One-dimensional (1D) nanomaterials are often nanowires (NW) with ten or larger height–diameter ratios, and nanoparticles (NPs) with a height–diameter ratio of around one are zero-dimensional (0D) nanomaterials. 1D and 0D nanomaterials have been the focus of research and applications due to their outstanding and novel characteristics. Nanowires are important building blocks for nanodevices. Nanoparticles have been applied in optical and biomedical areas. However, up to the present, all research on the nanomaterial’s size effects have been limited within their specific dimensions and no attention has been given to nanomaterials with a height–diameter ratio in-between 0D and 1D. Here, we name this kind of nanostructured material with an intermediate ratio a ‘half-dimensional (0.5D) nanomaterial’ and explore the properties of such materials by studying the photoelectric properties of individual zinc oxide (ZnO) nanomaterials with different dimensions through changing their lengths while keeping the same radius. As the nanowire reduces in height, changing size from 1D to 0D, the photoelectric response decreases, even though it is supposed to increase according to Ohm’s Law. A model is set up to explain this phenomenon, making it possible to control the photoelectric sensitivity of ZnO nanomaterials. Therefore, a landmark has been set for studying the properties of 0.5D nanomaterials.

The ZnO nanomaterials used in these experiments were grown by a vapor–liquid–solid (VLS) process on conductive silicon substrates, using Au particles as a catalyst. To characterize the properties of different dimensions, we deliberately controlled the ZnO nanostructures, growing them to different lengths but with a constant diameter of 50 nm (Figure 1a for 1D nanomaterials, Figure 1b for 0.5D nanomaterials, Figure 1c for 0D nanomaterials). There are several key strategies in the measurement, which benefit from achieving higher measurement accuracy. First, the Au particles, staying at the tips of the sample ZnO nanomaterials (Figure 1d), serve as good conduction contacts in the measurement. Additionally, ZnO nanomaterials synthesized by the VLS method possess perfect crystal structures, leading to an ultra-low current noise in the measurement (Figure 1e). The ZnO nanomaterials all grow along the [0001] direction and have side surfaces of [0110], as Figure 1f shows, providing a consistent experimental platform. Lastly, in order to reduce the complexity of the measurements, the ZnO nanomaterials have been grown with relatively low density, so that the atomic force microscope (AFM) tip can exclusively reach one individual ZnO nanomaterial without touching another.

The measurements were performed by a Current AFM (I-AFM, Park X-70) with a gold-coated silicon tip. The cantilever had a calibrated normal spring constant of 1.51 N/m (Figure 2a). ZnO nanomaterials were identified by scanning the AFM tip in non-contact mode. The conductive tip contacted the top of ZnO nanomaterial with a normal force of 20 nN and the current–voltage (IV) curves of ZnO nanomaterials under illumination (0.1 w/cm², microwave light source) and in the dark were successfully obtained. This is a direct method for measuring the conductivity of nanomaterials, which avoids the complex nano-electrode fabrication process. We conducted the same measurements on ZnO nanomaterials with different heights but the same diameter of 50 nm and the IV curves are shown in Figure 2b, c and d for 1D, 0.5D and 0D ZnO nanomaterials, respectively. The blue curves are the IV curves under illumination and the red curves are from the dark environment. Through decreasing the height of the ZnO nanomaterials, the additional dimension (height) will change from the macroscale to the nanoscale, where nano-confinement will happen.

The currents of 1D ZnO nanomaterials under illumination and in the dark are obviously different (Figure 2b). As shown in Figure 2c, the current difference of 0.5D ZnO nanomaterials in both environment is smaller when comparing to 1D ZnO nanomaterials. For 0D ZnO nanomaterials, the current curves in illuminated and dark environments overlap and cannot be identified separately (Figure 2d). This shows that, as nanomaterials change in dimension, the photoelectric effect varies significantly.

To study this phenomenon quantitatively, we performed multi-cycle tests by measuring currents of ZnO nanomaterials.
Figure 1. ZnO nanomaterials from 0D to 1D. (a) Aligned 1D ZnO nanowire arrays with 50 nm diameter and approximately 1 µm height. (b) Aligned 0.5D ZnO nanorod arrays with 50 nm diameter and approximately 150 nm height. (c) 0D ZnO nanomaterial arrays with 50 nm diameter and 40 nm height. (d) The TEM image of typical ZnO nanomaterials. (e) The high resolution TEM image of the ZnO nanomaterials, showing the perfect crystal structure without defects. (f) Diffraction pattern of the ZnO nanomaterials indicating the growth direction is along the [0001] direction.

Figure 2. Experimental design and measurement. (a) Experimental setup and procedures for measuring IV curves by touching the top of ZnO nanomaterials with a conductive AFM tip. The sample location is from scanning AFM in non-contact mode. IV curve acquirements are from conductive AFM tip touching the ZnO nanomaterial arrays in contact mode with light illumination or in dark. (b–d) IV curves measured on the nanomaterials of Figure 1 a, b, and c, respectively. Blue line represents IV curve under illumination, red line represents IV curve in the dark. The insets are the corresponding topographies of ZnO nanomaterials obtained by AFM working in non-contact mode. Scale bars are 25 nm. (e) Under a fixed voltage of 10 V, the measured current difference as the function of the height of ZnO nanomaterials with a fixed radius of 25 nm. Blue solid line is from Ohm’s law, red dash line is the fitted curve of the measured data. As the length of ZnO nanomaterial becomes less than a certain value, current difference δI deviates Ohm’s law.
with different heights repeatedly to reduce random errors. Monitoring the currents under a working voltage of 10 V, we found that the photoresponse $\Delta I$ (the difference between illumination current and dark current) becomes undetectable as the height decreases, as shown in Figure 2c. The orange points are data from experiments and the red dashed line is the fitted curve. The quantum effect can be neglected for this size.\[9\] According to Ohm’s Law, the $\Delta I$ should be:

$$\Delta I = \frac{Us}{\lambda} (\sigma_{\text{light}} - \sigma_{\text{dark}}) \tag{1}$$

where $U$ is the voltage; $s$ is the cross section of resistor; $I$ is the length; $\sigma_{\text{light}}$ is the conductivity under illumination, and; $\sigma_{\text{dark}}$ is the conductivity in the dark. As the blue solid line shows, theoretical Ohm’s Law deviates from the red line (fitted curve of experimental data) as the length of the nanomaterial drops below a certain value. These experimental results strongly indicate that photoelectric properties vary apparently with the nanomaterial’s dimension.

To set forth this phenomenon theoretically, we built an analytical model to describe the electron movement in the ZnO nanomaterials. For ZnO nanomaterials in the dark, oxygen is absorbed on the surface of ZnO in the form of negatively charged ions by capturing free electrons from the semiconductor and environment, resulting in a electron depletion layer with low electrical conductivity on the surface [O$^2- + e^- \rightarrow O^2-$] (as per Figure 3, the dark color along the edge). Electron density inside, when a ZnO nanomaterial is not connected in circuit, is stable and balanced for 1D, 0.5D (Figure 3a), and 0D ZnO nanomaterials (Figure 3b). When an external electrical field is applied, the electron density will change because electron transition between the valance and the conduction bands of ZnO is a dynamic equilibrium process.\[10\] When the ZnO nanomaterial is connected in circuit and an electrical potential is applied along the longitudinal direction, once electrons in the valance band are excited into the conduction band, they will move along the electrical field direction. Because the mean free path of electrons is the average distance that electrons travel before collision, the excited electrons do not have an opportunity to collide and fall into the valance band to recombine with holes along the mean free path, resulting in a rich electron layer (see the Supporting Information for more details). In other words, all electrons that can be excited have been excited into conduction band, and the valance band has no more electrons for further light excitation within the mean free path length. For 1D and 0.5D ZnO nanomaterials, the layer with highly excited electrons locates on the two ends (Figure 3c). For 0D ZnO nanoparticles, the electron depletion layer covers the whole ZnO material completely (Figure 3d; see the SI for details). Therefore, the current difference between ZnO nanomaterials under illuminated and dark conditions becomes smaller in terms of electron density as the height decreases from 1D to 0D nanomaterials.

Based on the model above, the average electron density of ZnO nanomaterials in the dark can be derived as (see the SI for details):

$$n_{\text{dark}} = \left[1 - \frac{r_p}{R_{\text{rod}}}\right] \left(n_{\text{thermal}} + \frac{2\lambda_{\text{mfp}} n_{\text{pe}}}{h_{\text{rod}}} \right) \tag{2}$$

where $n_{\text{thermal}}$ is the thermal electron density in the conduction band; $n_{\text{pe}}$ is the light excited electron density in the conduction band; $h_{\text{rod}}$ is the height of the ZnO nanomaterial; $R_{\text{rod}}$ is the radius of the ZnO nanomaterial; $r_p$ is the Bohr radius of ZnO; $\lambda_{\text{mfp}}$ is the mean free path of electrons in ZnO.

Figure 3 is a contour plot of electron density of a ZnO nanomaterial in the dark as a function of its radius and height, according to Equation (2). When the height or radius is small enough, the dark electron density will arrive at a constant value, i.e., thermal electron supersaturation. The curve in Figure 4b shows how the electron density changes with the height of nanomaterials with a fixed radius of 25 nm. The solid blue curve in Figure 4c is the calculation according to Equation (2), which fits the measured data well (see the SI). The light purple area represents ZnO nanomaterials with a height–diameter ratio from 1 to 20 (0.5D) and the light green area is ZnO nanomaterial with a height–diameter ratio above 20 (1D). The current response reaches a maximum when the
ZnO nanomaterial within the 0.5D region, which indicates that the photoelectric property experiences a significant change in 0.5D nanomaterials.

In summary, we have pioneered the study of half-dimensional (0.5D) nanomaterials, which is an intermediate nanoscale material between 1D and 0D materials. The photoelectric properties of zinc oxide (ZnO) nanowires, with a height–diameter ratio from one to ten, have been thoroughly investigated by characterizing the current difference in illumination and dark environments. As anticipated, the photoelectric property of 0.5D nanomaterials experiences significant changes as the 3D nanoconfinement is reinforced. The change does not follow the traditional Ohm’s law because of additional nanoconfinement from the third dimension, which did not previously exist on the range of the nanoscale. An analytical model based on carrier density has been built and interprets this photoelectric property change in 0.5D nanomaterials well. This makes it possible to tune the photoelectric characteristics of these nanomaterials by controlling the additional confinement, which will pave a new and effective way for optimal nanodevice design, fabrication, and performance. For instance, individual nanomaterials with controllable photoelectric properties can be grown as photoelectric sensor pixels, achieving nanoscale resolution.

In all, as a research area, 0.5D nanomaterials has now been opened, bridging the research gap between 1D and 0D nanomaterials. The study of 0.5D nanomaterials will consequently be expanded to more properties, more materials, and will profoundly impact the fields of nanoscience, nanodevices, and nanoelectronics. This will lead to not only new discoveries and understandings of property changes in 0.5D systems but also to novel applications of all nanomaterials including, but not limited to, semiconducting nanomaterials, carbon nanotubes,[12] graphene,[13] and more.

### Experimental Section

A silicon substrate with 10 nm thick Au as catalyst was placed into a tube furnace, where 100 cc/min argon (Airgas) and 30 cc/min oxygen (Airgas) were introduced to grow ZnO nanomaterials at 950 °C for 45 min. Notably, the ZnO nanomaterial can be grown with a broad variation in oxygen flow, from 10 cc/min to 50 cc/min. The oxygen partial pressure significantly affects the growth speed and nanomaterial length and diameter.

### Supporting Information

Supporting Information is available from the Wiley Online Library or from the author. It includes the details of VLS grown 1D, 0.5D nanomaterials and corresponding SEM images, and the details of the theoretical analytical model for the electron distribution in 0.5D nanomaterials.

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