The performance and industrial viability of organic photovoltaics are strongly influenced by the functionality and stability of interface layers. Many of the interface materials most commonly used in the lab are limited in their operational stability or their materials cost and are frequently not transferred toward large-scale production and industrial applications. In this work, an advanced aqueous-solution-processed cathode interface layer is demonstrated based on cost-effective organosilica nanodots (OSiNDs) synthesized via a simple one-step hydrothermal reaction. Compared to the interface layers optimized for inverted organic solar cells (i-OSCs), the OSiNDs cathode interlayer shows improved charge carrier extraction and excellent operational stability for various model photoactive systems, achieving a remarkably high power conversion efficiency up to 17.15%. More importantly, the OSiNDs’ interlayer is extremely stable under thermal stress or photoillumination (UV and AM 1.5G) and undergoes no photochemical reaction with the photoactive materials used. As a result, the operational stability of inverted OSCs under continuous 1 sun illumination (AM 1.5G, 100 mW cm\(^{-2}\)) is significantly improved by replacing the commonly used ZnO interlayer with OSiND-based interfaces.

The power conversion efficiency (PCE) of organic solar cells (OSCs) has been rapidly boosted by the recent development of novel nonfullerene small-molecule acceptors (NFAs) featuring significantly increased light absorption and reduced energy losses.[1–6] Recently, the PCE of single-junction OSCs is approaching the 18% milestone, exceeding the efficiency threshold expected for industrial viability.[7–10] Besides efficiency, long-term operational stability, such as thermal- and photostability, is a major concern for the practical application of OSCs.[11–15] On the one hand, the stability related to the microstructure of a bulk-heterojunction (BHJ) photoactive layer is essential for long-term stability; on the other hand, the stability of interface materials and the compatibility between the photoactive layer and the interface layer play a key role in determining efficiency and stability of OSCs.[16–20] By tuning the properties of the photoactive layer, such as tailoring the chemical structure of both donor (D) and acceptor (A), or incorporating a “phase compatibilizer” or “molecular lock” between D/A components, the microstructure stability of BHJ photoactive layer could be addressed.[21–25] However, interface-associated device’s instability is less frequently investigated and analyzed for

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state-of-the-art OSCs. As such, interface-induced device instabilities remain unresolved for many high-performance systems.

Zinc oxide (ZnO) is the most widely used cathode interlayer in inverted OSCs (i-OSCs), which possess better oxygen and humidity stability compared to the interface materials used in the conventional structure, such as LiF and Ca.\cite{26,27,28,29} To date, all of the i-OSCs with PCE over 15% were achieved by using a ZnO interlayer.\cite{31,32,33} However, the electronic properties of the ZnO interlayer are typically not well defined, and inevitably result in photo-instability issues upon ultraviolet (UV) illumination. On the one hand, the conductivity of the ZnO layer dramatically increases as a result of trap filling upon UV illumination, resulting in “photoinduced shunts” and enhanced charge carrier recombination at the ZnO/photoactive layer interface.\cite{34,35} On the other hand, as a well-known photocatalyst for organic compound, ZnO would facilitate the decomposition of NFAs such as IT-4F under UV irradiation.\cite{36,37} In addition, the “photoinduced shunts” have been proven to be a general phenomenon in OSCs comprising “neat or electrically doped” ZnO-based interlayers, regardless if the interlayer is prepared from nanoparticles’ dispersion or by vacuum-based techniques.\cite{34} Therefore, developing novel cathode interlayer materials that could realize highly efficient and photostable devices is urgently needed for the industrial scalability of OSCs.

Here, we demonstrate the use of aqueous-solution-processed organosilica nanodots (OSiNDs) as a promising cathode interlayer for high-performance i-OSCs, which is the first time for the organosilica materials to be used as an interlayer in OSCs. OSiNDs were synthesized via a simple one-step hydrothermal reaction between rose bengal (RB) and silane molecules with water as solvent. Ultraviolet photoelectron spectroscopy (UPS) measurements revealed that the OSiNDs’ film could reduce the work function (WF) of indium tin oxide (ITO) from 4.68 to 4.01 eV, which is an appropriate value to match with the lowest unoccupied molecular orbitals (LUMOs) of various kinds of electron acceptors. Compared to the ZnO cathode interlayer, the OSiNDs-based cathode interlayer showed improved charge carrier extraction and superior device performance for various model photoactive systems, including PM6:Y6, PM6:IT-4F, PTB7-Th:phenyl-C_{71}-butyric-acid-methyl ester (PC_{71}BM), and PM6:Y6:PC_{71}BM. A remarkably high PCE of 17.15% was achieved for OSCs incorporating the OSiNDs-based interlayer, which is the first time to achieve PCEs over 15% for i-OSCs without using ZnO as the cathode interlayer. More importantly, the OSiNDs-based interlayer significantly improved the photostability of OSCs as compared to pristine ZnO cathode interlayer. The OSiND-based devices maintained 96.1% of their initial performance after under continuous 1 sun illumination (AM 1.5G, 100 mW cm\(^{-2}\)) for 10 h, while devices based on a pristine ZnO interlayer only remained 67.2% of the original PCE under the same condition. The high photostability is attributed to the avoidance of photoinduced shunts and photocatalyst effect in OSiND-based OSCs. These results clearly show that OSiNDs are promising cathode interlayers, and may inspire the design and development of a new class of interlayer materials for highly efficient and photostable OSCs.

The OSiNDs were prepared by a facile one-pot hydrothermal method according to a previous report (Figure 1a).\cite{38} In detail, 30 mg of RB was dissolved in 4 mL of water. After the addition of 1 mL of 3-[2-(2-aminoethylamino)ethylamino]propyl-trimethoxysilane (AEEA), the mixture was transferred into a 10 mL Teflon-lined autoclave, which was sealed and maintained at a temperature of 160 °C for 4 h. After cooling down to room temperature, the resultant solution was dialyzed (500 Da) to remove the excess silane molecules.
As shown in Figure 1c, the stretching vibrations of Si–O and O–H bonds (1041 cm⁻¹) were observed. The Si–O stretch (≈1100 cm⁻¹) was attributed to the vibrations of amide bonds, while the ≈3400 cm⁻¹ peak also indicated the presence of amine groups in the OSiNDs. The presence of these silicon-involved bonds and amine groups was further verified by the Si 2p signal and N 1s signal in the XPS spectra (Figure S1, Supporting Information). The amine groups provide sufficient solubility in water and are expected to facilitate WPE modification of the beneath layer, which will be discussed in more detail in the following paragraphs. Compared to the interlayer materials based on polymers or small molecules, OSiNDs, as crystalline nanodot materials, would have better electrochemical stability in the charge carrier transfer process between interlayer and photoactive layer. The ultraviolet-visible (UV–vis) absorption and fluorescence spectra of OSiNDs are shown in Figure 1d.

The OSiNDs (2 mg mL⁻¹ in water) were used as cathode interlayer to fabricate i-OSCs with a device configuration of ITO/OSiNDs/PM6:Y6/MoO3/Al. Control devices with ZnO as the cathode interlayer were fabricated for comparison. The chemical structures of PM6 and Y6 are shown in Figure S2 (Supporting Information). The photovoltaic parameters of the devices are summarized in Table 1. Figure 2a illustrates the representative current density versus voltage (J–V) characteristics of OSCs incorporating different cathode interlayers under simulated AM 1.5G illumination at 100 mW cm⁻². The performance of OSCs optimized using different concentrations of OSiNDs is shown in Figure S3 and Table S1 (Supporting Information). The transmission spectra of glass/ITO and glass/ITO/OSiNDs (with optimal condition) are shown in Figure S4 (Supporting Information).

The ZnO-based device exhibited a maximum PCE (PCE_max) of 15.75% with an open-circuit voltage (Voc) of 0.83 V, a short-circuit current density (Jsc) of 25.07 mA cm⁻², and a fill factor (FF) of 75.69%, which are comparable to the values published in previous reports. Using OSiNDs as the cathode interlayer could slightly increase the Jsc to 25.54 mA cm⁻² and FF to >76%, resulting in a PCE_max of 16.15%. The average PCEs of OSiNDs versus ZnO-based devices progressed slightly from 15.67 ± 0.06% (for ZnO) to 16.01 ± 0.09% (for OSiNDs, box plots shown in Figure 2b, calculated from 15 identical devices prepared from different batches). Devices based on OSiNDs interlayer with different annealing conditions were measured (Figure 5 and Table S2, Supporting Information). There was negligible change in the device performance after 200 °C annealing of the OSiNDs for 1 h, indicating excellent thermal stability of the OSiNDs-based interlayer. External quantum efficiency (EQE) measurements were conducted to confirm the Jsc of the i-OSCs. As shown in Figure 2c, the EQE of OSiND-based device showed slightly enhanced photocurrent contributions in the 510–820 nm range compared to that of ZnO-based control device. The integrated Jsc values from EQE measurements are shown in Table 1, and are in good agreement with that obtained from J–V measurements (deviation within 3%). Figure 2d depicts the J–V characteristics of OSCs with different cathode interlayers in the dark. Compared to the ZnO-based device, the OSiND-based OSCs exhibited an improved shunt resistance and a comparable series resistance, indicating superior charge selectivity and charge transport ability of the cathode interlayer.

### Table 1. Photovoltaic parameters for devices with different active layer and electron transport layer under simulated AM 1.5G illumination at 100 mW cm⁻².

| Active layer | ETL   | Voc [V] | Jsc [mA cm⁻²] | FF [%] | PCE [%] (average) |
|--------------|-------|---------|----------------|--------|-------------------|
| PM6:Y6      | ZnO   | 0.83    | 25.07 (24.34)  | 75.69  | 15.75 (15.67 ± 0.06) |
| PM6:Y6      | OSiNDs| 0.83    | 25.54 (24.89)  | 76.19  | 16.15 (16.01 ± 0.09) |
| PM6:Y6      | ZnO/OSiNDs| 0.83 | 25.31 (24.65)  | 76.93  | 16.16 (16.03 ± 0.08) |
| PM6:Y6      | SnO₂  | 0.83    | 24.51 (23.83)  | 70.29  | 14.30 (14.08 ± 0.13) |
| PM6:Y6      | SnO₂/OSiNDs| 0.83 | 24.91 (24.25)  | 74.14  | 15.33 (15.08 ± 0.15) |
| PTB7-Th:PC₇₁BM | ZnO | 0.80    | 16.20 (15.74)  | 70.14  | 9.09 (8.93 ± 0.08)  |
| PTB7-Th:PC₇₁BM | OSiNDs| 0.80 | 16.78 (16.31)  | 71.74  | 9.63 (9.44 ± 0.11)  |
| PM6:IT-4F   | ZnO   | 0.84    | 20.57 (20.08)  | 74.02  | 12.79 (12.68 ± 0.07) |
| PM6:IT-4F   | OSiNDs| 0.84    | 20.98 (20.41)  | 76.04  | 13.40 (13.21 ± 0.11) |
| PM6:Y6:PC₇₁BM | ZnO | 0.85    | 25.67 (25.11)  | 76.22  | 16.63 (16.48 ± 0.09) |
| PM6:Y6:PC₇₁BM | OSiNDs| 0.85 | 26.02 (25.42)  | 77.54  | 17.15 (16.92 ± 0.14) |

*Average PCEs in brackets are based on 15 devices; Values in brackets are calculated from EQE.*
To study the mechanism of how OSiNDs function inside i-OSCs, UPS was used to investigate the \(W_F\) of ITO, ITO/ZnO, and ITO/OSiNDs substrates. As shown in Figure 3a, the \(W_F\) shifted from 4.68 eV for ITO to 4.24 eV for ITO/ZnO and 4.01 eV for ITO/OSiNDs. The \(W_F\) values for ITO and ITO/ZnO substrates are consistent with the previous reports, and

![Figure 3a](https://www.advancedsciencenews.com/)

**Figure 3.** a) UPS spectra of ITO, ITO/ZnO, and ITO/OSiNDs substrates. b) Photocurrent density \((J_{ph})\) versus effective voltage \((V_{eff})\) curves of the devices. c) Dependence of \(V_{oc}\) on light intensity for the devices. d) Dependence of \(J_{sc}\) on light intensity for the devices. Device structure: ITO/ZnO or OSiNDs/PM6:Y6/MoO3/Al.
the $W_F$ value of 4.01 eV for ITO/OSiNDs is attributed to the amine-containing groups of OSiNDs forming an interfacial dipole (Figure S6, Supporting Information) as reported for multiple amine-containing polymers such as poly[(9,9-bis(3’-(N,N-dimethylamino)propyl)-2,7-fluorene)-alt-2,7-(9,9-dioctylfluorene)] (PFN), polyethylenimine (PEI), and polyethylenimine ethoxylated (PEIE).[41–43] The decreased $W_F$ for ITO/OSiNDs compared to ITO/ZnO substrates was further investigated by Kelvin probe force microscopy (KPFM), as shown in Figure S7 (Supporting Information), and evidences a homogeneously lowered work function of OSiND-coated ITO. The atomic force microscopy (AFM) images corresponding to the KPFM measurements are shown in Figure S8 (Supporting Information). Moreover, the $W_F$ of 4.01 eV for ITO/OSiNDs is appropriate to match with the LUMOs for most of the reported fullerene acceptors and NFAs, indicating that this novel cathode interlayer could be widely used in i-OSCs based on many different photoactive layers (as will be demonstrated in the following paragraphs). The conductivity values of OSiNDs and ZnO were determined to be (2.31 ± 0.69) × 10⁻⁵ and (2.64 ± 0.37) × 10⁻⁴ S m⁻¹, respectively (Figure S9, Supporting Information). The surface morphology of PM6:Y6 active layer on ITO/ZnO and ITO/OSiNDs substrates was measured by AFM, as shown in Figure S10 (Supporting Information). The roughness for the active layer on OSiNDs was slightly higher than that for the active layer on ZnO interlayer, which could be resulted from the different surface energy of OSiNDs and ZnO interlayer (Figure S11 and Table S3, Supporting Information).

To understand the high performance for OSiND-based devices, the charge transport and extraction property were investigated first. The electron mobility was measured via the space-charge-limited-current (SCLC) method (Figure S12, Supporting Information). The electron mobility for encapsulated ZnO- and OSiND-based OSCs under continuous AM 1.5G illumination (100 mW cm⁻²) showed accelerated degradation, maintaining only 67.2% of the initial performance under the same condition. The long-term photostability of OSiND-based and ZnO-based OSCs was measured by using a metal halide lamp containing ultraviolet light (Figure S13, Supporting Information). The OSiND-based device showed much improved photostability with negligible burn-in degradation compared to the ZnO-based control device.

As depicted in Figure 4d, OSCs based on ZnO suffered from an almost two orders in magnitude increased leakage current after 1 h illumination. Such phenomena are known as photoshunts and indicate reduced charge carrier selectivity at the semiconductor/ZnO interface.[44] In clear contrast, OSiNDs-based OSCs exhibited almost unchanged dark $J$–$V$ characteristics after 1 h illumination, as shown in Figure 4e, underlining the excellent photostability of the OSiNDs-based interlayer. Figure 4f shows the UV–vis absorption spectra for Y6 on glass/ ZnO and glass/OSiNDs substrate before and after UV illumination (provided by a UV lamp at 5 mW cm⁻²) for 1 h. After UV illumination for 1 h, the absorption of Y6 on glass/ZnO substrate decreased significantly (the peak intensity reduced by 11%), indicating the decomposition of Y6 via the photocatalytic activity of ZnO, which is in agreement with the work by Zhou and co-workers, where ZnO was found to assist IT-4F decomposition under UV illumination.[45] For the Y6 film on glass/ OSiNDs substrate, the absorption spectra remained almost unchanged after UV illumination. As final evidence that the reduced photocatalytic activity of OSiNDs is responsible for the
lifetime enhancement, we investigated devices with a two-stack interface layer consisting of OSiNDs on top of ZnO interlayer (ZnO/OSiNDs bilayer interface) and found significantly improved photostability for the bilayer interface compared to ZnO-based control device (Figure S14, Supporting Information).

We further investigated the second selection criterion for interface materials—the wide applicability for various material systems. We decided to investigate the employing of OSiNDs as a bilayer interface on top of the most widely used metal oxide cathode interlayers, ZnO and SnO₂. Figure 5a presents the representative J–V characteristics of PM6:Y6 OSCs with these different cathode interlayers under AM 1.5G illumination at 100 mW cm⁻². EQE spectra of the corresponding OSCs are shown in Figure S15 (Supporting Information). Both ZnO/OSiNDs and SnO₂/OSiNDs bilayer cathode interlayers showed improved device performance compared to the control devices with a pristine metal oxide interface, indicating that OSiNDs are universal surface modifiers for various metal oxides including ITO, ZnO, and SnO₂, which might inspire the application of such interlayers in other organic optoelectronic devices such as organic light-emitting diodes, organic photodetectors, and perovskite solar cells. Next, we tested the universality of the interface with various model photoactive layers, including PM6:IT-4F, PTB7-Th:PC₇₁BM, and PM6:Y6:PC₇₁BM, whereas emphasis was placed to specifically vary the nature and LUMO of the electron acceptor. The photovoltaic parameters of OSCs are

Figure 4. a) The evolution of J–V curves for ZnO-based device under continuous AM 1.5G illumination (100 mW cm⁻²). b) The evolution of J–V curves for OSiND-based device under continuous AM 1.5G illumination (100 mW cm⁻²) for 10 h. c) The evolution of PCEs for the devices under continuous illumination. d) Dark J–V characteristics for ZnO-based device before and after illumination for 1 h in inert atmosphere. e) Dark J–V characteristics for OSiND-based device before and after illumination for 1 h. Device structure: ITO/ZnO or OSiND/PM6:Y6/MoO₃/Al. f) The absorption spectra of ZnO/Y6 and OSiND/Y6 films before and after UV-light illumination (365 nm) for 1 h.

Figure 5. a) J–V characteristics of the devices based on PM6:Y6 with different cathode interlayers under AM 1.5G illumination at 100 mW cm⁻². b) J–V characteristics of the devices based on PTB7-Th:PC₇₁BM, PM6:IT-4F, and PM6:Y6:PC₇₁BM with different cathode interlayers under AM 1.5G illumination at 100 mW cm⁻².
summarized in Table 1. Figure 5b presents the J–V characteristics of OSCs under AM 1.5G illumination at 100 mW cm\(^{-2}\). EQE spectra of the corresponding OSCs are depicted in Figure S16 (Supporting Information). It is worthwhile highlighting that the PCEs of optimized OSCs incorporating the OSiNDs-based interlayer are always slightly higher than those based on pristine ZnO interlayers. In all cases, we observed a slightly increased \( J_{sc} \) and FF, which we account to improved carrier extraction. An impressively high PCE\(_{max}\) of 17.15% was obtained for OSCs with OSiNDs as interface layer and PM6:Y6:PC\(_{71}\)BM as photoactive layer, which underlines our statement that OSiNDs are enabling a technology route for i-OSC s without a ZnO cathode interlayer.

In conclusion, we presented an extremely cost-effective, aqueous-solution-processed OSiND-based cathode interlayer for OSCs achieving excellent efficiency and photostability. It is for the first time that organosilica materials are demonstrated as most promising interlayer materials for OSCs. OSiNDs were synthesized via a simple one-step hydrothermal reaction in water. UPS and KPFM measurements revealed that the use of OSiNDs could reduce the \( W_F \) of ITO from 4.68 to 4.01 eV, which matched well with the LUMOs for most state-of-the-art electron acceptors. The OSCs based on OSiNDs showed a slightly improved efficiency compared to the ZnO-based control devices regardless of the employed photoactive layers (including PM6:Y6, PM6:IT4:F, PTB7-Th:PC\(_{71}\)BM, and PM6:Y6:PC\(_{71}\)BM). The more suitable \( W_F \), improved charge carrier extraction, and reduced charge carrier recombination in the OSiND-based devices contributed to the enhanced device performance, leading to an excellent PCE of 17.15% for the PM6:Y6:PC\(_{71}\)BM photoactive layer. More importantly, OSCs incorporating the OSiNDs interlayer maintained 96.1% of the initial efficiency after continuous illumination (AM 1.5G, 100 mW cm\(^{-2}\)) for 600 min, while the ZnO-based control device remained only 67.2% of its performance under the same condition. The high photostability of OSiND-based device was attributed to the avoidance of photoinduced shunts and photocatalytic effect, which are ineluctable shortcomings in ZnO-based i-OSC s. These results clearly show that OSiNDs are promising cathode interlayers for highly efficient and photostable OSCs, which take a giant step forward to the practical applications of OSCs.

For large-scale production and commercialization, the interface materials are expected to meet the following requirements: 1) excellent compatibility with state-of-the-art photoactive materials with minimized energetic and recombination losses; 2) cost-effective, as estimated in ref. [39]; 3) easy processing from green solvents; 4) the ink used to prepare the interlayer needs to be stably stored in the usual environment for a long time; 5) the thickness of the interlayer can be fine-tuned within a certain range to meet the production requirements; and 6) the interlayer should be stable under device operational conditions (under light and thermal stress), and does not react with active layers and electrodes.

**Supporting Information**

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