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Improved optoelectrical properties for organic solar cells by introducing silicon quantum dots via eco-friendly and simple process

Chang Ho Jung ^{a,b}, Hyoung Seok Lee ^{a,b}, Nam Gyu Yang ^{a,b}, Yong Woon Han ^{a,b}, Eui Jin Lee ^{a,b}, Young Hoon Kim ^{a,b}, Doo Kyung Moon ^{a,b,*}

^a Department of Chemical Engineering, Konkuk University, 1 Hwayang-dong, Gwangjin-gu, Seoul, 143-701, Republic of Korea

^b Nano and Information Materials Lab. (NIMs Lab.), Department of Chemical Engineering, Konkuk University, 120 Neungdong-ro, Gwangjin-gu, Seoul, 05029, Republic of Korea

ABSTRACT

In this study, we synthesized eco-friendly silicon quantum dots (SiQDs) with absorption \leq 400 nm and light emission of 440 nm and 500–550 nm. SiQDs were introduced into ZnO (sol-gel), an electron transport layer (ETL) of organic solar cells (OSCs) with an inverted structure.

The introduction of SiQDs led to a smoother and more uniform surface morphology of the ETL. SiQDs improved the carrier mobility of the device, and increased carrier transport by reducing carrier recombination and interfacial resistance. Furthermore, SiQDs were found to convert ultraviolet (UV) light to visible light via light conversion effect. They contributed to improved J_{SC} and FF in OSCs, and improved the power conversion efficiency (PCE) from 14.48 % to 15.31 % for the PM6: BTP-eC9 device (J_{SC} : 24.42 mA cm⁻² to 24.87 mA cm⁻², FF: 73.05 %–75.23 %) and from 15.43 % to 16.3 % for the PM6:L8-BO device (J_{SC} : 23.37 mA cm⁻² to 24.57 mA cm⁻², FF: 75.95 %–76.77 %).

SiQD-doped ZnO, with eco-friendly synthesized SiQDs, not only improved the efficiency with the ETL of OSCs, but also demonstrated good stability.

1. Introduction

Many countries around the world have continued to pledge targets of carbon neutrality in an effort to maintain the global temperature no greater than 1.5 °C above pre-industrial levels. CO_2 is released from the combustion of fossil fuels, and is one of the main contributors to global warming. Many governments and companies are leading efforts to develop eco-friendly energy to tackle CO_2 emissions and environmental pollution. Solar cells, including organic solar cells (OSCs), use solar energy, an infinite source of energy, and have garnered the most attention among other sources of renewable energy [1–6]. In particular, OSCs are third-generation solar cells with the advantages of low cost, lightweight, transparency through the solution process, potential applicability to wearable devices, and potential applications for building-integrated photovoltaics (BIPV) [2,6–11].

Generally, the most important aspects that determine the efficiency in OSCs include the molecular structures of the donor and acceptor, which consist of the active layer, and absorbance properties due to bandgap energy [1,12]. In 2019, Zou et al. [5] used PM6:Y6 as the active layer in an OSC and achieved high power conversion efficiency (PCE) up to 15.7 %. Among other non-fullerene acceptors (NFAs), high performance was achieved for Y6 developed by employing a ladder-type electron-deficient-core-based central fused ring. Since then, many researchers have adopted Y6-based derivatives as the acceptor and fabricated highly efficient NFA OSCs. In 2021, Wang et al. [13] blended NFA BTP-eC9 and PM6, Y6-based derivatives, as the active layer in OSCs, and reported a high PCE up to 15.76 % and good stability.

However, for OSCs, apart from the active layer, the device structure is also important to ensure good efficiency and stability. In general, the conventional structure of ITO/hole transport layer (HTL)/active layer/ electron transport layer (ETL)/electrode is used, and the PCE and stability decline due to ITO corrosion by poly(3,4ethylenedioxythiophene): poly(styrenesulfonic acid) (PEDOT:PSS), which is used as the HTL [14].

The inverted structure of ITO/ETL/active layer/HTL/electrode prevents corrosion due to PEDOT:PSS, and exhibits high PCE and long-term stability [15]. In 2022, Liu et al. [14] fabricated devices with inverted structure with PM6:BTP-eC9 as the active layer and ZnO (sol-gel) modified by methionine as the ETL. Consequently, they reduced surface defects, interface resistance, and charge recombination, which are traditionally prevalent in ZnO, and increased the PCE from 14.25 % to 15.34 % through enhanced charge transport properties. In 2023, Loi

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^{*} Corresponding author. Nano and Information Materials Lab. (NIMs Lab.), Department of Chemical Engineering, Konkuk University, 120 Neungdong-ro, Gwangjin-gu, Seoul, 05029, Republic of Korea.

E-mail address: dkmoon@konkuk.ac.kr (D.K. Moon).





Fig. 1. a) Schematic representation of the synthesis of SiQDs, b) HR-TEM image of SiQDs, c) size distribution of SiQDs.



Fig. 2. Absorbance properties of a) SiQDs solution and b) pristine ZnO solution & SiQDs-doped ZnO, c) emission properties of SiQDs by different excitation wavelength, emission properties of pristine ZnO & SiQDs-doped ZnO with d) excitation 340 nm and e) excitation 380 nm.

et al. [16] used ALD-SnO₂ as the ETL based on atomic layer deposition (ALD), decreased charge carrier recombination at the interface, and improved the efficiency from 16.84 % to 17.26 %.

Many studies have reported promising results to overcome resistance and charge recombination at the interface of ZnO (sol-gel) conventionally used as the ETL [17]. Furthermore, the currently used devices based on PM6:BTP-eC9 and PM6:L8-BO cannot absorb wavelength in the range of 300–400 nm in the absorbance properties of the donor and acceptor [18,19]. To overcome this issue, studies are being conducted regarding the introduction of quantum dots (QDs). QDs generally have a size of 1–100 nm, and are effective in improving the optical properties of OSCs as additives through quantum confinement [20–28]. QDs have the following roles in OSCs: 1) light conversion effects; 2) modification of the surface and interface; 3) accelerating carrier extraction; 4)



Fig. 3. a) SiQDs-doped ZnO OSCs device structure, b) images of SiQDs solutions under indo -or lamp & UV lamp (emission at 365 nm), c) bulk heterojunction (BHJ) active layer material.

improving OSC stability; and 5) tuning the bandgap energy [2,6,15,20, 29–33].

For instance, in 2020, our research group introduced graphene quantum dots in ZnO (sol-gel) and reported light conversion effects, improved carrier extraction, and improved PCE through good interface contact [6]. Additionally, in 2018, Zhu et al. [1] reported the results of using carbon quantum dots and ZnO (sol-gel) with inverted structure as the bilayer for the ETL.

In this study, we fabricated a device with the inverted structure of the BHJ-active layer with PM6 as the donor and BTP-eC9 and L8-BO as the acceptors. SiQD-doped ZnO, which included synthesized eco-friendly water-based SiQDs in ZnO, was introduced in the ETL [29,34,35]. Consequently, the fabricated OSCs (active layer: PM6/BTP-eC9) increased the short circuit current density (J_{SC}) from 24.42 mA cm⁻² to 24.87 mA cm⁻², improved the fill factor (FF) from 73.05 % to 75.23 %, and increased the PCE from 14.48 % to 15.31 %. Furthermore, PM6 and L8-BO-based OSCs exhibited increased J_{SC} from 23.37 mA cm⁻² to 24.57 mA cm⁻², improved FF from 75.95 % to 76.77 %, and increased PCE from 15.43 % to 16.3 %.

As a result, SiQD-doped ZnO (ETL) converted UV light to visible light and improved the PCE. More notably, SiQD addition was confirmed to significantly contribute to increases in J_{SC} and FF, instead of changes in the open circuit voltage (V_{OC}) of OSCs.

2. Experiment

2.1. Synthesis and characterization of SiQDs

Sodium-L-ascorbate (SA) and (3-aminopropyl) triethoxysilane (APTES, $H_2N(CH_2)_3Si(OC_2H_5)_3$) were purchased from Sigma-Aldrich (Germany). Water-dispersible SiQDs were synthesized using DI water, an eco-friendly solvent. Subsequently, 0.1 M sodium-L-ascorbate (SA) aqueous solution was violently mixed for 20 min, and 0.25 M (3-aminopropyl) triethoxysilane (APTES, $H_2N(CH_2)_3Si(OC_2H_5)_3$) aqueous

solution (5.0 mL) was added and violently mixed for 20 min. Then, 1.25 mL of SA solution was added and mixed for 40 min at 75 $^{\circ}$ C [29,34–36]. Finally, aqueous SiQDs were obtained in the colloidal state [26,37].

2.2. Fabrication of OSCs

PM6, BTP-eC9, and L8-BO were purchased from Derthon (China). For fabrication of OSCs, the cleaning process was conducted on patterned ITO glass, with neutral detergent, isopropyl alcohol, and deionized water through ultrasonication. The cleaned glass was subjected to UV-ozone treatment with the UVO cleaner. The OSCs with inverted structure (ITO/ZnO/photoactive layer/MoO₃/Ag) were fabricated. Sol-gel ZnO was used for the ZnO layer. For ZnO (sol-gel), zinc acetate dihydrate and ethanolamine (1:1 M ratio) were dissolved in 2methoxyethanol (0.75 M). Then, the solution was agitated at 50 $^\circ$ C for 12 h and filtered, and the final ZnO precursor was obtained as the clear solution [38]. The prepared ZnO precursor was coated on the cleaned ITO glass at 4000 rpm and annealed at 150 °C for 60 min. To introduce emissive dopants, the SiQD solution was dispersed at the concentration of 0.5 vol% in the ZnO precursor [1,6,16,39]. Two bulk heterojunction types of solution were used for the photoactive layer, and consisted of PM6:BTP-eC9 (13.2 mg mL⁻¹) in the ratio 1:1 and PM6:L8-BO (15 mg mL⁻¹) in the ratio 1:1. After coating the photoactive layer, the films were annealed at 100 °C for 10 min. Finally, the hole transport layer (HTL) MoO₃ and the top electrode Ag were formed in the vacuum chamber (under 10^{-7} Torr) through the thermal evaporation process at the thickness of 5 nm and 100 nm, respectively. The active area of the fabricated device was 0.04 cm².

2.3. Characterization of the fabricated device

The emission properties of the SiQD solution were measured by a UV hand lamp (emitted at 365 nm, VL-4L). The absorption properties of the pristine ZnO, SiQD solution and SiQD-doped ZnO solution were



Fig. 4. a) Current density-voltage (J–V) characteristics of PM6:BTP-eC9 device and b) PM6:L8-BO device, c) external quantum efficiency (EQE) characteristics of PM6:BTP-eC9 device and d) PM6:L8-BO device.

Table 1	
Photovoltaic performances of fabricated OSCs under 1 Sun Irradiatio.	

Condition	V _{OC} (V)	J _{SC} (mA/ cm ²)	FF (%)	PCE (%)
 ZnO (PM6:BTP-eC9) SiQDs-doped ZnO (PM6:BTP-	0.812	24.42	73.05	14.48
eC9)	0.818	24.87	75.23	15.31
3. ZnO (PM6:L8-BO)	0.869	23.37	75.95	15.43
4. SiQDs-doped ZnO (PM6:L8-BO)	0.864	24.57	76.77	16.3

measured by a UV-vis spectrometer (Agilent 8453). The emission properties of the pristine ZnO, SiQD solution and SiQD-doped ZnO solution were measured by a photoluminescence spectrometer (LabRAM HR UV/Vis/NIR). High-resolution transmission electron microscopy (HR-TEM) images were measured by JEM-2100F. The current densityvoltage (J-V) and dark current density-voltage characteristics were measured by a power source meter (keithley 2400) and solar simulator (Oriel, AM 1.5G under an illumination of 100 mW/cm² with an Xe lamp). The external quantum efficiency (EQE) was measured by the incident photon-to-current efficiency (IPCE) measurement system (Polaronix K3100, Mc Science). The optical energy level was calculated by the Tauc plot with the UV-vis spectrometer. The surface morphology characteristics were analyzed by field emission scanning electron microscopy (FE-SEM; SU8010, Hitachi) and atomic force microscopy (AFM). The interface resistance of the fabricated OSCs was measured by electrochemical impedance spectroscopy (AM 1.5, 100 mW/cm²) with an applied frequency of 100 Hz to 7 MHz. To measure the amorphous properties of SiQDs, X-ray diffraction (smartlab, theta-2theta) was conducted.

3. Results and discussion

3.1. Optical properties of the synthesized SiQDs

Fig. 1a illustrates the synthesis pathway and chemical structure of SiQDs used in this study. The surface morphology and particle size of the obtained nanoparticles were confirmed by high-resolution transmission electron microscopy (HR-TEM). Fig. 1b and c shows the HR-TEM image and particle size distribution of the nanoparticles, respectively. From the HR-TEM image in Fig. 1b, the obtained particles are confirmed to have an amorphous structure. In addition, we performed the FT-IR analysis and X-ray photoelectron spectroscopy (XPS) analysis. In Figure s1, FT-IR spectrum of SiQDs the peak 1049 cm⁻¹ attributed to stretching vibration of Si–O –Si. The peak 3398 cm⁻¹ attributed to stretch of Si–OH band. The peak 2973 cm⁻¹ attributed to N–H stretch. The peak 2334 cm⁻¹ and 1649 cm⁻¹ attributed to Si–C band. The peak 902 cm⁻¹ attributed to Si–N band. The peaks in 600–800 cm⁻¹ attributed to O–H band. Also, we did XPS analysis of SiQDs. Characteristics peaks of Si 2p, Si 2s, C 1s, N 1s, O 1s are at 103.6, 155.8, 286.4, 400.6, 532.5 eV respectively. The results demonstrate FT-IR spectrum is consistent with the analysis of XPS, indicating we successfully synthesize SiQDs similar to results of Liu et al. [29,35,40]. As illustrated in Fig. 1c, the obtained SiQDs are confirmed to have a maximum particle size of 3 nm and a mean diameter of 3.660 nm [2,35,39,41].

These results are consistent with the surface morphology data, which are discussed later, and suggest that SiQDs have a smoother and more dispersed surface than QDs [2,21,35,39,42].

To obtain more evidence for the amorphous properties of SiQDs confirmed in HR-TEM, X-ray diffraction (XRD) analysis was conducted. Figure s2 shows mostly broad spectra, but a weak peak at 32°. These

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Fig. 5. Morphology characteristics measure by AFM and FE-SEM, AFM of a) pristine ZnO layer and b) SiQDs-doped ZnO layer, FE-SEM of c) pristine ZnO layer, d) SiQDs-doped ZnO layer. The insets of image c and d are the partial enlarged images.

results indicate that the synthesized SiQDs have limited crystallinity and are amorphous, and the results are consistent with the aforementioned results of HR-TEM [34,43,44]. Additionally, in Figure s2, the peaks at 47° , 54° , 56° , 61° are for silicon wafer used as the base.

Fig. 2 shows the UV–visible absorption spectra of the synthesized SiQDs (Fig. 2a) and ZnO and SiQD-doped ZnO (Fig. 2b). As shown in Fig. 2a, the absorbance range of the synthesized SiQDs is \leq 400 nm. As shown in Fig. 2b, ZnO and SiQD-doped ZnO have a UV area \leq 300 nm. The absorption peak for SiQD-doped ZnO shows a more red shift than that of ZnO, and a new shoulder peak is observed around 300 nm [1,15, 25,29,33–35,45]. It is confirmed that the introduction of small SiQDs leads to a red shift in the absorption range of ZnO, resulting in new absorbance properties for the UV range. In addition, Figure s3 shows the UV–visible absorption area of the active materials. As shown in figure s3, the main absorption area of the active materials used in the experiment is over 500 nm.

Figure s4 illustrates the optical energy properties of pristine ZnO and SiQD-doped ZnO as well as the absorption properties measured by UV–vis spectroscopy. The optical energy band gap for pristine ZnO and SiQD-doped ZnO is measured as 3.87 eV and 4.01 eV, respectively. Also, We performed ultraviolet photoelectron spectroscopy (UPS) in Figure s4 to analyze HOMO and LUMO of the ZnO and SiQDs-modified ZnO. The valence band energy levels (E_{VB}) of pristine ZnO and SiQDs-doped ZnO were calculated using the equation below.

$E_{\rm VB} = hv - E_{\rm cutoff} + E_{\rm onset}$

The results are as follows. For the pristine ZnO layer, the $E_{\text{cutoff}} = 16.38\text{eV}$ and the $E_{\text{onset}} = 2.78\text{eV}$, and for the SiQDs-doped ZnO layer, the $E_{\text{cutoff}} = 16.45\text{eV}$ and the $E_{\text{onset}} = 3.09\text{eV}$. As a result of calculation, SiQDs-doped ZnO has lower HOMO energy level than pristine ZnO.

Accordingly, it results in a bigger energy bandgap in the ETL, which functions as a hole-blocking layer more effectively than traditional ZnO layer and consequently, can contribute to improved electron mobility [6].

Fig. 2c shows the results of emission properties of SiQDs and SiQDdoped ZnO. The emission data is shown when the excitation wavelength is excited to SiQD solution at 20 nm intervals from 340 nm to 400 nm. It is evident that excitation at 340 nm as well as 360 nm and 440 nm, leads to a mixture of emission peaks at 440 nm and 500 nm [42]. However, excitation at 380 nm, leads to an emission peak at 520 nm with bigger PL intensity than the existing emission peak at 440 nm. For excitation at 400 nm, the emission peak at 440 nm disappears, and emission properties are observed between 500 nm and 550 nm [6,18,29, 35,46,47].

The PL data in Fig. 2d and e compare the emission properties of pristine ZnO and SiQD-doped ZnO at the excitation wavelengths of 340 nm and 380 nm. In Fig. 2d, excitation at 340 nm leads to the emission peak of SiQD-doped ZnO at 420 nm. It is affected by the emission peak of ZnO, and is consistent with the absorbance properties affected by ZnO [1,6,29,34].

In Fig. 2e, excitation at 380 nm leads to an emission peak at 480 nm. Excitation at 380 nm is affected by ZnO, but the effect is less than excitation at lower wavelengths. This is confirmed from the absorbance properties of ZnO.

Consequently, the properties of the absorbing wavelengths in the UV range and emitting wavelengths in the visible light range are confirmed for the pristine ZnO, SiQD solution and SiQD-doped ZnO solution. These results confirm that SiQD-doped ZnO, when introduced in the ETL, leads to more light conversion, allowing more light in the visual light range to reach the active layer, and thereby, helps achieve higher efficiency [6,



Fig. 6. a) J_{SC} and b) V_{OC} dependence with irradiated light intensity of PM6:BTP-eC9 device, c) J_{SC} and d) V_{OC} dependence with irradiated light intensity of PM6:L8-BO device.

22,39].

3.2. Photovoltaic properties of fabricated hybrid OSCs

Fig. 3a shows the inverted structure (ITO/ZnO/photoactive layer/ MoO_3/Ag) of the device with the fabricated SiQD-OSCs. In the device, which uses Ag as the anode, the ZnO precursor (ETL) was synthesized in accordance with the method in Ref. [38]. Then, the synthesized SiQD aqueous solution was dispersed in the ZnO precursor at the concentration of 0.5 vol% [1,6,16,39]. The SiQD-doped ZnO (ETL) with added SiQDs, was coated at 4000 rpm on cleaned ITO glass. Then, thin films were annealed at 150 °C for 60 min. Fig. 3b illustrates the colors of the SiQD solutions irradiated by the indoor light and UV lamp. Fig. 3c and d shows the energy level alignment and structure of the donor (PM6) and acceptor (BTP-eC9, L8-BO) introduced in the photoactive layer.

The photoactive layer was introduced with spin coating by using a bulk heterojunction type of solution, in which the donor and acceptor were mixed in the ratio 1:1. The photoactive layer films were annealed at 100 °C for 10 min. Finally, the hole transport layer (HTL) MoO₃ and the top electrode Ag were formed in the vacuum chamber (under 10^{-7} Torr) through the thermal evaporation process at the thickness of 5 nm and 100 nm, respectively. The active area of the fabricated device was 0.04 cm².

Fig. 4 shows the J-V curve and EQE results of the devices under 1 sun conditions in which ZnO and SiQD-doped ZnO were introduced in the

ETL, while Table 1 lists the PCE results [14]. For the PM6:BTP-eC9 based inverted structure device, as indicated in Fig. 4a, the reference device (ETL:ZnO) exhibits a PCE of 14.48 % ($J_{SC} = 24.42 \text{ mA cm}^{-2}$, $V_{OC} = 0.8116 \text{ V}$, FF = 73.05 %). The device with SiQD-doped ZnO in the ETL, has a comparatively increased PCE (by 5.73 %) of 15.31 % ($J_{SC} = 24.87 \text{ mA cm}^{-2}$, $V_{OC} = 0.8183 \text{ V}$, FF = 75.23 %). As described in Fig. 4b, the reference device with the PM6:L8-BO based inverted structure (ETL: ZnO) exhibits a PCE of 15.43 % ($J_{SC} = 23.37 \text{ mA cm}^{-2}$, $V_{OC} = 0.8692 \text{ V}$, FF = 75.95 %). When SiQD-doped ZnO is introduced in the ETL, the PCE is increased by 6.8 %–16.3 % ($J_{SC} = 24.57 \text{ mA cm}^{-2}$, $V_{OC} = 0.8641 \text{ V}$, FF = 76.77 %). Although different acceptors were used, with the introduction of SiQDs to the ETL (ZnO), both devices have improved J_{SC} and FF, and increased PCE compared to the reference device.

Consequently, when SiQD-doped ZnO is introduced in the ETL, there is no notable difference in the V_{OC} of the device. Meanwhile, the J_{SC} value slightly increases, the FF increases considerably, and it is confirmed to contribute to improved device efficiency.

As observed in Fig. 4c and d, the external quantum efficiency (EQE) characteristics are consistent with the optical property data mentioned earlier. Fig. 4c and d shows the EQE values of the devices with PM6:BTP-eC9 and PM6:L8-BO as the active layer. Both devices have increased EQE at 350 nm and 450–550 nm when SiQD-doped ZnO, rather than ZnO, is introduced in the ETL [2,6,15,37,39]. However, at 400 nm, both devices have a slight decrease in EQE, which is confirmed to be due to the absorption of SiQDs. As in the PL spectra, these results are consistent



Fig. 7. SCLC curves of electron only devices a) PM6:BTP-eC9 and b) PM6:L8-BO, dark J-V curves of c) PM6:BTP-eC9 and d) PM6:L8-BO.

Table 2

Electron mobility and Shunt resistance properties of fabricated device, Parameters employed for the fitting the impedance spectra by use of and equivalent circuit model.

Condition	μ _e	R _{sh} (KΩcm²)	R1 (Ω)	R2 (Ω)	CPE
1. ZnO (PM6:BTP-eC9)	1.06 x 10 ⁻⁴	16.96	4.53	101.0	1.133 x 10 ⁻⁸
2. SiQDs-doped ZnO (PM6:BTP-eC9)	1.90 x 10 ⁻⁴	20.77	6.07	75.61	1.483 x 10 ⁻⁸
3. ZnO (PM6:L8-BO)	1.65 x 10 ⁻⁴	26.19	3.23	89.86	2.031 x 10 ⁻⁸
4. SiQDs-doped ZnO (PM6:L8-BO)	2.47 x 10 ⁻⁴	36.77	7.37	72.01	1.827 x 10 ⁻⁸

with the two emission peaks observed at other excitation wavelengths. Accordingly, with the EQE characteristics, SiQD-doped ZnO improves the J_{SC} value even when another acceptor is introduced in the active layer [6,39].

3.3. Surface morphology properties

Fig. 5 shows the results of atomic force microscopy (AFM) and field emission scanning electron microscopy (FE-SEM) on the pristine ZnO and SiQD-doped ZnO layers. The measurement of AFM was carried out under the same conditions.

In the AFM results in Fig. 5a, large white parts of pristine ZnO are observed. It means that surface morphology's height is higher than surroundings. But in the case of SiQDs-doped ZnO, those white parts become uniform by SiQDs dopant. In addition, RMS roughness value of pristine ZnO was $R_q = 1.147$ nm. After introducing SiQDs, RMS roughness value was $R_q = 0.872$ nm [1,6,11,19]. As a result, it can be explained that the morphology was more uniformly distributed. This is attributed to modification in the surface properties with the introduction of amorphous SiQDs, and is consistent with the results of the increased FF of the device.

The FE-SEM images in Fig. 5c and d confirm that SiQDs are uniformly distributed in ZnO layer [48].

3.4. Optoelectrical properties of the fabricated SiQD-doped ZnO device

To gain insights into changes in charge recombination in the device with SiQD addition, the J-V curve was measured for light intensity from 10 mW/cm² to 100 mW/cm². Fig. 6a–d shows the dependence of J_{SC} and V_{OC} on the light intensity. Charge recombination can be interpreted from the slope of the relationship between J_{SC} and light intensity. A slope closer to 1 implies weak bimolecular recombination [30,49–51].

For the PM6:BTP-eC9 device in Fig. 6a, when ZnO and SiQD-doped ZnO are introduced in the ETL, the slope (α) is measured to be 1.037 and 1.027, respectively. For the PM6:L8-BO device in Fig. 5c, the slope is



Fig. 8. a) Nyquist plots of fabricated PM6:BTP-eC9 and PM6:L8-BO devices. Inset is an equiva -lent circuit employed in fitting different impedance curves. Photocurrent density-effective voltage (J_{ph}-V_{eff}) characteristics of b) PM6:BTP-eC9 and c) PM6:L8-BO devices.

1.045 and 1.025, respectively. These results demonstrate that the introduction of SiQDs partially prevents bimolecular recombination, and is consistent with increased J_{SC} in the device.

Bimolecular recombination often occurs when the slope is closer to kT/q (where q is the elementary charge, T is the temperature, and k is the Boltzmann constant) in the relationship between V_{oc} and light intensity, while trap-assisted charge recombination often occurs when the slope is closer to 2kT/q [30,49–51]. As shown in Fig. 6b, kT/q is calculated as 1.084 and 1.055 for the PM6:BTP-eC9 device, in which ZnO and SiQD-doped ZnO are introduced as the ETL, respectively. Similarly, for the PM6:L8-BO device (Fig. 6d), kT/q is calculated as 1.076 and 1.056. Consequently, when SiQD-doped ZnO is used as the ETL, the value of kT/q is smaller, confirming that SiQD-doped ZnO reduces trap-assisted charge recombination [17,30,49–51].

The charge transport behavior of OSCs fabricated by the introduction of SiQDs was measured. The space-charge limited current (SCLC) method was used for measurement, and the charge carrier mobility was measured in the fabricated electron-only device (ITO/ZnO (SiQDsdoped ZnO)/active layer/Ag).

Fig. 7a and b illustrate the J-V curve of the electron-only device (in dark) in PM6:BTP-eC9, PM6:L8-BO, and SiQD-doped ZnO. The electron mobility (μ_e) is calculated by the Mott-Gurney equation.

$J = (9 / 8) \varepsilon_r \varepsilon_0 \mu_{eff} \left(V^2 / L^3 \right)$

J, ε_r , ε_0 , μ_{eff} , V, and L refer to the current density, dielectric constant, free space permittivity, carrier mobility, applied voltage, and film thickness, respectively [51–53].

Table 2 shows the measurement results of the electron mobility (μ_e), shunt resistance (R_{sh}), and impedance. The electron mobility values of PM6:BTP-eC9, when ZnO and SiQD-doped ZnO are used as the ETL, are calculated as 1.06×10^{-4} and 1.90×10^{-4} , respectively. However, for PM6:L8-BO, the electron mobility is calculated as 1.65×10^{-4} and 2.47×10^{-4} , respectively. In both devices, the introduction of SiQDs improves electron mobility, which is consistent with increased J_{SC} and FF in the photovoltaic data presented earlier.

Similar to the dark J-V curve in Fig. 7c and d, when another active material is used, the leakage current is lower at reverse bias in both devices when SiQD-doped ZnO is used. Hence, the shunt resistance is increased by the introduction of SiQDs to ZnO as shown in Table 2 (PM6: BTP-eC9: 16.96 \rightarrow 20.77 k Ω cm², PM6:L8-BO; 26.19 \rightarrow 36.77 k Ω cm²).

From these results, it is evident that the introduction of SiQDs in ZnO reduces the number of trap sites involved in electron mobility, and SiQDs serve as additional pathways for electron mobility, and therefore, facilitate electron mobility. Consequently, the introduction of SiQDs contributes to improved J_{SC} [6,17,24,30,39].

3.5. Electrical and electronic properties

The improved J_{SC} and FF in the photovoltaic data are related to

carrier transport, which is confirmed by changes in the interfacial resistance. To confirm interfacial resistance, we used electrochemical impedance spectroscopy (EIS), which can measure the electrochemical characteristics. Fig. 8 shows Nyquist plot data measuring and fitting the equivalent circuit model and the fabricated device under 1 sun conditions [53,54].

As shown in Fig. 8a and Table 2, SiQD-doped ZnO used for the ETL has a lower R₂ value than ZnO, where R₂ refers to the carrier transport resistance. For PM6:BTP-eC9, R_2 is 101.0 Ω when ZnO is used as the ETL and 75.61 Ω when SiQD-doped ZnO is introduced. Meanwhile, PM6:L8-BO shows R_2 values of 89.86 Ω and 72.01 Ω . Consequently, when SiQDdoped ZnO is used, the interfacial resistance of the device decreases. These results suggest that SiQDs play an important role in improving carrier transport properties [2,14,28,53-55]. In addition, the results are consistent with the improved J_{SC} and FF in the photovoltaic data mentioned earlier. Finally, to analyze carrier dissociation and transport trends in the devices with SiQD-doped ZnO (ETL), Fig. 8b and c shows the measurement results of the photocurrent density-effective voltage $(J_{ph}-V_{eff})$ dependence. In $J_{ph}-V_{eff}$ dependence, $J_{ph} = J_L-J_D$ (where J_L is the current density under light illumination, and $J_{\rm D}$ is the current density under dark conditions) and $V_{eff} = V_o - V_{app}$ (where V_{app} is the applied voltage, and V_0 is V_{app} when the current density is J_{ph} [6,17,53].

Fig. 8b and c shows that the saturated J_{ph} tends to be higher in the devices with SiQD-doped ZnO (ETL). This means that SiQDs cause strong exciton generation and carrier dissociation, and contribute to improved J_{SC} and FF [30,51].

In addition, this results in improved stability in the device. As shown in Figure s5, the non-encapsulated PM6:L8-BO (ETL:ZnO) device was stored in the glovebox for 400 h. The PCE decreases slightly, as evident in the measurement results (95 %). The devices with SiQD-doped ZnO in the ETL, maintain a PCE of 98 %. The non-encapsulated PM6:BTP-eC9 (ETL:ZnO) device was stored in the glovebox for 650 h. The PCE decreases drastically, as evident in the measurement results (86 %). The devices with SiQD-doped ZnO in the ETL, maintain almost PCE of 99 %. Both devices with SiQDs-doped ZnO in the ETL show good stability. On the other hand, devices with pristine ZnO show reduced efficiency due to decreased FF. This can be attributed to improved carrier transport properties and lower trap-assisted recombination through reduced interfacial resistance in the aforementioned data [6,12,39].

4. Conclusion

In this study, we used an eco-friendly and simple method to synthesize SiQDs, which showed absorption \leq 400 nm and light emission of 440 nm and 500–550 nm. SiQDs were introduced in ZnO (sol-gel), the ETL of the device with the inverted structure, resulting in improved efficiency due to increased J_{SC} and FF. For the PM6:BTP-eC9 device, the PCE is enhanced from 14.48 % to 15.31 %, while for the PM6:L8-BO device, the PCE is improved from 15.43 % to 16.3 %.

The introduction of SiQDs leads to a smoother and more uniform surface morphology of the ZnO layer, and increases carrier transport by reducing carrier recombination in the device, improving carrier mobility, and reducing interfacial resistance. SiQD-doped ZnO, which introduces eco-friendly synthesized SiQDs, demonstrates not only improved efficiency in the ETL for OSCs, but also, good stability.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Changho Jung reports financial support was provided by Konkuk University.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.orgel.2023.106940.

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