UV photodetectors might be due to the process of producing 2D ZnO, which are more complicated compared to the ones used for the 1D ZnO structures.

Acknowledgements

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