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**Novel p-type wide bandgap manganese oxide quantum dots operating at deep UV range
for optoelectronic devices**

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Abstract

Wide bandgap semiconductor (WBGs)-based deep UV (DUV) devices lag behind those operating in the visible and IR range, as no stable p-type WBGs that operates in the DUV region (< 300 nm) presently exist. Here, solution-processed p-type manganese oxide WBGs quantum dots (MnO QDs) are explored. Highly crystalline MnO QDs were synthesized via femtosecond-laser ablation in liquid. The p-type nature of these QDs is demonstrated by Kelvin probe and field effect transistor measurements, along with density functional theory calculations. As a proof of concept, we developed high-performance, self-powered, and solar-blind Schottky DUV photodetector based on such QDs that is capable of detecting under ambient conditions. The carrier collection efficiency is enhanced by asymmetric electrode structure, leading to high responsivity. This novel p-type MnO QD material can lead to cost-effective industrial production of high-performance solution-processed DUV optoelectronics for large-scale applications.

All modern technologies based on electronics, optoelectronics, sensors, bio-devices, and photovoltaic cells require semiconductor devices, including diodes, transistors, and laser diodes that consist of p–n junctions. Optoelectronic applications based on wide bandgap semiconductors (WBGs) operating in the deep ultraviolet (DUV) spectral range below 300 nm (UV-C), are of particular interest for researchers and industry practitioners due to their significance in a wide range of industrial applications, such as homeland security, medical diagnostics, food curing, sanitation, chemical and biological threat detection, space-to-space communications, missile detection, military surveillance, target detection and acquisition, transparent thin-film transistors, solar cells, white lighting, sterilization, medical treatment, and touch display panels.^[1-7] For example, the most commercial DUV photodetectors are produced using UV-enhanced narrow bandgap semiconductors, mainly Si-based photodetector.^[8,9] However, the narrow bandgap materials are ineffective in rejecting signals in the UV–visible–IR spectral region, making them unsuitable for DUV applications. Thus, high-quality DUV WBGs are still needed to produce high-performance DUV optoelectronic devices.

In each of the aforementioned fields, researchers and industry practitioners are looking to overcome different challenges. There is a growing demand for both p-type and n-type WBGs that possess good stability and conductivity. The main obstacle to the attainment of this goal stems from the lack of p-type wide bandgap materials operating in the DUV range below 300 nm (i.e., > 4.1 eV) that exhibit good p-type stability. Currently, the p-type materials having bandgap in the UV-A range (such as p-type GaN, Cu₂O and SnO) are utilized in DUV optoelectronics, which severely downgrades device performance, as their bandgaps are limited to the UV-A to visible spectral region (320–400 nm).^[10,11] Moreover, though n-type WBGs (e.g., ZnO, Ga₂O₃, and AlGaN) with good conductivity and stability can operate in the UV and DUV range (280–390 nm), it is not possible to convert them to a p-type material with good stability and conductivity due to their intrinsic electronic properties.^[2,6,11-16] Consequently, no

highly stable conductive p-type DUV WBGS operating in both UV-B and UV-C region presently exists.^[17]

Further advances in the field of DUV optoelectronics are hindered by other issues, such as the difficulty in developing new cost-effective material production and fabrication methods that could replace the expensive and high vacuum-based technologies presently in use. As DUV-WBGS based devices tend to be prohibitively expensive, they are difficult to produce on a large scale.^[18,19] Moreover, the defects in the interface between layers, such as lattice mismatch and dislocation defects significantly hinder the performance of DUV devices.^[1,5,7,10-15] To overcome these issues, many research groups are working towards hybrid heterojunction DUV photodetectors.^[20-22] At the same time, solution-processed materials, as well as two-dimensional materials, are becoming more relevant for DUV photodetector applications.^[22-29] Therefore, for a material to be suitable for all DUV-based technology applications, it must be easy to fabricate using cost-effective methods, and the device structure has to be free from the aforementioned issues.^[30]

In this work, we have addressed these problems very effectively, and have used several experimental and theoretical approaches to confirm the validity of our findings. In addition to exploring a highly stable p-type WBGS operating in the DUV region, we also demonstrated that high-performance solution-processed MnO QDs are the best choice to overcome the aforementioned issues. Highly crystalline p-type wide bandgap manganese oxide-based quantum dots (p-MnO QDs) are explored. These MnO QDs were synthesized by cost-effective solution-processed femtosecond laser ablation technique in liquid (FLAL). Finally, high-performance solar-blind self-powered DUV ($\lambda < 300$ nm) Schottky junction photodetectors based on MnO QDs solely were fabricated as a proof of concept.

The high resolution-transmission electron microscopy (HR-TEM) images presented in **Figure 1** demonstrate the crystallographic and dimensional properties of MnO QDs synthesized via the FLAL technique. Figure 1a shows the MnO QD structure, whereby the mean diameter

was calculated at 4.8 ± 0.2 nm, as indicated by the distribution graph presented in Figure 1b. The inter-planar spacing along the (200) and (111) planes was found to be 2.22 Å and 2.57 Å, respectively, which is in good accordance with the results reported in the pertinent literature.^[31]

Figure 1. Structural and material characterization by TEM. (a) TEM image of MnO QDs drop-casted on a TEM grid. (b) Size distribution of MnO QDs obtained using computer software (ImageJ, NIH) based on several high-magnification TEM images. (c) HR-TEM image of MnO QDs exhibiting typical fringes of MnO crystalline structures. (d) A single QD on which the EELS has been performed. (e) The color mapping of manganese (red), oxygen (yellow), and carbon (green).

The atomic compositions were confirmed by electron energy loss spectroscopy (EELS) mapping, as shown in Figure 1d and Figure 1e, depicting individual elements in a single MnO QD. The Mn, O, and C atoms are located in the red, yellow and green regions, respectively, confirming that the Mn and O atoms are homogeneously distributed within a single MnO QD. Similar evidence for the presence of both Mn and O atoms in the structure was provided by energy-dispersive X-ray (EDX) spectroscopy measurements (Figure S1, Supporting Information). Both HR-TEM measurements and compositional maps demonstrate the atomic distribution of the MnO QDs with good crystallinity.

High-resolution X-ray photoelectron spectroscopy (XPS) was performed to identify the chemical composition and oxidation states, as shown in **Figure 2**, indicating the chemical compounds comprising this novel QD material. The XPS spectrum of the Mn $2p$ core level shows that the major components comprising the Mn $2p_{3/2}$ portion of the spectrum (Figure 2a) could be decomposed mathematically, unveiling three phases that correspond to the combined spectra of MnO, MnOOH, and Mn₂O₃.^[32] Based on the average value obtained by performing repeated XPS measurements on several specimens, the MnO phase (81.5%) was found to be predominant and was accompanied by smaller contributions of MnOOH (12.0%) and Mn₂O₃ (6.5%), producing unique characteristics. It should be noted that MnO QDs are passivated by hydroxyl group (-OH), as confirmed by Fourier transform infrared spectroscopy (FTIR) findings shown in Figure S2 (Supporting Information).^[33-35] The doublet peaks shown in the high-resolution XPS spectrum of the Mn $3s$ (Figure 2b) are typically examined to confirm the Mn oxidation state. The distance between such doublet peaks was about 5.8 eV, which serves as another strong indicator of the high prevalence of MnO in the composition of these QDs.^[36,37]

Room temperature absorption spectrum of MnO QD confirms that the wide bandgap of this material is within the DUV (UV-C) range (4.1–4.5 eV), as shown in Figure S3 in Supporting Information (the photo of MnO QDs in ethanol is shown in the inset). Figure S3 show the absorption spectra of as-prepared and aged colloidal MnO QDs in ethanol, which was aged for several days in the solution, indicating no significant change in the main absorption edge at 4.1.

Figure 2. X-ray photoelectron spectroscopy (XPS) of MnO QDs. (a) High-resolution XPS spectrum of the Mn 2p core level arising from manganese oxide QDs. The black scattered curve (square pattern) represents the experimental data of the Mn 2p spectrum. The orange, red and blue curves represent the best fittings of the experimental (black scattered) curve and correspond to MnO, MnOOH and Mn₂O₃, respectively. The weak black line below all curves represents the background. (b) High-resolution XPS spectrum of the Mn 3s core level produced by Mn particles.

In order to elucidate the electronic properties of the obtained QDs, we studied (MnO)₄ theoretically that is one of the most stable nanoclusters based on manganese oxide compounds,^[38,39] as shown in **Figure 3a**. Density functional theory (DFT) was employed to understand the electronic properties of these QDs and examine their bandgap behavior. As can be seen in Figure 3, the binding energy value of the OH-passivated system is 0.07 eV higher than that of the pure (MnO)₄ (resulting in a wider bandgap), which is in line with the values reported for bulk MnO.^[40-42] The calculated total DOS is presented in Figure 3b, indicating that the OH-passivated configuration is a spin-polarized material, as it exhibits spin-up and spin-down bandgaps similar to the bulk MnO crystal.^[42] The bandgap of the passivated OH-(MnO)₄ is 4.1 eV, which is 0.15 eV greater than that of the unpassivated (MnO)₄. Although the calculated bandgap is smaller than that obtained experimentally, it is approximately in line with the findings yielded by our absorption experiment (Figure S3). Figure 3c shows the projected

density of states (PDOS) of $\text{OH}-(\text{MnO})_4$ that delineate the individual atomic contributions, indicating the contribution of the OH group in the band structure formation. The valence band maximum comprises of a dominant contribution of the Mn-*d* and O-*p* orbitals, along with that of the OH group. On the other hand, conduction band minimum is a result of the major contribution from Mn-*d*, with a much smaller OH contribution.

Figure 3. Density functional theory calculations of density of states of $(\text{MnO})_4$. (a) Geometric structure of OH-passivated $(\text{MnO})_4$, whereby the table provides the binding energy of pristine and passivated MnO structures. (b) The total DOS. (c) PDOS of the OH-passivated $(\text{MnO})_4$. The pink dashed line indicates the Fermi level position.

The p-type electrical properties of MnO QDs were demonstrated by producing a field effect transistor (FET) based on the spray-coated MnO QD film on Si-SiO₂ substrate (**Figure 4**). The cross-section SEM images (Figure S4, Supporting Information) confirms very good coverage of the spray-coated MnO QD films. Figure 4a shows the asymmetric electrode (AE) structure of Au and Ti, while high-contrast optical microscope (OM) image showing electrical paths through the MnO QDs networks is presented in Figure 4b. The MnO QDs FET evidently

exhibited p-type electrical characteristics governed by holes as the majority carriers (Figure 4c). A high source-drain (SD) voltage of 10 V was required to activate a hole conducting channel due to the large channel length of 50 μm and a porous morphology of the MnO QDs layer. Under negative gate voltages, holes as the majority carriers are accumulated sufficiently enough to open the hole channel, which means that the gate voltage offsets or pushes out negative charges in the vicinity of the interface between the MnO QDs and the SiO₂ substrate.^[44]

Figure 4. Device structure and electrical properties of the MnO QD film incorporated in a device.

(a) An optical microscope (OM) image of the MnO QD film coated on the Ti–Au asymmetric IDE/SiO₂ substrate. (b) A magnified OM image displaying the MnO QDs networks within the Ti–Au IDE. (c) The transfer characteristic of the MnO QD device as a function of gate voltage. (d) The KPM color map of work function (ϕ) distribution across the MnO QDs layer and the Au surface. (e) A band diagram before contact, clearly showing the work function difference ($\phi_{\text{Ti}} < \phi_{\text{MnOQDs}} < \phi_{\text{Au}}$). E_F is above the valence band maximum (E_v) and E_c denotes the conduction band minimum. (f) The equilibrium band diagram after contact, demonstrating a favorable potential slope for electron–hole pair splitting.

To further confirm the p-type material characteristics, Kelvin probe measurements (KPM) were carried out. Figure 4d shows the work function distribution of MnO QDs (ϕ_{MnOQDs}), with the average (ϕ_{MnOQDs}) of 4.87 ± 0.02 eV, calculated by applying the empirical formula given in Equation 3 (in the Experimental Section). In addition, we obtained both $\phi_{\text{Au}} \sim 5.1$ eV and $\phi_{\text{Ti}} \sim 4.3$ eV to precisely construct the band diagram of the MnO QD device. Figure 4e and 4f depict the flat-band and the equilibrium diagram of the Ti-MnO QD-Au device architecture, clearly showing that the Fermi level (E_F) is above the valence band maximum. Since the ϕ_{Au} value is close to the ϕ_{MnOQDs} (Figure 4f), the valence band of the MnO QDs can be aligned with that of the Au electrode, while the contact between the Ti electrode and the MnO QDs can result in a Schottky barrier. Therefore, in the equilibrium contact, this AE structure can efficiently release a greater quantity of photogenerated carriers into one electrode even at no external bias.^[43] Moreover, photocarrier collection efficiency in this AE structure was enhanced due to the hole (as majority carriers) transport in the MnO QDs, further confirming the p-type nature of the QD material.

As a part of this investigation, different Schottky junction photodetectors based on the p-type MnO QDs solely were fabricated by spray-coated them on the IDE SiO₂ as a proof of concept to confirm the optical and electrical properties and stability of practical devices operating in the DUV range. Photodetector devices are distinguished by their device architectures aimed at detecting DUV (UV-C) illumination. **Figure 5a** demonstrates highly efficient photocurrent (I_{ph}) generation. Under illumination, at zero bias voltage, the device of the optimized AE (Ti–Au) configuration exhibited the I_{ph} of about 5 nA, while producing 12 nA under forward bias mode, indicating high carrier density, while both symmetric devices (Au–Au or Ti–Ti) produced negligible I_{ph} , as shown in Figure 5a. The amount of I_{ph} in the AE architecture depends on the release direction, denoted as either forward or reverse mode (Figure 5b inset).

Figure 5. The Ti–Au asymmetric IDE architecture is advantageous for efficient photocarrier generation and release. (a) Self-powered generation of I_{ph} in three MnO QDs devices of different IDE types (Ti–Au, Ti–Ti, and Au–Au) upon exposure to 244 nm laser illumination. (b) The effect of carrier releasement direction on I_{ph} under 244 nm laser illumination at 42 mW/cm² power density. The band diagram (c) under forward bias (negative Au) and (d) under reverse bias (negative Ti).

Under 244 nm laser illumination at 42 mW/cm² (Figure 5b), the I_{ph} of about 12 nA was generated in the forward bias mode (red), while no saturated I_{ph} was obtained in the reverse mode (blue), except for abruptly increasing and dissipating moments. The predominant generation of I_{ph} in the forward mode can be explained by referring to the band diagrams shown in Figure 5c and Figure 5d. At zero voltage, the Schottky potential formed at the Ti–MnO QDs junction (Figure 4f) is higher than that of the counter side (Au), limiting the transport of hole carriers. Therefore, to facilitate hole release into the valence band, forward bias (positive Ti and

negative Au) is required to reduce the potential barrier, as shown in Figure 5c. Under these conditions, majority of the holes photogenerated under DUV illumination can be easily released into the Au side, thereby producing high I_{ph} . This finding demonstrates that the MnO QDs are generating carriers with sufficient density under DUV (UV-C) illumination. In contrast, when device is operated in the reverse bias mode (negative Ti and positive Au), higher and deeper Schottky potential is produced, trapping the majority of holes at the Ti–MnO QDs junction interface. Under the reverse mode, electrons (as the minority carriers), from the conduction band, as well as a few holes (as the majority carriers) are thermally transferred through the valence band edges, and can thus produce infinitesimally small I_{ph} .

In order to obtain a p–n junction photodetector working in the DUV region, we have also fabricated n-type Ga_2O_3 –p-type MnO QDs photodetector. It is observed that photodetector based on n-type Ga_2O_3 and p-type MnO exhibits superior performance relative to that based solely on n-type Ga_2O_3 , as shown in Figure S5 in Supporting Information. Therefore, this work further confirms that it is possible to obtain p–n junction devices operating in the DUV region, which has not been achieved to date due to the scarcity of p-type materials.

Figure 6a shows that, in self-powered mode at 0 V bias, I_{ph} gradually increases with the incident light power density. The graph also reveals an abrupt emergence of a peak is observed followed by I_{ph} saturation, the level of which increased in line with the laser power increment. This phenomenon can be related to the fast release of initially existing and/or photogenerated holes from the MnO QDs surface, followed by rapid recombination due to shallow trap sites at the surface. However, no voltage-dependent peaks were produced at 10 mW/cm² (Figure 6b). During five ON-OFF cycles performed as a part of this investigation, both base and saturation currents remained at their initial levels, demonstrating a stable and reliable DUV detection. Figure 6c shows device responsivity versus power density, obtained using the I_{ph} values related to the peaks and saturation points, respectively. As can be seen from the graph, as the power density decreases, the responsivity gradually increases due to efficient photogeneration of

electron–hole pairs even at low light power. In self-powered mode, responsivity reached 11 mA/W under 244 nm laser exposure, thus confirming that electron–hole pairs are generated at 0 V bias. This finding also indicates that free carrier transport across the device can be achieved, a phenomenon that has never been observed in other p-type DUV materials due to their insulating nature. To further highlight the importance of these findings, the performance of our device is compared with the previously produced solution-processed DUV photodetectors^[22,26-29] and the pertinent data is presented in Supporting Information (Table TS1).

The rise and decay time are also in the acceptable range (hundreds of milliseconds), as shown in Figure 6d, as well as discussed in more detail in in Figure S6, Supporting Information. However, treating the QD surface defects can improve the response time, while adopting a heterojunction structure, having optimized band alignment, can further enhance the carrier collection efficiency, as well as response time.^[20,22,44, 45]

Enabling selective DUV detection is essential for the development of high-performance DUV optoelectronics. Figure 6e shows normalized device photoresponse under exposure to various monochromatic light wavelengths. When subjected wavelength below 300 nm illumination, the photoresponse markedly decreased (Figure 6e, inset) eventually reaching zero. This phenomenon is observed because of light of longer wavelengths (with energy below the MnO QD bandgap) cannot sufficiently excite electron–hole pairs. This result confirms strong solar-blind properties that can be harnessed for sensors that do not interact with solar radiation. UV-C or DUV radiation is absent from the Earth’s atmosphere, as these wavelengths are mostly absorbed by the ozone layer. Therefore, solar-blind photodetectors based on a DUV material can avoid most of the interference from solar radiation, unlike photodetectors based on Si.^[46] In addition, these results indicate strong transparency to UV-B and visible radiation, suggesting that this material can be employed in any UV or DUV device.

Figure 6. Solar-blind DUV photodetection characteristics of the MnO QDs device. A graph of 244 nm laser detection (a) under various power densities (0.35, 10, 42, 98, and 185 mW/cm²) at 0 V, and (b) under different voltages (0, 0.5, and 1 V) at 98 mW/cm² power density. (c) Responsivity (the highest responsivity of the MnO QDs device under 244 nm laser exposure was about 11 mA/W at 0 V and it reached 25 mA/W at 1 V) and (d) rise and decay time as a function of power density, which was extracted from the I_{ph} results shown in Figure 6a. (e) Typical photoresponse behaviors and relative responsivities as a function of incident light wavelength, with the relative responsivity shown in the inset. (f) Absolute responsivity and detectivity results under monochromatic light illumination (200, 220, 240, and 280 nm) at different power densities (0.5, 1.8, 5, and 6.8 mW/cm²).

Figure 6f shows the responsivities (R) of MnO QDs photodetectors, which reached 227 mA/W. We also investigated detectivity (D^*), as shown in Figure 6f (right axis) to determine the optical detection limit of the MnO QDs device. The D^* values obtained at 200, 220, 240, and 280 nm wavelengths were 2.57, 1.63, 1.49, and 1.17 ($\times 10^{11}$ Jones), respectively. These D^* values signify that the device is capable of efficient and selective generation of electron-hole pairs within the DUV range. At the same time, the device shows very good stability over time.

To examine the stability further, photoresponse of the MnO QDs devices was measure after four months and the results are shown in Supporting Information. No significant decline in photoresponse is observed, as shown in Figure S7. Thus, it can be comparable or superior to high-performance conventional photodetectors fabricated using expensive, time-consuming, and high-vacuum processes.

In summary, we have explored the synthesis of highly stable p-type WBGS MnO QDs (with a bandgap of 4.1–4.5 eV) by solution-processed FLAL technique. We demonstrated both experimentally and theoretically that it is possible to attain p-type MnO QDs. MnO QDs were confirmed to be the sole active layer in DUV Schottky photodetectors that exhibit efficient and stable photogeneration with high stability and reproducibility. MnO QDs photodetectors also exhibit good detectivity and solar-blind properties. The asymmetric structure adopted in this work enables self-powered characteristics, which is advantageous for power consumption. The highly stable p-type and crystalline nature of these MnO QDs would be immensely beneficial for a wide range of applications in electric and optoelectronic devices, as no p-type WBGS operating in the DUV range presently exists. Heterojunction devices incorporating any material can be easily built using such solution-processed QDs, as they are free from other issues, such as lattice mismatch layer and expensive fabrication, broadening the range of their use, especially in flexible devices. Thus, this exploration has resulted in a significant breakthrough in a very broad scientific and commercial context.

Experimental Section

FLAL QDs synthesis: FLAL using ultrashort femtosecond pulses has many advantages over other chemical methods.^[29,47] FLAL is a simple synthesis method that can be performed under atmospheric conditions. In this work, we used a titanium-sapphire (coherent-Mira 900) femtosecond (fs) laser with optimum operating conditions of 150 fs pulse width and 76 MHz pulse repetition rate at 800 nm wavelength. As adoption of this technique does not induce any ablation damage to the manganese oxide target, the likelihood of formation of undesired composites consisting of complex stoichiometric compositions (e.g., $\text{Mn}_x\text{O}_{1-x}$) during the fabrication process is minimized.^[29]

Transmission electron microscopy (TEM): HR-TEM measurements (using Titan 60-300 microscope, from FEI Co, equipped with Cs probe corrector and Quantum 966 imaging filter) were performed to examine the structural properties of our FLAL-synthesized MnO QDs. Electron energy loss spectroscopy (EELS) was conducted using the Titan TEM system to confirm the material composition, while XPS studies were carried out in a Kratos Axis Supra DLD spectrometer equipped with a monochromatic Al $K\alpha$ x-ray source ($h\nu = 1486.6$ eV) operating at 150 W, with a multichannel plate and delay line detector under a vacuum of $1\sim 10^{-9}$ mbar. The survey and high-resolution spectra were collected at fixed analyzer pass energies of 160 eV and 20 eV, respectively. Room temperature absorption measurements were performed using UV-Vis Varian Cary 5000 spectrophotometer.

X-ray photoelectron spectroscopy (XPS): A thin film of MnO QDs was obtained by spray coating colloidal MnO QDs on a glass substrate. Samples were mounted in floating mode to avoid differential charging. Charge neutralization was required for all samples. Binding energies were referenced to the C 1s peak of C–C, C–H bond which was set at 284.8 eV. The data were analyzed using commercially available software, CasaXPS A Shirley, and background was applied across the Mn $2p_{3/2}$ portion of the spectrum. We further employed the fitting procedure developed by Biesinger et al.^[32] to establish the chemical state of Mn

quantitatively, as shown in Figure 2a. A semi-empirical approach was adopted in the fitting procedures to determine the photoelectron count for each chemical state. This value was then directly related to the relative percentage of each chemical state at the sample surface.

Device fabrication: The spraying of the MnO QDs through the N₂ blowing gun was controlled at a constant N₂ pressure and a pre-set temperature (80 °C) of the loading plate. Two-probe resistance measurements were used to examine the conduction between the contacts on the film. The IDE silicon oxide substrate (SiO₂) was fabricated via electron beam evaporation (Oxford Instruments, UK) using a shadow mask. Three types of electrode configurations were prepared for symmetric (Ti–Ti, Au–Au) and asymmetric devices (Ti–Au). The device architecture was constructed based on the asymmetric Ti–Au (each of 100 nm thickness) IDE with a channel length of 50 µm, as shown in the optical microscope (OM) image presented in Figure 4a. In this device, the carriers can flow through electrical paths within the MnO QDs networks, as seen in the high-contrast OM image presented in Figure 4b.

DFT calculations: We performed the density-functional theory calculations using the *ab initio* software package VASP.^[48] For this purpose, the Perdew-Burke-Ernzherof exchange (PBE) correlation functional with generalized-gradient approximation (GGA) was adopted. The interaction between core and valence electrons was described via the projector augmented-wave method. All atoms were relaxed until the force and energy tolerances declined below 0.01 eV/Å and 10⁻⁵ eV, respectively. A plane wave energy cut-off of 500 eV was chosen. In order to avoid interactions with neighboring cells, a vacuum layer thicker than 12 Å was adopted in all three directions. Since the PBE functional underestimates the bandgap,^[50] we calculated the density of states (DOS) of OH-Mn₄O₄ using PBE0 functional, as it yielded more accurate results for MnO crystal.^[33] The calculated bond lengths of core (passivated) Mn–O and O–H are 1.80 Å (1.77 Å) and 0.97 Å. Upon passivation with the OH group, a core MnO bond length 0.01 Å

smaller than that of the pure (MnO)₄ was obtained. To check the OH-(MnO)₄ stability, we also calculated the binding energy of the system using the expression:

$$E_b = (E(T) - x \cdot E(\text{Mn}) - y \cdot E(\text{O}) - z \cdot E(\text{H})) / (x + y + z) \quad (1)$$

where $E(T)$, $E(\text{Mn})$, $E(\text{O})$, and $E(\text{H})$ are the total energies of pristine or OH-terminated (MnO)₄, isolated Mn atom, isolated O atom, and isolated hydrogen atom, respectively. The x , y , and z are the total number of Mn, O, and H atoms in the system, respectively.^[40,49]

Device characterizations: The 244 nm laser beam wavelength was generated using Lexel CW DUV and Visible laser (Cambridge Lasers Lab, Inc.). The forward and backward photocurrent was measured under a power density (defined as a light power projected per unit active area) of 10 mW/cm². A shutter (Thorlab) was attached to laser output and was electronically programmed to perform On/Off transient measurements. To measure the I–V characteristics, devices were probed and connected to a Keithley 2400 Source Meter (Tektronix, China) using electrical feedthrough. To modulate the light wavelength, Edinburgh Instruments FLS980 spectrometer attached to a 1000 W Xe lamp (Newport) equipped with customized shutter and optics was utilized. To evaluate the DUV detection efficiency, the responsivity (R)—defined as the ratio of generated I_{ph} to the incident light power—was calculated and the different incident light densities were corrected. R was calculated by dividing the generated photocurrent (I_{ph}) by the illuminated optical power on the effective area (P_o):

$$R = \frac{I_{ph}}{P_o}, \quad (2)$$

Assuming that the dark current is mainly dominated by the shot noise, D^* can be approximated to $D^* = \frac{R_\lambda A^{1/2}}{\sqrt{2 \cdot e \cdot I_{dark}}}$, where R_λ is the responsivity, A is the projected active area of the MnO QDs device, e is the electron charge, and I_{dark} is the dark current in the absence of light. The rise time (T_{rise}) and the decay time (T_{decay}) were defined as the time required to reach at least 90% value of the saturated current and to return to less than 10% value of the saturated current, respectively.

Kelvin probe measurements: When adopting the Kelvin probe technique, a vibrating metal tip is placed very close to the sample surface and both are connected to a feedback loop. A sinusoidal voltage $V_{ac}\sin(\omega t)$ is applied to the metal tip (in this case gold tip), resulting in oscillating electrostatic force between the sample and the tip. The electrons will start to flow and this process will continue until the Fermi levels are aligned. This phenomenon results in potential buildup across the tip and the sample, which can be nullified by applying DC voltage from the feedback loop externally. This nullifying voltage is denoted as contact potential difference (CPD) between the tip and the sample. The work function of the sample ϕ can be calculated using the following relation:

$$\phi = 5100 - CPD_{Au} + CPD_{sample}, \quad (3)$$

where, 5100 is the ϕ of Au in meV and CPD_{sample} is the CPD between the tip and the sample surface.^[43] All measurements were performed inside a Faraday cage within a glovebox, and the sample surface area of $100 \mu m \times 100 \mu m$ was scanned, while the relative CPD changes were also recorded (KP Technology).

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Table of Content

P-type wide bandgap semiconductor, manganese oxide quantum dots (MnO QDs) was synthesized for the first time by femtosecond laser ablation method. Schottky device based on solution-processed p-type MnO QDs shows superior photoresponse in deep UV region. Asymmetric electrode structure further helps to achieve self-powered photodetection.

Keyword: p-type material, deep ultraviolet photodetector, quantum dots, asymmetric electrode

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Novel p-type wide bandgap manganese oxide quantum dots operating at deep UV range for optoelectronic devices

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Supporting Information

**Novel p-type wide bandgap manganese oxide quantum dots operating at deep UV range
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Section S1: Energy-dispersive x-ray (EDX) spectroscopy of Manganese Oxide quantum dots (MnO QDs)

Section S2: Fourier transform infrared spectroscopy (FTIR) of MnO QDs

Section S3: Absorption Spectrum of MnO QDs

Section S4: Scanning electron microscopy (SEM) images of spray-coated MnO QDs

Section S5: p-n junction (p-type MnO and n-type Ga₂O₃) DUV photodetector

Section S6: Comparison between our device and the previously obtained DUV photodetectors based on solution-processed nano-devices.

Section S7: Rise and decay time calculation

Section S8: Photoresponse stability of the device over time

Section S1: Energy-dispersive x-ray (EDX) spectroscopy of MnO QDs

Energy-dispersive x-ray (EDX) spectroscopy findings confirm the presence of manganese (Mn) and oxygen (O) component, as shown in Figure S1.

Figure S1.: EDX measurements of the MnO QDs confirming the presence of Mn and O.

Section S2: Fourier transform infrared spectroscopy (FTIR) of MnO QDs

To verify the surface termination of the colloidal sample, FTIR results are discussed in this section. FTIR-iS10 instrument with Smart iTR setup has a diamond probe, permitting measurements in attenuated total reflection (ATR) mode. For these assessments, colloidal samples were drop-casted on the holder and then dried for a few minutes prior to collecting the FTIR spectra in the ATR mode. Lower vibrational frequencies corresponding to 620 cm^{-1} and 770 cm^{-1} are attributed to the Mn–O–Mn bond stretching vibration.^[23,24] The vibrational frequencies related to the 1350 cm^{-1} , 1384 cm^{-1} , 1418 cm^{-1} and 1585 cm^{-1} wavelengths are due to the Mn–OH bending, confirming the OH passivation of the QDs.^[25]

Figure S2. Fourier transform infrared spectroscopy (FTIR) of MnO QDs.

Section S3: Absorption spectrum of manganese oxide nanoparticles (MnO QDs)

Room temperature absorption measurements were conducted using UV-VIS Varian Cary 5000 spectrophotometer. Figure S3 showed the absorption spectra of both as-prepared and aged colloidal solution of MnO QDs, which was aged for four days in ethanol solution. No significant change in the main DUV absorption edge (at 250 nm) apart from a slight change in the tail that can be due to passivation of the dangling bonds in the surface. This result indicates good stability of the MnO QDs in colloidal form. The absorption result confirms that these MnO QDs possess a wide bandgap (4.1 eV).

Figure S3. Absorption spectra of as-prepared (black) and aged (red) colloidal MnO QDs in ethanol (inset shows the image of MnO QDs in ethanol).

Section S4: Scanning electron microscopy (SEM) images of spray-coated MnO QDs

Figure S4a and Figure S4b respectively provide cross-section images of MnO QD film obtained by spray-coating MnO QDs colloidal solution in different quantities (30 and 5 ml, respectively) and for different durations (around 60 and 10 min, respectively). The duration of the spray coating and the amount of solution was varied to modify the MnO QD film thickness, as shown in Figure S4a and S4b. The findings indicate that the colloidal solution concentration remains constant, while Figure S4c confirms very good coverage of the spray-coated MnO QD film.

Figure S4: Cross-section SEM images of the MnO QD film spray-coated on Si-SiO₂ substrate (a) 30 ml and (b) 5 ml of MnO QDs colloidal solution. (c) Surface morphology of the spray-coated MnO QD film.

Section S5: p-n junction (p-type MnO and n-type Ga₂O₃) DUV photodetector

We have fabricated p-type MnO and n-type Ga₂O₃ based DUV photodetector. MnO QDs are spray coated on the Ga₂O₃ flakes on a silicon oxide substrate. Titanium contact was deposited on the two sides of the flakes. The photodetector measurement was performed under 254 nm illumination. Figure S4 shows the current-voltage characteristics of the device and it can be noticed that the rectification behavior is present. We can also observe that the n-type Ga₂O₃ with p-type MnO QDs responds much better under DUV illumination as shown in the inset of Figure S5.

Figure S5: I-V characteristics of the n-type Ga₂O₃ the p-type MnO shows rectifying behavior. Transient photocurrent generation (on-off) under UV illumination shown in the inset.

Section S6: Comparison between our device and the previously obtained DUV photodetectors based on solution-processed nano-devices.

Table TS1: Comparison with the all solution-processed solar-blind DUV photodetectors reported in literature.

Photodetector	Type	Self-powered	Detectivity (Jones)	Rise /decay time (s)	Maximum R (mA/W)	I _{ph} /I _{dark}	Wavelength (nm)	Fabrication method	Ref.
Gr/GQD/Gr	Schottky	No	$<1 \times 10^{11}$	-	50 (not solar-blind)	-	300 nm	Solution-processed	1
Graphene QDs	Schottky	No	9.5×10^{11}	$t_r=0.064$ $t_d=0.043$	2.1	-	254 nm	Solution-processed	2
ZnS QDs	Schottky	No	3.83×10^9	$t_r=1.1$ $t_d=0.05$	1.60	8.3 (15V)	254 nm	Solution-processed	3
ZnS QDs	Schottky	No	-	$t_r=0.35$ $t_d=0.07$	0.1	-	265 nm	Solution-processed	4
C-ZnO QDs	Schottky	No	-	$t_r<0.08$ $t_d<0.08$	295	-	224 nm	Solution-processed	5
CsPbX ₃ QDs to Si nanowires	Hybrid	No	-	$t_r=0.00048$ $t_d=0.001$	54 32	-	200 nm 270 nm	Solution-processed	6
p-Gr/ZnS QDs/4H-SiC	Hybrid Heterojunction	Yes	1.41×10^{10}	$t_r=0.000028$ $t_d=0.00075$	0.29	1.6 (3V)	250	Solution-processed	7
p-type MnO QDs	Schottky	Yes	1.49×10^{11}	$t_r=0.29$ $t_d=0.29$	227	3(0V)	244	Solution-processed	This work

Section S7: Rise and decay time calculation

The rise and decay times were extracted from the transient DUV detection results shown in Figure S6a and Figure S6b, as they are significant figures of merit typically used to estimate photodetector detection speed roughly. As indicated in Figure 6d, the T_{Rise} and T_{Decay} are within hundreds of milliseconds (e.g., $T_{\text{Rise}} = 291$ ms and $T_{\text{Decay}} = 292$ ms was obtained at 10 mW/cm^2), which has not been achieved in extant studies on NP- or QD-based DUV detection in self-powered mode.

Figure S6. a) Rise time component between turning on and saturation and b) Decay time behavior at 0 V bias under light illumination with a power density of 10 mW/cm^2 .

Section S8: Photoresponse stability of the device over time

Figure S7 shows the transient photoresponse at 0 V of the same device measured at different times. The as-prepared device was measured within a week of the QD synthesis, as well as after four months. While no significant change in photocurrent generation has been observed, the response time has been slightly modified. We attribute this phenomenon to the oxide passivation of the surface over time under ambient conditions.

Figure S7: Transient photoresponse of the as-prepared and aged device.

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