Dye sensitized solar cells (DSSCs) are one of the most efficient and cost-effective photovoltaic devices at present.\cite{1} The traditional DSSCs (n-type DSSCs), which are generally composed of an active photoanode sensitized with a visible light absorption dye such as N719 and a passive cathode,\cite{2} suffer from insensitivity to infrared light which constitutes up to 49% of the solar spectrum\cite{3} and expanding the light harvesting region to near-infrared (NIR) is an effective way to improve the photovoltaic performance. Light trapping strategies such as coabsorption by the photoanode have recently been proposed.\cite{4,5,6} However, although coabsorption can enhance light absorption, the power conversion efficiency is not improved substantially because of fast charge recombination caused by hole injection from light coabsorbers in the photoanode. Hence, it is challenging to produce n-type DSSCs with a wide solar response and high power conversion efficiency simultaneously. In this respect, adoption of NIR light active photocathodes and visible light responsive photoanodes is a feasible means to produce wideband DSSCs with the desirable carrier transport efficiency.

Expanded light harvesting and enhanced device performance have been observed from p–n type DSSCs composed of light-active NiO-based photocathodes but the efficiency is still low.\cite{7,8,9} Meanwhile, there is no photocathode-based structure for n-type DSSCs because of the difficulty in fabricating an efficient NIR light active photocathode based on the traditional cathode. Therefore, it is highly desirable to develop a new photocathode which not only exhibits high NIR absorption but also serves as a charge transfer layer with low electron recombination.

Black phosphorus (BP), a relatively new member of the 2D materials family, has attracted tremendous interest because of its anisotropic nature and unique semiconducting properties.\cite{10,11,12} Unlike semimetallic graphene with a zero bandgap and MoS$_2$ with a direct band gap of $\approx$1.8 eV only in the monolayered form, BP exhibits a layer-dependent direct bandgap varying from $\approx$-0.3 eV (bulk) to $\approx$-1.5 eV (monolayer).\cite{13,14} Consequently, there have been investigations on the potential application of few-layer BP to phototransistors,\cite{15,16} photovoltaics,\cite{17,18} NIR photodetectors,\cite{19,20} supercapacitors,\cite{21} as well as modulators.\cite{22} However, its use in DSSCs has not been explored experimentally probably due to the difficulty to obtain the clean solution-processable form of BP. Recently, many groups have reported the synthesis of few-layer BP nanosheets by liquid-phase exfoliation of bulk BP in organic solvents such as N-methyl-2-pyrrolidone (NMP) and dimethyl sulfoxide (DMSO).\cite{23,24,25} In particular, Zhang et al.\cite{26} and our group\cite{27} have demonstrated NMP-based synthesis of ultrasmall BP nanosheets (named BP quantum dots, BPQDs) which have a homogeneous thickness of less than 2 nm and large extinction coefficient in the NIR region.\cite{28} However, these solvents have high boiling points which render them very difficult to remove thereby adversely affecting the conversion of BP into a composite or film.

Herein, a BPQDs based photocathode suitable for wideband quasi-solid-state bifacial n-type DSSCs is described. By using a scalable and clean method to exfoliate BP crystals in ethanol, BPQDs are synthesized and incorporated into a polyaniline (PANI) film to fabricate a photocathode which exhibits NIR light absorption in addition to complementary absorption by the photoanode, leading to significant enhancement in electron transport and recombination. The quasi-solid-state bifacial n-type DSSCs comprising the BPQDs-based photocathode show a power conversion efficiency of 6.85% and short-circuit current ($J_{\text{sc}}$) of 24.31 mA cm$^{-2}$, which is almost 120% of that obtained from the bifacial n-type DSSCs without the BPQDs.

The BPQDs are synthesized by liquid-phase exfoliation involving an ultrasonic probe followed by ice-bath sonication of bulk BP crystals in absolute ethanol. Figure 1a shows the crystal structure of the layered BP. The transmission electron microscopy (TEM) images in Figure 1b,c depict the morphology...
of the BPQDs. The high-resolution TEM (HR-TEM) image in Figure 1d reveals lattice fringes of 0.256 nm arising from the (111) plane of the BP crystal.\[^{30,31}\] The atomic force microscopy (AFM) image in Figure 1e presents the topography of the BPQDs and the measured heights are 0.82, 1.42, 1.55, and 1.65, respectively. According to the statistical TEM and AFM analysis of 200 BPQDs (Figure S1, Supporting Information), the average lateral size is 3.5 \(\pm\) 0.6 nm and average thickness is 1.6 \(\pm\) 0.5 nm corresponding to a stack of 2 \(\pm\) 1 quintuple layers (QLs) of BPs. As shown by the Raman scattering results in Figure 1f, the three typical vibrational modes of the out-of-plane phonon modes at 359.8, 436.0, and 463.1 cm\(^{-1}\) correspond to the \(A_1\)\(^{\text{g}}\), \(B_2\)\(^{\text{g}}\), and \(A_2\)\(^{\text{g}}\) modes, respectively. Compared to bulk BP, the \(A_1\)\(^{\text{g}}\), \(B_2\)\(^{\text{g}}\), and \(A_2\)\(^{\text{g}}\) modes of the BPQDs blue-shift by about 1.6, 2.5, and 3.1 cm\(^{-1}\), respectively.\[^{27}\]

UV/vis–NIR spectrophotometry is employed to determine the optical properties of the BPQDs (Figure 1g). The BPQDs are well dispersed in ethanol and show a light yellow color (inset in Figure 1g). The optical band gap energy (\(E_g\)) of the BPQDs is calculated by the equation of \(E_g = 1240/\lambda_{\text{intersection}}\)\[^{32}\] and \(\lambda_{\text{intersection}}\) is 1015 nm (Figure 1g) which corresponds to the \(E_g\) value of 1.22 eV of BPQDs and a stack of 2 QLs of BPs.\[^{33}\] The normalized absorption intensity over the characteristic length of the cell (\(A/L\)) at \(\alpha\) of 808 nm, a typical NIR wavelength, at different concentrations (C) is determined (see Figure S2, Supporting Information) and the amount of BPQDs is determined by inductively coupled plasma atomic-emission spectroscopy. In agreement with the Lambert–Beer law (\(A/L = \alpha C\)), a linear trend is observed from the \(A/L\) versus concentration and the extinction coefficient of BPQDs at 808 nm is determined to be 14.3 L g\(^{-1}\) cm\(^{-1}\). It is larger than that of typical NIR absorbing nanomaterials such as Au nanorods (3.9 L g\(^{-1}\) cm\(^{-1}\)) and GO nanosheets (3.6 L g\(^{-1}\) cm\(^{-1}\)).\[^{34}\]

Figure 2a shows the schematic of the fabrication of the quasi-solid-state bifacial n-type DSSCs. The BPQDs are incorporated into a PANI film as the photocathode and a TiO\(_2\)/N719 film is the photoanode. Figure 2b shows the energy levels of the materials and simple electron transfer process in which the valence band of the BPQDs is \(-4.8\) eV according to Lin’s study.\[^{20}\] In the device, Dye N719 in the photoanode and BPQDs in the photocathode are used to absorb visible and NIR light, respectively. Under illumination, the N719 dye is excited by visible light and the photogenerated electrons are injected into the conduction band of TiO\(_2\). The oxidized dye is reduced by electrons from the donor in the redox couples. Under illumination, NIR light is transmitted to the photocathode and absorbed by the BPQDs to produce photogenerated electrons which are transferred to the BPQDs/electrolyte interface to oxidize the acceptor in the redox couples. The bifacial structure enhances light harvesting and better photovoltaic performance is expected compared to traditional front-illuminated DSSCs.

Incorporation of the BPQDs into the PANI film is illustrated in Figure 2c–g. Figure 2c,d shows the morphology of the bare PANI and PANI/BPQDs films, respectively. The films are composed of 50 nm PANI nanoparticles showing distinct particle boundaries and some particle aggregation (300–400 nm). The inset in Figure 2c presents the high-resolution SEM image revealing the porous structure of the PANI film. After BPQDs
incorporation, the PANI particle boundaries become blurry (Figure 2d), suggesting that a surface layer covers the PANI nanoparticles. The inset in Figure 2d exhibits the elemental maps of the boxed area acquired by energy-dispersive X-ray spectroscopy (EDS) and reveals the existence of P in the film. The TEM images in Figure 2e,f confirm the presence of BPQDs in the PANI/BPQDs film and EDS (Figure 2g) and X-ray photoelectron spectroscopy (Figure S3, Supporting Information) further corroborate the existence of BPQDs.

To better understand the interactions between the BPQDs and PANI, Fourier transform infrared (FTIR) spectroscopy is conducted on the bare PANI and PANI/BPQDs films (Figure 2h). The absorption bands at 3423, 2920, 1646, 1560, and 1105 cm\(^{-1}\) are assigned to the O–H antisymmetrical stretching mode, C=O, N–H bending and C=N stretching, vibration, and C–H stretching mode of the quinoid ring in PANI, respectively.\[^{35,36}\] Compared to the bare PANI film, the vibration of O–H at 3443 cm\(^{-1}\) in the PANI/BPQDs shifts to a larger wavenumber of about 20 nm indicative of the interactions between the –OH groups on the surface of the BPQDs and in the PANI.\[^{37}\] The asymmetrical stretching vibration of P=O bond in the P=O–P chain is observed at 1072 cm\(^{-1}\) \[^{38}\] from the PANI/BPQDs film revealing the formation of P=O\(_x\) in the BPQDs which are sensitive to oxygen under visible light irradiation.\[^{29}\]

The absorption and transmittance spectra of the bare PANI and PANI/BPQDs photocathodes are presented in Figure 3a,b, respectively. The three typical absorption bands at 343, 402, and 840 nm observed from the PANI films are associated with the characteristic absorption peak of the π–π* transition of the benzene ring in PANI as well as excitation transition of polarons and bipolarons in doped PANI, respectively.\[^{39,40}\] The bare
PANI photocathode without BPQDs shows strong light absorption in the infrared region arising from the interband transitions of $\pi$-electrons and bipolarons in the PANI molecules and is influenced by the change of the $\pi-\pi^*$ and bipolaron transition band gap of PANI. However, NIR light absorption from the PANI interband electron transitions is not considered to contribute substantially to the photogenerated electrons in the photocathode of DSSCs. After incorporating the BPQDs, enhancement of NIR light absorption from 750 to 1100 nm is observed from the PANI/BPQDs photocathode and it is attributed to the infrared light response properties of BPQDs due to the band gap as indicated in Figure 1 g. Figure 3 b shows that the PANI/BPQDs ($T_{\text{max}} = 45\%$) exhibit slightly reduced transmittance than PANI ($T_{\text{max}} = 53\%$), indicating that it is suitable for transparent photocathodes in bifacial n-type DSSCs. As shown in Figure 3 a, the TiO$_2$/N719 photoanode shows moderate absorption in the visible region between 300 and 750 nm but weak absorption in the NIR region between 750 and 1100 nm. Hence, the photocathode with the PANI/BPQDs film shows complementary light absorption indicating wide-band absorption by the DSSCs comprising both the optically active TiO$_2$/N719 photoanode and PANI/BPQDs photocathode.

The $J-V$ curves are derived to characterize the photovoltaic performance of the bifacial n-type DSSCs with PANI and PANI/BPQDs as the photocathodes when illuminated from both the front and rear sides (Figure 3 c). The photovoltaic parameters are summarized in Table S1 in the Supporting Information. In the front and rear illuminated bifacial n-type DSSCs, a mirror is placed on the rear side of the device to reflect light from the light source in order to enhance light harvesting at the rear side. \cite{41} Figure 3 c shows that the power conversion efficiency of the devices with different photocathodes exhibiting the following trend: PANI/BPQDs $> \text{PANI based bifacial n-type DSSCs}$. The quasi-solid-state device based on the PANI/BPQDs photocathode achieves a power conversion efficiency of 6.85\% with $J_{\text{sc}}$ of 24.31 mA cm$^{-2}$ and $V_{\text{oc}}$ of 0.64 V and this reflects almost 20\% enhancement in the efficiency compared to the PANI cathode device (5.82\%).

To further study the role of BPQDs in the photocathode of DSSCs, the photovoltaic characteristics of DSSCs with the PANI/N719 photocathode are determined for comparison (Figures S4 and S5 and Table S1, Supporting Information). The DSSC with the PANI/N719 photocathode shows lower power conversion efficiency (6.26\%) than that with the PANI/BPQDs photocathode (6.85\%). It is known that N719 is a molecular dye with excellent light absorption ability but without charge transport properties, whereas BPQDs play dual roles as the NIR light absorber and good charge transport materials. \cite{20} Therefore, better power conversion efficiency can be obtained from the PANI/BPQDs photocathode. In addition, the optical properties and electrochemical and photovoltaic performance of the DSSCs with TiO$_2$/N719/BPQDs photoanode are studied to determine the role of BPQDs in the photoanode (Figure S6 and Tables S2 and S3, Supporting Information). Little improvement in the light-to-electron conversion efficiency is observed from the DSSCs with the TiO$_2$/N719/BPQDs photoanode compared...
to those without BPQDs. It is because of the limited charge transfer from BPQDs to TiO$_2$/N719 in the DSSC caused by the unmatched energy levels among N719, BPQDs, and redox couple in the device.

The reported optimal power conversion efficiency of the DSSCs with N719 dye is 10%–12% but it is for DSSCs based on a liquid electrolyte. Because liquid electrolytes are difficult to package and have limited long-term stability, efforts have been made to replace liquid electrolytes with solid-state electrolytes including p-type inorganic semiconductors, organic hole transporting materials, and polymer composite electrolytes. Among them, polymer electrolytes are particularly attractive due to the relatively high ionic conductivity and promising long-term cell performance. Up to now, the best power conversion efficiency observed from solid-state DSSCs with N719 is around 8%–9%. Here, the agaro-based polymer electrolyte is used as the solid-state medium in the DSSCs and the efficiency is 6.85%, which is comparable to the best efficiency of previously reported solid-state DSSCs.

BP generally suffers from instability because it is very reactive to oxygen and water and the electronic and optical properties can degrade. Thus, the stability of $J_{sc}$, $V_{oc}$, and $\eta$ with time is evaluated under ambient conditions (Figure 3d). It can be observed that the DSSCs show good stability by incorporation of the BPQDs into the PANI film. The normalized efficiency of the bifacial n-type DSSC with the PANI cathode exhibits a ≈50% decrease after 14 days (without sealing), whereas the cell with the PANI/BPQDs photocathode shows slow degradation (≈30%) under the same conditions. The observed decrease in the DSSC efficiency is probably due to slight corrosion of the PANI by the residual NMP in the quasi-solid-state polymer electrolyte. However, the BPQDs are stable in the NMP (29) and so the PANI/BPQDs photocathode shows better stability and maintains the performance better than the bare PANI cathode.

To further evaluate the electrochemical performance and charge transfer and recombination processes of the bifacial n-type DSSCs based on the PANI and PANI/BPQDs photocathodes, cyclic voltammetry (CV), Tafel plots, electrochemical impedance spectroscopy (EIS), and intensity-modulated photocurrent/photovoltage spectroscopy (IMPS/VS) are conducted (Figure 4). The CV curves of the PANI and PANI/BPQDs photocathodes are acquired from 1.5 to −0.6 V at a scanning rate of 50 mV s$^{-1}$ as shown in Figure 4a. All the samples show two pairs of reduction and oxidation peaks. The relatively positive peak on the right (noted as Red$_1$ and Ox$_1$) is assigned to the redox reaction of 3I$_2$ + 2e$^-$ ↔ 2I$_2$ and the left peak (noted as Red$_3$ and Ox$_3$) corresponds to the redox reaction of I$_3^-$ + 2e$^-$ ↔ 3I$^-$. Both the reduction and oxidation peak current densities increase in the following order: PANI/BPQDs > PANI. A larger peak current density indicates better catalytic activity and the PANI/BPQDs photocathode shows better catalytic activity than PANI based on the large peak current density. It indicates efficient charge transfer at the interface between the electrolyte and PANI/BPQDs photocathode leading to better $J_{sc}$ of the bifacial n-type DSSC than the PANI based DSSC. NIR light absorption by the BPQDs creates new photogenerated electrons and the good electron transport characteristic of BPQDs promotes electron transfer at the interface to accelerate the reaction of I$_3^-$ + 2e$^-$ ↔ 3I$^-$. The cyclic voltammograms of the different photocathodes acquired at various scanning rates are presented in Figure S7 in the Supporting Information.

The Tafel polarization curves of the symmetrical cells with the PANI and PANI/BPQDs photocathodes are shown in Figure 4b which reveals the interfacial charge transfer at the interface of the photocathode/electrolyte. The Tafel curve can be divided into three zones: polarization zone at a small overpotential ($|U| < 120$ mV), Tafel zone at the intermediate overpotential (with a sharp slope), and diffusion zone at a large overpotential. The exchange current density ($j_0$) can be derived from the Tafel zone and diffusion zone slope and $j_0$ is used to evaluate the catalytic activity of the photocathodes. The PANI/BPQDs photocathode exhibits larger slopes in the anodic and cathodic branch, indicating a larger $j_0$ and better catalytic activity in reducing triiodide at the photocathode/electrolyte interface than PANI, which is consistent with the CV analysis (Figure 4a). In comparison with PANI, the larger $j_0$ observed from the PANI/BPQDs photocathode stems from more photogenerated electrons by the BPQDs and rapid charge transfer from BPQDs to the electrolyte as mentioned above.

Figure 4c presents the Nyquist plots of the bifacial n-type DSSCs with the PANI and PANI/BPQDs photocathodes and the EIS results are interpreted with three semicircles. The EIS spectra are fitted with the equivalent circuit shown in Figure 4c using the Z-View software. (All the Nyquist plots in this manuscript are fitted by the same equivalent circuit.) The fitting series resistance $R_s$, charge transfer resistance $R_1$, and ion diffusion resistance $R_3$ of the devices with different photocathodes are listed in Table S4 in the Supporting Information. The PANI/BPQDs ($R_s = 39.1$ Ω) based device shows a smaller $R_s$ than the PANI based bifacial n-type DSSC ($R_s = 52.1$ Ω) and a smaller $R_3$ is beneficial to the photovoltaic performance. In EIS, $R_1$ usually represents the charge transfer resistance at the photocathode/electrolyte interface and $R_2$ is related to the redox transport resistance in the electrolyte. The bifacial n-type DSSC with the PANI/BPQDs photocathode has smaller $R_1$ and $R_2$ than the PANI cathode, indicating better electrocatalytic activity of the PANI/BPQDs photocathode, reduced redox transport resistance at the BPQDs-based photocathode/electrolyte interface resulting in larger $j_{sc}$ and better power efficiency as shown in Figure 3. The smaller $R_2$ corresponds to the enhanced triiodide reduction process (I$_3^-$ + 2e$^-$ ↔ 3I$^-$). It may be attributed to the larger electron concentration and faster electron transport at the photocathode/electrolyte interface caused by BPQDs thereby playing dual roles as the light absorber and charge transporting layer. The enhanced triiodide reduction process in the electrolyte increases ion diffusion or reduces the redox transport resistance in the electrolyte thus producing smaller $R_2$. These results are consistent with the CV and Tafel analysis further corroborating the excellent charge transfer in the BPQDs.

To probe the NIR light response of the PANI/BPQDs photocathodes, the normalized transmittance of the bare PANI and PANI/BPQDs photocathodes is determined on the pump–probe system (1050 nm and average power of 73 μJ) (Figure 4d). When the pulse arrives at the PANI/BPQDs films ($t = 0$), the normalized transmittance of the weak probe laser pulse increases rapidly implying a large number in the electron hole separation. Afterward, the dynamic relaxation process.
begins and decreases the normalized transmittance in the following picoseconds range. The ultrafast carrier dynamic relaxation in the nonlinear response is obtained by biexponential function fitting to the experimental results. As shown in Figure 4d, the PANI/BPQDs photocathode exhibits a biexponential decay process with a short relaxation time $\tau_1$ of 0.14 ps and long relaxation time $\tau_2$ of 5.41 ps. The fast decay ($\tau_1$) is associated with intraband relaxation stemming from defect-assisted carrier cooling [55] and the slow decay ($\tau_2$) is related to electron–hole recombination. [56] The nonlinear response and recovery of the PANI/BPQDs photocathode is more obvious compared to the bare PANI photocathode. It suggests that electron hole separation occurs in the PANI/BPQDs photocathode probably resulting from the photogenerated electrons produced by the NIR light active BPQDs.

To further demonstrate the effects of the BPQDs on electron transport in the DSSCs, IMPS/VS is performed on the DSSCs with different photocathodes as shown in Figure 4. Table S5 in the Supporting Information shows the electron transfer time constant $\tau_c$ ($\tau_c = 1/(2\pi f_c)$), electron diffusion coefficient $D_e$ ($D_e = \omega^2/(2.35\tau_c)$), electron recombination time constant $\tau_r$ ($\tau_r = 1/(2\pi f_r)$), and electron transfer length $L$ ($L = (D_e\tau_c)^{1/2}$) according to the IMPS/VS results, where $f_c$ and $f_r$ are the characteristic frequency minimum of the IMPS (Figure 4e) and IMVS (Figure 4f) curves, respectively, [57] and $\omega$ is the thickness of the photoanode film ($\omega = 12$ µm for the cells studied.

Figure 4. a) Cyclic voltammograms of the PANI and PANI/BPQDs photocathodes at a scanning rate of 50 mV s$^{-1}$ in 10 $\times$ 10$^{-3}$ M LiI and 1 $\times$ 10$^{-3}$ M I$_2$ NMP solution containing 0.1 M LiClO$_4$ as the electrolyte; b) Tafel plots of the symmetrical cells based on the PANI and PANI/BPQDs photocathodes; c) Nyquist plots and fitted lines of DSSCs with the PANI and PANI/BPQDs photocathodes obtained at the open circuit voltage under irradiation of 100 mW cm$^{-2}$ with the inset being the equivalent circuit used to fit the impedance data; d) fast relaxation dynamics of the PANI/BPQDs and pure PANI photocathodes with a laser wavelength of 1050 nm and average pulse power of 73 µJ together with the fitting results; e) IMPS and f) IMVS of the DSSCs with the PANI and PANI/BPQDs photocathodes.
At the same time, an improvement in tron lifetime and lower electron recombination in the DSSCs.

The larger Voc is attributed to longer electron lifetime as a result of the enhanced electron density in the DSSCs caused by extra NIR-light-generated electrons from the BPQDs and improved electron transport in the DSSCs.

To compare with photocathodes composed of other types of high-mobility 2D materials, the PANI/graphene photocathode is studied. Figure S8 in the Supporting Information presents the optical, IMPS/VS, and I–V results of the DSSCs with PANI/BPQDs and PANI/graphene photocathodes and the results are summarized in Tables S6 and S7 in the Supporting Information. It can be observed that the PANI/BPQDs photocathode has better optical absorption than the PANI/graphene photocathode. The DSSCs with the PANI/BPQDs photocathode also deliver better electron transport and recombination performance than the device with the PANI/graphene photocathode. Correspondingly, the DSSCs with PANI/BPQDs have better power conversion efficiency (6.85%) than that with the PANI/graphene photocathode (5.59%). The better performance arises from the enhanced NIR absorption and semiconducting properties of BP compared to graphene.

In summary, a BPQDs based photocathode is incorporated into quasi-solid-state bifacial n-type DSSCs to improve the photovoltaic performance. Different from most NIR active molecule dyes which can only be used as a light absorber, the BPQDs here act as both an NIR light absorber and charge transfer layer, thus producing significant improvement in NIR light absorption, charge transport, and electron recombination. Correspondingly, the power conversion efficiency of the BPQDs based DSSCs is 6.85% which is almost 20% higher than that of the PANI cathode device (5.82%). This study not only reveals a practical means to realize wideband bifacial n-type DSSCs, but also provides insights pertaining to the use of solution-processable BP in next-generation photovoltaic and optoelectronic devices.

Supporting Information

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

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Supporting Information for

Black phosphorus quantum dots based photocathodes in wideband bifacial dye-sensitized solar cells

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Experimental Section

Preparation of BPQDs. The high-quality BP crystals were purchased from Smart Elements and stored in a dark glovebox filled with Ar gas. The absolute ethanol (99.5 %, anhydrous) was purchased from Aladdin chemistry Co. Ltd. All the other chemical reagents used in this work were analytical reagent grade and used without further purification.

The BPQDs were prepared from bulk black phosphorus crystals by a simple probe ultrasonic processing in addition to an ultrasound bath treatment. The bulk BP (30 mg) was ground and dispersed in ethanol, sealed in a cylindrical plastic tube, and sonicated with a power of 1200 W for 3 h. The ultrasound probe was operated for 2 s and stopped for 4 s in a frequency range between 19 and 25 KHz. The following treatment involved sonication of the dispersion ultrasonically with the power at 300 W for 10 h. The temperature in the probe ultrasonic
processing and ultrasound bath treatment was below 277 K controlled by an ice bath. The dispersion was centrifuged at 7,000 rpm for 20 min to collect the supernatant containing the BPQDs. The BPQDs solution was centrifuged at 12,000 rpm for another 20 min to obtain the precipitate which was re-suspended in ethanol for further use. The concentration of the BPQDs in ethanol was about 4 μg/mL. Except the sonication and centrifugation steps, the experiments were conducted in an Ar glovebox.

**Characterization of BPQDs.** TEM and HR-TEM were performed on the Tecnai G2 F20 S-Twin transmission electron microscope at 200 kV. AFM was conducted on the drop-cast flakes on Si/SiO$_2$ substrates using the MFP-3D-S atomic force microscope (Asylum Research, USA) using the AC mode (tapping mode) in air. Raman scattering was carried out on a Horiba Jobin-Yvon Lab Ram HR VIS high-resolution confocal Raman microscope equipped with a 633 nm laser as the excitation source at room temperature. The UV–vis–NIR absorption spectra were acquired on a Lambda25 spectrophotometer (PerkinElmer) using QS-grade quartz cuvettes at room temperature.

**Synthesis of PANI based photocathode.** Poly (vinyl pyrrolidone) (4 wt%, PVP, 99.8% purity, Urchem) and ammonium persulfate (25 mM, APS, 98% purity, TCI) were added to hydrochloric acid (0.5 M, HCl, 50 mL) containing aniline (25 mM, ANI, 99% purity, TCI). A FTO glass (surface resistance =15 Ω sq$^{-1}$) was immersed in the solution at -3 °C for 20 min to obtain HCl-doped PANI films. After rinsing repeatedly with DI water and 1 M HCl, the transparent PANI film was dipped in HCl (1 M) for 4 h and dried at 80 °C in vacuum for 30 min. The thickness of the obtained PANI film was optimized to be about 1 μm (Figure S9). The PANI/BPQDs photocathodes were prepared by soaking the PANI film with a thickness of 1 μm in the BPQDs ethanol solutions (4 and 20 μg/mL) for about 4 h under N$_2$ in a glove box, respectively. A comparative study of the BPQDs loadings with different BPQDs solution concentrations (0, 4 and 20 μg/mL) for the PANI/BPQDs photocathode was evaluated as shown in Figure S10 and Table S8. The BPQDs concentration loading in the
PANI/BPQDs photocathode was chosen as 4 μg/mL in the manuscript for comparing with the bare PANI photocathode and the corresponding DSSCs. For comparison, the PANI/N719 photocathode was fabricated by immersing the PANI film in the N719 (0.5 mM) ethanol solution for about 12 h. The PANI/graphene photocathode was prepared by dipping the PANI film in the graphene ethanol solution (20 μg/mL) for 4 h.

**Synthesis of BPQDs based photoanode.** The N719 dyed TiO₂ photoanodes prepared as reported previously[1] was immersed in BPQDs ethanol solution (4 μg/mL) for 4 h and then dried in glove box under room temperature to obtain TiO₂/N719/BPQDs photoanode.

**Assembly of quasi-solid-state bifacial n-type DSSCs.** The N719 dyed TiO₂ photoanodes and agarose polymer electrolytes were prepared as described previously.[1] To assemble the bifacial n-type DSSCs with different photocathodes, the polymer electrolyte was added to the N719 dyed TiO₂ photoanode at 75 °C and the pure PANI, PANI/N719 and BPQDs/PANI photocathodes were sandwiched into the TiO₂/electrolyte structure to construct the DSSCs when the polymer electrolyte became viscous. The devices were dried at 75 °C for 2.5 h to remove the solvent to produce the quasi-solid-state DSSCs. All the bifacial n-type DSSCs were assembled and tested in air without sealing.

**Characterization of the photocathodes and quasi-solid-state bifacial n-type DSSCs.** The surface morphology and structure of the PANI and BPQDs/PANI photocathodes were characterized by scanning electron microscopy (SEM, JSM-6360LV, JEOL, Japan) and transmission electron microscopy (TEM, Tecnai G220 S-Twin, FEI, USA), respectively. EDS measurement was conducted during the SEM and TEM examination. FTIR (Fourier transform infrared spectroscopy) was performed on the Nxus 670 (Thermo Nicolet Corporation, USA) and XPS was carried out on the Thermo Fisher-VG Scientific ESCALAB 250Xi XPS. The UV-Vis-NIR absorption and transmittance spectra were acquired on the ultraviolet-visible spectrophotometer (UV-Vis, Hitachi, Tokyo, Japan) and electrochemical impedance spectra (EIS) were obtained between 10⁵ and 10⁻¹ Hz with a bias of -0.8 V on an electrochemical
analyzer (CHI604D, Chenhua, Shanghai, China) under illumination of 100 mW/cm² and the AC amplitude was 10 mV. The Tafel polarization plots were acquired on the CHI604D at a scanning rate of 10 mV/s and the J-V characteristics were determined from DSSCs under simulated AM 1.5 G solar illumination at 100 mW/cm² from a xenon arc lamp (CHF–XM500, Trust–tech, China) under ambient conditions and recorded with the CHI604D (the active cell area of 0.16 cm²). The light intensity was calibrated by a Si-1787 photodiode (spectral response range 320-730 nm).

The pump-probe measurements were performed with a femto-second pulse laser with a pulse duration of 35 fs and pulse repetition rate of 2 kHz. The laser pulse was produced by an optical parametric amplifier (TOPAS, USF-UV2) pumped by a Ti:Sapphire regenerative amplifier (Spectra-Physics, Spitfire ACE-35F-2KXP Maitai SP and Empower 30). The laser beam was focused by a lens with the focal distance of 250 mm. The wavelength of the pumped light and probe light was 1050 nm.

The IMPS/VS measurements were carried out on an LED driver system (AUT.LEDKIT, Metrohm, Swiss) in which a red LED (627 nm) LED provided the sinusoidal optical perturbation signal. The IMPS/VS signals were recorded by the PGSTAT302N Electrochemical Workstation (Metrohm, Swiss). The frequency range was set between 1000 Hz and 0.1 Hz in the IMPS and IMVS measurements.
Figure S1. (a) Statistical analysis of the size of 200 BPQDs shown by the TEM images and (b) Statistical analysis of the heights of 200 BPQDs measured by AFM.
Figure S2. (a) Absorbance spectra of the BPQDs dispersed in ethanol with different concentrations (1.3, 2.5, 5.1, 10.1, and 20.2 ppm). (b) The normalized absorbance intensity over the characteristic length of the cell ($A/L$) at different concentrations at $\lambda = 808$ nm.
Figure S3. (a) XPS spectra of the PANI and PANI/BPQDs films and (b) P2p spectrum of the BPQDs in PANI film. The PANI film shows the Cl2p2/3, C1s, and N1s at 199.0, 283.2 and 398.6 eV, respectively, which are attributed to the HCl-doped PANI. A small O1s peak is observed at 532.1 eV, which results from PVP in PANI film. After incorporating BPQDs, both the Cl2p2/3 and N1s peaks disappear from the PANI and the intensity of O1s is bigger. It is because the surface is covered of the dye or the BPQDs attenuate the Cl2p2/3 and N1s signals introducing more –OH from BPQDs. The high-resolution P2p peak at 136.0 eV observed from the PANI/BPQDs film can be attributed to P2O5.[2] Surface oxidation of the BPQDs is unavoidable during the film fabrication process but does not reduce NIR absorption by the BPQDs.[3]
Figure S4. J-V curves of the bifacial n-type DSSCs with the PANI, PANI/N719 and PANI/BPQDs photocathodes under different illumination conditions (front illumination: 100 mW/cm²).
Table S1. $J_{sc}$, $V_{oc}$, FF, and $\eta$ of the quasi-solid-state bifacial n-type DSSCs with various photocathodes under different illumination conditions.

<table>
<thead>
<tr>
<th>Illumination</th>
<th>Photocathodes</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>$V_{oc}$ (V)</th>
<th>FF</th>
<th>$\eta$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Front</td>
<td>PANI</td>
<td>21.13</td>
<td>0.59</td>
<td>0.46</td>
<td>5.73</td>
</tr>
<tr>
<td>Front</td>
<td>PANI/ BPQDs</td>
<td>23.19</td>
<td>0.64</td>
<td>0.43</td>
<td>6.38</td>
</tr>
<tr>
<td>Front</td>
<td>PANI/N719</td>
<td>21.88</td>
<td>0.64</td>
<td>0.43</td>
<td>6.02</td>
</tr>
<tr>
<td>Rear</td>
<td>PANI</td>
<td>16.88</td>
<td>0.59</td>
<td>0.51</td>
<td>5.08</td>
</tr>
<tr>
<td>Rear</td>
<td>PANI/ BPQDs</td>
<td>20.13</td>
<td>0.62</td>
<td>0.47</td>
<td>5.87</td>
</tr>
<tr>
<td>Rear</td>
<td>PANI/N719</td>
<td>19.19</td>
<td>0.66</td>
<td>0.44</td>
<td>5.57</td>
</tr>
<tr>
<td>Front + rear</td>
<td>PANI</td>
<td>21.44</td>
<td>0.59</td>
<td>0.46</td>
<td>5.82</td>
</tr>
<tr>
<td>Front + rear</td>
<td>PANI/ BPQDs</td>
<td>24.31</td>
<td>0.64</td>
<td>0.44</td>
<td>6.85</td>
</tr>
<tr>
<td>Front + rear</td>
<td>PANI/N719</td>
<td>21.75</td>
<td>0.64</td>
<td>0.45</td>
<td>6.26</td>
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</table>
Figure S5. (a) Absorption and transmittance spectra of the PANI/N719 photocathodes; (b) Cyclic voltammograms of the PANI/N719 photocathodes at a scanning rate of 50 mV/s in 10 mM LiI and 1mM I₂ in NMP solution containing 0.1M LiClO₄ as the electrolyte; (c) Tafel plots of the symmetrical cells based on the PANI/N719 photocathodes; (d) Nyquist plot and the fitting line of the bifacial n-type DSSCs with the PANI/N719 photocathodes obtained at the open circuit voltage under irradiation of 100 mW/cm², and the fitting result is obtained with the same equivalent circuit shown in Figure 4c.
Figure S6. (a) Energy level diagram of the bifacial DSSCs with the photoanode co-sensitized by both N719 and BPQDs; (b) Absorption by the TiO\textsubscript{2}/N719 and TiO\textsubscript{2}/N719/BPQDs photoanodes; (c) Nyquist plots and the fitted lines (the fitting results are obtained with the same equivalent circuit shown in Figure 4c); (d) IMPS, (e) IMVS and (f) I-V curves of the bifacial n-type DSSCs with the TiO\textsubscript{2}/N719 and TiO\textsubscript{2}/N719/BPQDs photoanodes assembled with a Pt counter electrode. Both the EIS and I-V test are performed under illumination with a power of 100 mW/cm\textsuperscript{2}. Incorporating BPQDs into the TiO\textsubscript{2}/N719 photoanode shows small enhancement in the light absorption in the whole range. The larger $R_1$ and $R_3$ and smaller $D_n$ and $L$ observed from the device with the TiO\textsubscript{2}/N719/BPQDs photoanode indicate slower charge transfer in the DSSCs compared to those with TiO\textsubscript{2}/N719. This results in small improvement in the light-to-electron conversion efficiency in the DSSCs after introducing BPQDs into the photoanode.
### Table S2. Fitted EIS results and photovoltaic parameters of the bifacial n-type DSSCs with various photoanodes.

<table>
<thead>
<tr>
<th>Photoanode</th>
<th>R₁ (Ω)</th>
<th>R₂ (Ω)</th>
<th>R₃ (Ω)</th>
<th>Jₘc (mA/cm²)</th>
<th>Vₒc (V)</th>
<th>FF</th>
<th>η (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO₂/N719</td>
<td>114.3</td>
<td>76.1</td>
<td>12.6</td>
<td>16.3</td>
<td>0.58</td>
<td>0.47</td>
<td>4.44</td>
</tr>
<tr>
<td>TiO₂/N719/BPQDs</td>
<td>123.3</td>
<td>78.2</td>
<td>50.7</td>
<td>17.4</td>
<td>0.58</td>
<td>0.45</td>
<td>4.54</td>
</tr>
</tbody>
</table>

### Table S3. IMVS/PS parameters of the bifacial n-type DSSCs with various photoanodes.

<table>
<thead>
<tr>
<th>Photoanode</th>
<th>fₙ (Hz)</th>
<th>τₙ (ms)</th>
<th>Dₙ (μm²/ms)</th>
<th>fᵣ (Hz)</th>
<th>τᵣ (ms)</th>
<th>L (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO₂/N719</td>
<td>20.0</td>
<td>8.0</td>
<td>7.7</td>
<td>3.2</td>
<td>49.7</td>
<td>19.6</td>
</tr>
<tr>
<td>TiO₂/N719/BPQDs</td>
<td>16.0</td>
<td>10.0</td>
<td>6.1</td>
<td>3.2</td>
<td>49.7</td>
<td>17.4</td>
</tr>
</tbody>
</table>
Figure S7. Cyclic voltammograms: (a) PANI, (b) PANI/N719, and (c) PANI/BPQDs photocathodes at different scanning rates from 5–100 mV/s with the anodic and cathodic peak current densities as a function of the square root of the scanning rates for (d) PANI, (e) PANI/N719 and (f) PANI/BPQDs photocathodes.
Table S4. The fitting EIS parameters of the bifacial n-type DSSCs with different photocathodes (PANI, PANI/N719 and PANI/BPQDs).

<table>
<thead>
<tr>
<th>Photocathodes</th>
<th>$R_s$ (Ω)</th>
<th>$R_I$ (Ω)</th>
<th>$R_3$ (Ω)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PANI</td>
<td>52.1</td>
<td>17.6</td>
<td>45.9</td>
</tr>
<tr>
<td>PANI/BPQDs</td>
<td>39.1</td>
<td>10.7</td>
<td>21.7</td>
</tr>
<tr>
<td>PANI/N719</td>
<td>33.2</td>
<td>9.8</td>
<td>53.4</td>
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Table S5. IMPS/VS parameters of the quasi-solid-state DSSCs with different photocathodes (PANI, and PANI/BPQDs).

<table>
<thead>
<tr>
<th></th>
<th>$f_c$ (Hz)</th>
<th>$\tau_c$ (ms)</th>
<th>$D_n$ ($\mu m^2/\text{ms}$)</th>
<th>$f_r$ (Hz)</th>
<th>$\tau_r$ (ms)</th>
<th>$L$ ($\mu m$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PANI</td>
<td>20.0</td>
<td>8.0</td>
<td>7.7</td>
<td>5.0</td>
<td>31.8</td>
<td>15.6</td>
</tr>
<tr>
<td>PANI/BPQDs</td>
<td>25.1</td>
<td>6.3</td>
<td>9.7</td>
<td>3.2</td>
<td>49.7</td>
<td>22.0</td>
</tr>
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</table>
Figure S8. (a) UV-Vis-NIR absorption, and (b) IMPS curves, (c) IMVS curves, and (d) I-V curves of the DSSCs with the PANI/BPQDs and PANI/graphene photocathodes. The I-V tests are carried out under illumination with a power of 100 mW/cm². The PANI/BPQDs photocathode shows better optical absorption in the whole range between 300 and 1100 nm than the PANI/graphene photocathode. The IMPS/VS results provide confirmation of the larger $D_n$ and $\tau_r$ for the PANI/BPQDs based device compared to that with the PANI/graphene. Because of the both improvement in both NIR light absorption and charge transporting performances, the DSSC with PANI/BPQDs shows better power conversion efficiency (6.85\%) than that of device with the PANI/graphene photocathode (5.03\%).
Table S6. IMPS/VS parameters of the quasi-solid-state DSSCs with the PANI/BPQDs and PANI/graphene photocathodes.

<table>
<thead>
<tr>
<th>Photocathodes</th>
<th>$f_c$</th>
<th>$\tau_c$</th>
<th>$D_n$</th>
<th>$f_r$</th>
<th>$\tau_r$</th>
<th>$L$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(Hz)</td>
<td>(ms)</td>
<td>($\mu$m$^2$/ms)</td>
<td>(Hz)</td>
<td>(ms)</td>
<td>($\mu$m)</td>
</tr>
<tr>
<td>PANI/BPQDs</td>
<td>25.1</td>
<td>6.3</td>
<td>9.7</td>
<td>5.0</td>
<td>31.8</td>
<td>17.6</td>
</tr>
<tr>
<td>PANI/graphene</td>
<td>20.0</td>
<td>8.0</td>
<td>7.7</td>
<td>10.0</td>
<td>15.9</td>
<td>11.1</td>
</tr>
</tbody>
</table>

Table S7. The photovoltaic parameters of the quasi-solid-state DSSCs with the PANI/BPQDs and PANI/graphene photocathodes.

<table>
<thead>
<tr>
<th></th>
<th>$J_{sc}$</th>
<th>$V_{oc}$</th>
<th>FF</th>
<th>$\eta$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(mA/cm$^2$)</td>
<td>(V)</td>
<td>(%)</td>
<td></td>
</tr>
<tr>
<td>PANI/BPQDs</td>
<td>24.31</td>
<td>0.64</td>
<td>0.44</td>
<td>6.85</td>
</tr>
<tr>
<td>PANI/graphene</td>
<td>19.98</td>
<td>0.56</td>
<td>0.45</td>
<td>5.03</td>
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</tbody>
</table>
Figure S9. (a) UV-vis-NIR absorption spectra of the PANI photocathode for different polymerization times; (b) The I-V curves and (c) the power conversion efficiency of the devices fabricated with the using PANI photocathode for different polymerization times; (d) Cross-sectional SEM image of the PANI photocathode with the polymerization time of 20 min. A longer polymerization time increases the thickness of the PANI film and, whose light absorption becomes stronger. The optimal photovoltaic performance is observed from the device fabricated with a polymerization time of 20 min and a corresponding film thickness of 1 μm. A thicker PANI film may adversely affect charge transport in the DSSC because of worse catalytic and electrochemical properties caused by the increased aggregations and trapping states in the PANI.
Figure S10. (a) UV-Vis-NIR absorption spectra of the PANI and PANI/BPQDs photocathodes modified with the 0, 4, and 20 μg/mL BPQDs solutions; (b) IMPS, (c) IMVS, and (d) I-V curves of the DSSCs with PANI and PANI/BPQDs photocathodes modified with the 0, 4, and 20 μg/mL BPQDs solutions. The device loading prepared with the diluted BPQDs solution (4 μg/mL) shows better optical and electron transporting performances, which may be attributed to more homogeneous deposition of the BPQDs and decreased BPQDs aggregation formation on the PANI surface, thereby resulting in improving the photovoltaic properties of the DSSC.
### Table S8. The IMPS/VS and photovoltaic parameters of the devices with different BPQDs concentrations loading.

<table>
<thead>
<tr>
<th></th>
<th>$f_c$ (Hz)</th>
<th>$\tau_c$ (ms)</th>
<th>$D_n$ ($\mu$m$^2$/ms)</th>
<th>$f_r$ (Hz)</th>
<th>$\tau_r$ (ms)</th>
<th>$L$ ($\mu$m)</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>$V_{oc}$ (V)</th>
<th>$FF$ (%)</th>
<th>$\eta$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PANI</td>
<td>20.0</td>
<td>8.0</td>
<td>7.7</td>
<td>5.0</td>
<td>31.8</td>
<td>15.6</td>
<td>21.44</td>
<td>0.59</td>
<td>0.46</td>
<td>5.82</td>
</tr>
<tr>
<td>PANI/BPQDs (4μg/mL)</td>
<td>25.1</td>
<td>6.3</td>
<td>9.7</td>
<td>3.2</td>
<td>49.7</td>
<td>22.0</td>
<td>24.31</td>
<td>0.64</td>
<td>0.44</td>
<td>6.85</td>
</tr>
<tr>
<td>PANI/BPQDs (20μg/mL)</td>
<td>25.1</td>
<td>6.3</td>
<td>9.7</td>
<td>5.0</td>
<td>31.8</td>
<td>17.6</td>
<td>22.39</td>
<td>0.58</td>
<td>0.42</td>
<td>5.45</td>
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</table>
