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Flexible Quantum Dot Light Emitting Devices for Photomedicine

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Abstract
We demonstrate highly efficient quantum dots with narrow spectra and specific peak wavelengths for photomedical applications. Flexible quantum dot light emitting devices with peak EQE of 8.2% and luminance over 20,000 Cd/m² were achieved which will be employed for treatment of oral cancers or diabetic wounds.

Author Keywords
Flexible Quantum dot light emitting devices, photomedicine, photodynamic therapy, photobiomodulation

1. Background
Photodynamic therapy (PDT) and photobiomodulation (PBM) are two branches of photomedicine that involve the application of light with respect to disease and health. In PDT, light of a specific wavelength is used to excite photosensitizers (i.e. a drug that is nontoxic itself, but can be activated by light exposure selectively) and turn molecular oxygen into singlet oxygen that can kill unwanted tissues, cells including cancer cells, bacteria, fungi and viruses, and thus lead to the treatments of cancers, infections, etc. In PBM, light can enhance cellular function leading to beneficial clinical effects, such as wound repair or hair regrowth [1].

Although PDT and PBM have already been clinically demonstrated as effective minimally invasive or noninvasive strategies to treat cancers and infections, improve wound repair, reduce pain, and grow hair, etc., they still haven’t received widespread acceptance mainly because of challenging light source requirements. The ideal light source needs to have the right color with a narrow emission spectrum to match the absorption of photosensitizers, with a high enough power density for sufficient excitation, but low heat emission to avoid pain for the patients, and flexible form factors with homogeneous emission so that it can be easily applied to patients without worrying about over or under treatments.

Currently, laser and LED arrays are the dominant light sources used in photomedicine because they can provide sufficient power density at the proper wavelength window [2]. However, these expensive, hot, rigid, heavy and inhomogeneous light sources are not commonly available in small clinics and treatments are thus only available at limited locations and often require expensive hospital visits, limiting their further penetration into practical clinical use.

OLEDs were once proposed to work as light-emitting bandages for PDT [3] because of their unique form factors as thin, flexible, lightweight and uniformly large area luminaires. But this method was later abandoned, mainly because a relatively high brightness (>20,000 Cd/m² or ~10 mW/cm²) at wavelengths of deep red region is demanded in the photomedical field in order to have deep tissue penetration while still maintaining sufficient energy for molecular excitation [1]. Existing OLEDs with either fluorescent or phosphorescent emitters can’t achieve such high brightness at the right wavelength windows because of significant efficiency roll-off problems of OLEDs at high current density [4] and the lack of efficient deep red emitters with narrow spectra [5].

Recently, our group has developed ultrabright and efficient deep red quantum dot light-emitting devices (QLEDs) [6]. The devices have a peak emission wavelength of 620 nm, a narrow bandwidth of 22 nm and can achieve high current efficiency (20.5 Cd/A at ~20, 000 Cd/m²) and small efficiency roll-off at high driving current density. Ultrahigh brightness of 165, 000 Cd/m² can be achieved at a current density of 1000 mA/cm², which sets a new brightness record for existing organic related red light emitting devices.

Table 1. Competitive advantages of QLEDs over other light source technologies for photomedicine.

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<tr>
<th>Color</th>
<th>Wavelength</th>
<th>Power Density</th>
<th>Heat</th>
<th>Flexibility</th>
<th>Large Area</th>
<th>Light Weight</th>
<th>Cost</th>
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<tbody>
<tr>
<td>Laser</td>
<td>mm/PM</td>
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<td>LED array</td>
<td>mm/PM</td>
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<td>OLED</td>
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<tr>
<td>Our QLED</td>
<td>mm/PM</td>
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With the potential to be low cost, wearable, disposable light emitting bandage products, these ultrabright deep red QLEDs enjoy all form factor merits like OLEDs, while having emission peak width 3-5 times narrower, and with a 2-4 times higher power density (under similar driving conditions) than OLEDs. These advantages can translate into a greater than one order improvement in photomedical treatment efficacy over traditional OLEDs. Being solution processable at low costs, QLEDs...
represent the ideal photomedical light sources with all desired features over other lighting strategies as summarized in Table 1. Preliminary PBM and PDT tests with these ultrabright QLEDs as light sources have been carried out in vitro and were reported last year [7, 8]. The experimental results demonstrated that QLEDs for PBM could increase cell metabolism in multiple cell lines by ~11-25% over control systems [7, 8] and QLED PDT could efficiently kill bacterial and cancerous cells, in a similar fashion with parallel studies using inorganic LEDs as comparisons [8]. The demonstration of ultrabright deep red QLEDs and their effectiveness for PBM and PDT warrant further studies investigating QLED devices for photomedical applications.

In this paper, we present our new developments of QD materials and demonstration of flexible QLEDs. QDs were synthesized with precisely controlled emission peaks at the absorption wavelengths of photosensitizers for wound repair, inflammation and cancer treatment applications. QLED devices were also successfully transferred onto a flexible substrate and well encapsulated to achieve low cost, wearable, disposable light emitting bandage products.

2. Experiment and Results

1) QDs with different wavelengths

While we had reported the promising results of QLEDs based PDT and PBM, it should be noted that the emission wavelength of the QLEDs we used is 620 nm. Although this falls into the favorite range for most photomedical applications (620-670 nm), highly effective phototherapy calls for better wavelength specific spectral control to maximize the absorption for photosensitizers (for PDT) or cytochrome C (for PBM) from QLED.

Thanks to quantum confinement effect, by tuning the quantum dot synthesis conditions (QDs size and composition), we have achieved highly efficient quantum dot materials with precisely controlled emission peaks at the following wavelengths for cancer treatment and wound repair applications (shown in Figure 1): 1) 631 nm for porfimer sodium (Photofrin®), a FDA approved photosensitizer widely used for various PDT cancer treatments; 2) 646 nm which is close to the absorption peak (652 nm) of Temoporfin, a photosensitizer (based on chlorin) used in photodynamic therapy for the treatment of squamous cell carcinoma of the head and neck.

![Quantum Dot Emission Spectra](image1)

**Figure 1.** The absorption spectra (dashed line) of some common photosensitizers (PS) and the experimental emission spectra of quantum dots under UV excitation. Porfimer sodium (Photofrin®), aminolevulinic acid (ALA) and temoporfin are three photosensitizers widely used for various PDT cancer treatments.

QDs with different wavelengths of 625nm, 631nm and 646 nm all exhibit narrow spectra (FWHM< 22nm) as shown in Figure 1. Better results for QLEDs based PDT and PBM are expected using these QDs that fit well into the absorption spectra of photosensitizers.

In addition, QDs emission can also be tuned to the absorption of newly developed photosensitizers. Currently such wavelength control is realized by expensive, bulky lasers, although the laser light needs to be waveguided with optical fibers and spread out with diffusers for large area applications. Obviously, QLEDs have a great advantage over lasers in terms of their lower expense and complexity.

2) Flexible devices

Flexible QLEDs are in obligatory demand to achieve a solution that is functional for a wearable bandage light source. A transparent indium tin oxide cathode (ITO) conductor with silicon nitride layer beneath on polyethylene naphthalate (PEN) substrate was employed for our flexible QLED fabrication. The devices were later encapsulated with a laminated barrier film developed by Holst Centre (i.e. a hybrid thin-film encapsulation stack consisting of two inorganic barrier layers of silicon nitride deposited at low temperature with an organic layer in between) [9] for testing in air (Figure 2).

![Flexible QLEDs](image2)

**Figure 2.** (a) Photograph of one flexible QLED device lighting up in air, (b) Structure of the flexible devices on PEN substrate.

Our flexible devices consist of multiple layers as ITO/ZnO nanoparticles/Cs2CO3/CdSe-ZnS-CdZnS core-shell-shell QDs/2,2',7,7'-tetrakis[N-naphthalenyl(phenyl)-amino]-9,9-spirobi fluororene/1,4,5,8,9,11-hexaazatriphenylene-hexacarbonitrile/Al anode (Figure 2. b). These organic-inorganic hybrid QLED devices were fabricated by a combination of solution-processing and vacuum vaporization techniques as reported in [6].

After encapsulation, the devices were tested in ambient conditions. The electroluminescence spectrum, as exhibited in Figure 3 a, displays a saturated quantum dot emission profile with a FWHM of 28 nm at a peak wavelength of 630 nm, falling right into the absorption range of Photofrin® as shown in Figure 1.

**Figure 3 b** demonstrates the current-density/luminance/voltage (J-L-V) characteristics of the flexible devices. With a turn-on voltage of 1.9V, the QLEDs could achieve a peak external quantum efficiency (EQE) of 8.2% at a current density of 19 mA/cm², corresponding to a luminance of 1800 cd/m². Luminance can reach up to over 20,000 cd/m², which is sufficient for photomedicine treatment, at current density of 283 mA/cm². It should be noted that the devices also exhibit low efficiency roll-off that EQE only lose 1.5% when luminance increased from 1100 nits (8.2%) to 20,000 nits (6.7%).
Though the lifetime of these flexible QLEDs are limited in air at the present time, the established knowledge from OLEDs field for flexible devices encapsulation (e.g. ALD or PECVD encapsulation) could help enable the further development of QLEDs and prolong the lifetime of QLEDs to satisfy clinical requirements. Ultrabright flexible QLEDs with long lifetimes could represent the ideal light source to work as highly efficient, low-cost and disposable bandage products for office-visit photomedical treatment in terms of their high luminance, wavelength tunability and narrow spectra.


The vast opportunities of photomedicine posed a special challenge for research decisions. After careful evaluation, oral cancer and diabetic wound treatments were selected as initial QLED treatment targets because of the technical feasibility, high social impacts and commercialization potential. The treatment of oral cancer and diabetic wounds have urgent requirements of device flexibility, light homogeneity, while the device size can be small (<2 cm²) and can thus be fabricated in a research or pilot scale laboratory at low cost (i.e. <$10/piece).

Oral cancer has been considered to be a global health crisis because of its high incidence in India. Although largely preventable, cancers of the oral cavity account for over 30% of cancers reported in India. This is one of the highest oral cancer rates in the world and is largely due to the widespread popularity of chewing gutka, a tobacco mixture with crushed betel nut and acacia extract. Treatment typically consists of surgery and/or radiotherapy, which requires expertise and medical infrastructure that are often not available in the settings where they are most needed. Even if the disease is detected relatively early, these interventions can be disfiguring and present major quality of life issues including the ability to chew, swallow, speak, and work, thus increasing the societal economic burden on an already burdened economy. On the other hand, early clinical studies showed that PDT is a safe and effective approach, with remarkable healing and is especially effective for early stage cancerous and precancerous lesions of the oral cavity. While the PDT photosensitizer is readily available, the expensive laser light source setup and lower the overall treatment cost for both oral cancer and diabetic wound repair treatment [14,15].

4. Impact

In this paper, we demonstrated QDs with high efficiency, narrow spectral and specific wavelengths. The emission spectra of these QDs could well match the absorption spectra of photosensitizers for PDT or cytochrome C for PBM, and thus improve the efficacy of photomedical treatment. Flexible QLEDs which could be the perfect light source for photomedicine were fabricated and presented. Peak EQE of these devices could reach up to 8.2% while luminance could exceed 20,000 Cd/m².

We believe this work could create a huge opportunity for OLEDs, QLEDs and photomedicine with tremendous potential technical, economic and social impacts. For mature OLED technology, their established knowledge of flexible devices will be important for further development of flexible QLEDs which, as an emerging technology, have clear advantages in color tunability, color purity and high power density over state-of-the art OLEDs. The joint efforts of OLED and QLED communities will enable advanced thin, flexible, light weight, homogeneously large area QLED devices that will gear up the adoption of photomedicine in multiple hundred-billion-dollar healthcare markets [16,17], helping manage cancer, acute and chronic wounds, inflammation, and antimicrobial resistance among others.

Figure 3. Flexible inverted quantum-dot light emitting devices (QLEDs) (a) Spectra of QLED electroluminescence at 3V (b) Luminance and current density versus driving voltage and (c) External quantum efficiency and luminous power efficiency versus luminance for typical devices. Device was tested at ambient condition (temperature: ~25°C; humidity: ~70%).
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6. References
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