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# Photoconductivity characteristics of ZnO nanoparticles assembled in nanogap electrodes for portable photodetector applications

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ABSTRACT

In the present report, ZnO nanoparticles of size ~9 nm have been assembled by optimized dielectrophoresis process on the pre-fabricated nanogap (60 nm) electrodes. The fabricated ZnO nanoparticles based nano-device was studied for its *I–V* characteristic and typical non-linear semiconducting behavior was observed. When illuminated with ultraviolet (UV) radiation of wavelength 365 nm, a tremendous change in conductivity of almost one order of magnitude was observed indicating a high sensitivity of the fabricated nano-device. Temporal photoresponse characteristics were studied at a fixed level of UV illumination intensity (1.0 mW/cm$^2$) and the response time under 10 ms was recorded. The photoresponse curve exhibited a perfect rise and recovery without any slow component. Absence of slow component in the photoresponse characteristic suggested that shallow trapping centers were inactive and the photoconductivity could be due to the true quantum yield of photogenerated charge carriers through interband and deep trapping centers transitions.



## 1. Introduction

Detection of ultraviolet (UV) radiation is becoming an important area of research and has taken special consideration from material scientists and physicists. Many materials have been investigated for designing UV sensors based on thin films and nanostructures but could not hold interest either due to limit of responsivity or complexity in design of such sensors. Out of the various materials studied, Zinc oxide (ZnO) has drawn broad attention due to its remarkable features such as good UV photoconductivity, resistance to radiation hardness, and established growth techniques in thin film form or nanostructures [1–12]. Research in the photoconductivity of ZnO began almost 70 years ago when Mollow [11] studied the photoconductivity in ZnO single crystals in 1940s. Since then, many studies have been performed on the transient photoresponse of ZnO. With the development of growth technology, ZnO materials of different kinds have been grown and their photoconductivity characteristics have been studied. Researchers have given considerable arguments to explain the observed photoresponse behavior in ZnO materials either due to surface or deep defects. It is well documented in the literature that ZnO exhibits a fast photoresponse when deep defects dominate the shallow defects which give rise to slowness in photoconductivity [5–10]. Each of these states or defects has their own contribution on the observed photoresponse behavior; however materials with large surface-to-volume ratio are fundamentally more suitable for optical sensor applications due to enhance photoresponsivity [4,7]. This indicates that nanomaterials can be potentially more viable for realizing optical sensors with improved responsivity. The exploration of photoconductivity in ZnO nanostructures gained momentum after Kind et al. [4] reported UV photoresponse of single ZnO nanowire on electrodes with a gap of ~10 μm. Since then the photoconductivity in ZnO nanostructures such as nanowires, nanorods, and nano-needles have been considerably investigated [1–4,12–14] for the fundamental studies and UV sensor applications as well. Bera and Basak [15] studied the photoconductivity in ZnO nanowires (diameter 29–36 nm) grown by aqueous solution technique. The electrodes used in this study were comprised of two gold (Au) circular dots (1 mm diameter) that were 3 mm apart and the response behavior was explained by surface and deep defects. Soci et al. [2] reported ZnO nanowire based photodetector (spacing between the electrodes was 2 μm) exhibiting high internal gain and attributed the observed behavior to the oxygen related hole trapping or surface states. In our previous work, we observed an improvement in the photoresponse of a structure consisting of ZnO nano-needles grown on the surface of ZnO thin film [1]. These studies and many similar other work reveal that increase in surface-to-volume ratio leads to improvement in the photoresponse behavior. It may be noted that nanowires and nanorods are normally 20–50 nm in diameter and their length varies from 1–2 μm. It would of interest to

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investigate photoconductivity in a system where the nanostructures are grown within 10 nm of size and assembled into nanometer gap electrodes.

In the present report, ZnO nanoparticles (~9 nm) have been assembled into nanogap electrodes (60 nm) using ac dielectrophoresis process. The fabricated ZnO nanoparticles based electrical device has been characterized under a fixed UV illumination intensity to study the transient photoresponse.

## 2. Experimental details

To fabricate nano-device for photoconductivity measurement, Au nanogap electrodes were fabricated on oxide-coated silicon substrate using standard electron-beam lithography and lift-off technique [16–17]. One chip consisted of 10 pairs of electrodes with a gap size of 60 nm each. ZnO nanoparticles were grown by a simple chemical route of sol–gel process [18]. The average diameter of the ZnO nanoparticles estimated by X-ray diffraction analysis was found to be ~9 nm. The grown ZnO nanoparticles were dispersed in di-ionised (DI) water in volume ratio of 1:50 and sonicated to prepare a solution of ZnO nano-colloid. The experimental setup used for assembling ZnO nanoparticles into nanogap electrodes consists of a function generator and an oscilloscope. Prior to nanoparticles assembly, the chips were passed through a cleaning process such as $O_2$ plasma cleaning and rinsing in ethanol [16]. Scanning electron microscopy (SEM) (Jeol, Model: JSM-7401F) was used to examine the alignment of nanoparticles into nanogap electrodes. Current–voltage ($I$–$V$) characteristics of the fabricated ZnO nanoparticles based nano-device were investigated by using $I$–$V$ measurement system (Keithley; Model: 4200-FCS). A Black-ray UV lamp ($\lambda$=365 nm) was used as a source of UV radiation for photoconductivity measurement.

## 3. Results and discussion

### 3.1. Dielectrophoretic assembly of ZnO nanoparticles

To assemble ZnO nanoparticles (~9 nm) into nanogap electrodes (60 nm), dielectrophoresis (DEP) process was used. DEP is one of the most effective bottom-up approaches for manipulation and alignment of micro- to nano-sized particles in electrodes gap where the motion of polarizable suspended material is controlled by the externally applied non-uniform electric field [16,17]. A successful assembling of ZnO nanoparticles in nanogap electrodes requires optimization of experimental DEP parameters. DEP strongly depends on three parameters i.e. applied frequency, applied peak-to-peak voltage, and time during which DEP is done. The experimental sequence is as follows: a drop of prepared ZnO nano-colloid was placed in the center of chip using a micropipette and immediately ac voltage was applied across the electrodes to initiate the DEP process. Fig. 1(a) shows the schematic diagram to perform the DEP of ZnO nanoparticles. An ac signal of suitable frequency and peak-to-peak voltage is applied across a pair of nanogap electrodes for a fixed duration of time. The DEP process is stopped after a certain internal of time when the nanoparticles align themselves in the nanogap electrodes (Fig. 1(b)). Finally the assembling of ZnO nanoparticles in nanogap electrodes is examined under an SEM. Based on our prior study a minimum number of nanoparticles was assembled into nanogap electrodes under the applied DEP parameters such as frequency, peak-to-peak voltage, and time of 150 kHz, 3 V, and 30 s, respectively. A detail discussion based on the dielectrophoretic assembly of ZnO nanoparticles can be found elsewhere [16]. Fig. 1(c) shows an SEM image of a nano-device consisting of dielectrophoretically assembled ZnO nanoparticles into nanogap electrodes, and this device has been used for photoconductivity measurements.

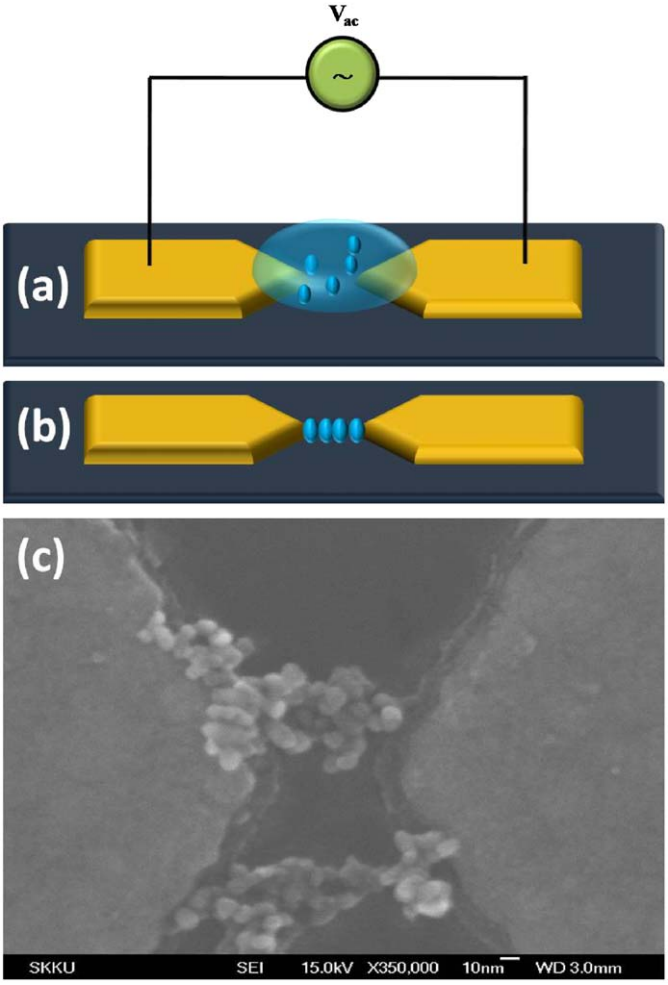


**Fig. 1.** Schematic diagram of the setup used for the DEP of ZnO nanoparticles into nanogap electrodes: (a) Experimental setup consists of a chip containing nanogap electrodes connected to a function generator. A period voltage signal is applied across the electrodes using a function generator to start the DEP process; (b) Assembled ZnO nanoparticles in nanogap electrodes after the DEP process is done; (c) An SEM image of the assembled ZnO nanoparticles into nanogap electrodes when the DEP was carried out at a fixed frequency of 150 kHz, applied peak-to-peak voltage of 3 V, and time of 30 s.

### 3.2. I–V characteristics and transient photoresponse

Fig. 2(a) shows the $I$–$V$ characteristics of the fabricated nano-device consisting of ZnO nanoparticles assembled in nanogap electrodes. The $I$–$V$ curves were taken in air at room temperature under a fixed level of UV illumination intensity ($\lambda$=365 nm; Intensity=1.0 mW/cm$^2$). Inset of Fig. 2(a) shows the schematic diagram of the photoconductivity measurement in assembled ZnO nanoparticles into nanogap electrodes. The $I$–$V$ curve measured in the absence of UV radiation is also shown for comparison. It may be noted that both the curves exhibited non-ohmic characteristics showing the semiconducting behavior of ZnO nanoparticles. Under an UV illumination the nano-device exhibited a tremendous change in conductivity and on UV removal the $I$–$V$ retraces the curve as observed under dark within a few seconds of measurement. This shows the fabricated nano-sensor is very quickly responding to UV illumination. Most

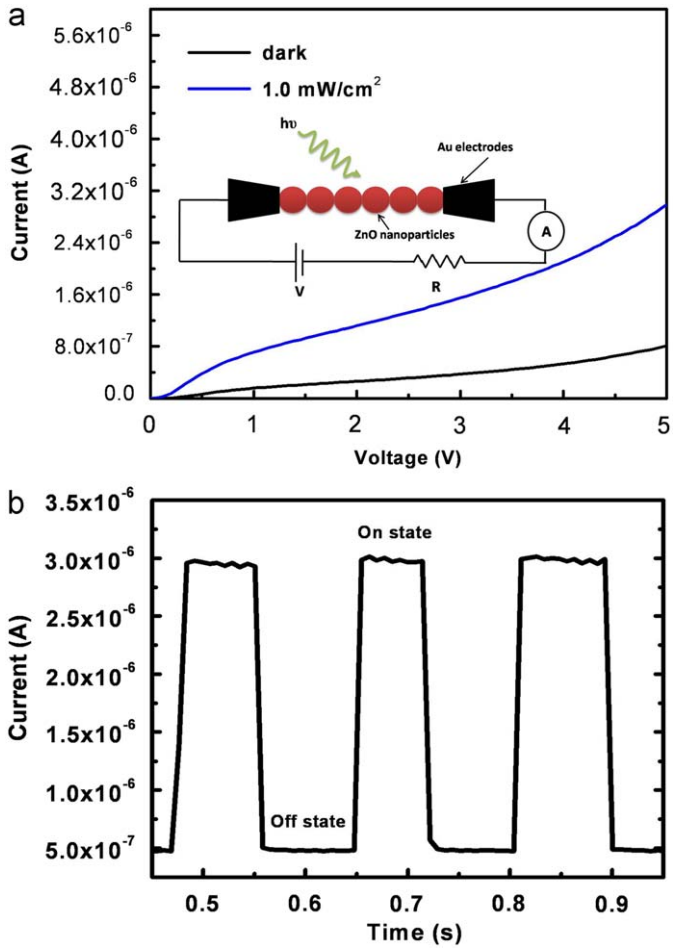


**Fig. 2.** (a). *I–V* characteristics of the fabricated ZnO nanoparticles based device measured with and without UV illumination intensity of 1.0 mW/cm$^2$. Inset shows the schematic diagram of the photoconductivity measurement in assembled ZnO nanoparticles into nanogap electrodes; (b) UV photoresponse transient observed at a bias of 5 V. The repetitive photoresponse curves exhibit similar trend of quick rise and recovery under UV illumination and removal, respectively.

importantly, the recovery to the dark value also took minimum time. To investigate the response time, it was necessary to study the temporal response of the fabricated ZnO nano-device. Fig. 2(b) shows the transient photoresponse of ZnO nanoparticles based nano-device. The transient photoresponse was measured under a bias of 5 V. Under UV illumination intensity a sudden rise in conductivity was observed from off-state to on-state and the conductivity was found to saturate. The photoconductivity remained saturated until UV illumination was removed. On UV removal, the conductivity dropped to off-state in almost similar duration of time which was taken during the rise of conductivity from off-state to on-state. It was found that rise time and recovery time of the photoresponse curve were almost 7 and 8 ms, respectively. Such short response time is essential for the design and development of ultrafast optical sensors. The experiments were performed by chopping the UV illumination at different intervals to see whether there exists any persistent in photoconductivity. It was observed that the device exhibited similar photoresponse curves (with similar rise and decay time) under period illumination when tested continuously for several minutes of repetitive cycles of UV on and off. This indicates the tremendous potential of fabricated nano-device for highly sensitive UV sensors. The response time (7–8 ms) observed in the present work is much smaller than the values reported for ZnO nanowires (23–33 s) [2,15].

Normally photoconductivity in ZnO depends on two factors. One is surface related photoconductivity which is due to the presence of shallow traps and the other is bulk related photoconductivity which is due to the presence of deep traps. Shallow traps are considered to give rise to slowness in photoresponse behavior and the deep traps contribute to the fast component in the photoresponse curve. ZnO is naturally n-type and many theories and models have been proposed describing Zn interstitial, oxygen vacancies, or interstitial defects as the cause of n-type behavior [6,15]. However its exact origin is still not very well understood and debated. The photoconductivity in ZnO is largely influenced by these arbitrary defect centers in the lattice and interstitial sites.

The surface related photoconductivity is primarily governed by the adsorption and desorption of the chemisorbed oxygen at the surface of ZnO. The oxygen molecules of the air are chemisorbed at the surface of ZnO by trapping free electrons from ZnO and thus form a depletion layer i.e. $O_2(g)+e^- \rightarrow O_2^-$ (adsorbed species). Due to the large surface-to-volume ratio, the adsorption of $O_2$ significantly decreases the conductivity of ZnO. Upon UV illumination, the photogenerated holes are produced and release the captured adsorbed species i.e. $O_2^-$ ion by leaving behind an electron i.e. $O_2^- + h^+ \rightarrow O_2(g)+e^-$. In the bulk related process, some $O_2$ neutrals are embedded in the grain boundaries and form oxygen ions by taking up electrons. Upon UV illumination, these species liberate electrons by capturing the photogenerated holes, and the photogenerated electrons drift in the electric field and contribute to the photoconductivity. This bulk related process is considered to be fast in comparison to the surface related process [1–6]. Nanostructures of ZnO such as nano-needles were reported to exhibit interesting dual behavior of slow and fast photoconductivity and the observed behavior was explained based on shallow traps exhibiting multiple trapping centers and deep defects with few trapping centers [1]. Ghosh et al. [9] attributed the slow photoresponse in ZnO nanowires based on the shallow or surface traps. From this discussion it is apparent that if surface states are maintained to minimum then slow behavior in photoresponse characteristic could be reduced conditionally there are deep traps or recombination centers to cause fast photoresponse effect. Realization of such materials with controlled deep and shallow traps seems not only difficult to achieve but practically challenging to grow.

In the present work, we have attempted to reduce the effects due to the surface states on the photoresponse characteristic of ZnO nanoparticles. We have designed a photodetector such that the sensing material is ZnO nanoparticles of average size ~9 nm and these nanoparticles are carefully manipulated and assembled into nanogap (60 nm) electrodes. Application of a voltage ~5 V across the nanogap (60 nm) electrodes results a strong electric field ($8.3 \times 10^7$ V/m). Under such strong electric field, any charge if trapped can be quickly accelerated. Moreover, the active material area of ZnO nanoparticles is only limited to 60 nm in length and ~30 nm in width (Fig. 1(c)). In such small region, it is highly unlikely that oxygen neutral chemisorbed on the surface of ZnO nanoparticles may have any significant influence on the photoresponse characteristics in comparison to previous reports where a large surface-to-volume ratio allows more oxygen to remain adsorbed on the surface of ZnO which brings slowness in photoresponse behavior [1,9,14]. This indicates that confining nanoparticles into nanogaps where a strong electric field exits the photogenerated charges will quickly drift in the strong field than relaxing at the surface states if present. It is important to mention that when the density of surface states is high the life time of the photogenerated charge carriers is prolonged. This may be due to the fact that the establishment of equilibrium between the charge carriers available in the conduction band and the shallow

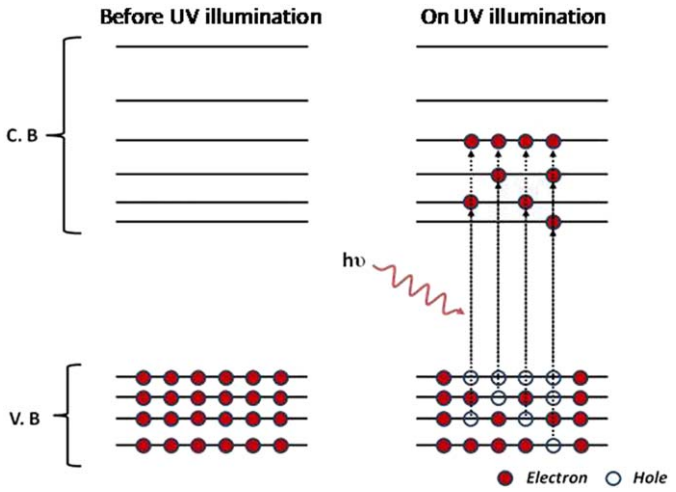


**Fig. 3.** Mechanism of UV photoconductivity in assembled ZnO nanoparticles into nanogap electrodes. Band transition profile of ZnO nanoparticles shows the creation of photogenerated charge carriers under UV illumination. The electrons from the balance band excite to the corresponding high energy states in the conduction band under UV excitation with the assumption that surface states are not active. Under the influence of strong electric field the photogenerated carriers are swept by the field than being captured by the surface states, if present and contribute to the photocurrent.

trapping levels requires a time that could be more than the recombination life time. Absence of any slow component in the photoresponse curve obtained in the present work indicates that surface states are not active that might be attributed to the small area available to the neutral oxygen to remain absorbed on the surface of ZnO nanoparticles assembled in nanogap electrodes.

Fig. 3 shows the band transitions in ZnO nanoparticles in the presence of a strong electric field and under UV illumination. ZnO nanoparticles being smaller in size ($\sim$9 nm) can be considered to exhibit discrete energy levels. Under UV illumination electrons occupying states in the valence band excite to high energy states into the conduction band and occupy the energy states by absorbing energy corresponding to illuminating UV radiation. The electrons present on the Fermi level drift under the applied electric field and contribute to the photocurrent. On UV removal, the excited electrons relax back to the ground state in the valence band and the photocurrent drops to the dark current value. The absence of slow component in the photoresponse curve shows that photoconductivity is mostly governed by the true quantum yield of the photogenerated charge carriers through interband and deep trapping centers transitions. The preliminary results presented in this paper show the potential of realizing ultrafast nano optical sensors based on ZnO nanoparticles assembled in nanogap electrodes. A detailed study on the photoconductivity of ZnO nanoparticles based nano-device under various wavelengths of illumination and a further insight into the deep traps are under investigation and would be published elsewhere.

In conclusion, we have studied the electrical and photoconducting characteristics of a nano-device consisting of ZnO nanoparticles assembled in nanogap electrodes. The fabricated nano-device exhibited enhanced photoresponse characteristics with a fast rise and recovery time of 7 and 8 ms, respectively. Such device has potential to be useful in designing ultrafast optical sensors for portable photodetector applications.

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