

Luminescence Enhancement in Polymer/Nanoparticle Composite Electro-Optic Devices

Numerous technical advances in the area of polymer light emitting diodes (PLEDs) have been made since their discovery in 1990 by Friend *et al* at Cambridge University^[1]. PLEDs are derivatives from the more commonly known LED (light emitting diode) devices. LEDs are solid-state semiconductor devices that convert electrical energy into light. They are typically used as indicator lights and numeric displays on many consumer electronic devices. The first LEDs were made of AlGaAs (aluminum gallium arsenic) and today the brightest and most abundant LEDs are comprised of AlInP (aluminum gallium indium phosphide) and InGaN (indium gallium nitride)^[2].

PLEDs utilize the same physic principles as LEDs but use polymers as the active light-emitting layer. PLEDs have many advantages when compared to normal inorganic LEDs. Simple and cost-efficient manufacturing and the ability to generate a uniform area of light demonstrate that PLEDs exhibit excellent promise for current and future electronic and optical applications. The first PLEDs used poly(phenylene vinylene) PPV as the emitting layer^[3]. PPV is an undoped conjugated polymer, which has a molecular structure given in Figure 1.

Today many other polymers have been used to emit light such as polythiopenes, polypyridine, poly(pyridyl vinylenes) and polyphenylene^[3]. Light emitting diodes consist of active or emitting layers placed between a cathode (typically aluminum or calcium) and an anode (ITO, indium tin oxide). A diagram of a typical PLED is shown in Figure 2. When the two electrodes are connected electrons are injected from the cathode into the p^* -band semiconducting polymer and holes are injected from an electrode into the p -band. The oppositely charged carriers in the two bands meet within the polymer films and recombine (return to their ground state) radiatively to give off light^[4].

The major drawbacks of the PLEDs have been operating life times and insufficient device radiances. Recently, it has been shown that incorporating oxide nanoparticles into a PPV derivative enhances the PLED current density and radiance by an order of magnitude. In addition CdS nanoparticles have been used in heterostructure devices with a polymer emitting layer to improve polymer photovoltaic device performance. The exact mechanism of this enhanced performance in polymer/nanoparticle devices is still widely debated. Synthesis and possible mechanisms which aim to explain the improvement in charge injection and charge transport in the oxide and CdS nanoparticle composite devices will be discussed in this review.

Synthesis of Polymer/Nanoparticle

Incorporating the nanoparticles into the active polymer emitting layer can be achieved by different synthetic methods. One method to prepare SiO_2 and TiO_2 colloids is by the hydrolysis of SiCl_4 and TiCl_4 respectively in a water-in-cyclohexane reverse microemulsion with dioctylsulfosuccinate as surfactant, and purified by dialysis against pH-adjusted MeOH^[5,6]. Next a PPV precursor poly(p-

xylene tetrahydrothiophenium chloride) is mixed with the SiO₂ and TiO₂ nanoparticles and centrifuged. The hydrophilicity of SiO₂ and TiO₂ nanoparticles can be lowered by capping them with a 10:1 mixture of ethyl and ammoniopropyl groups, which also result in a positively charged surface. After thermal treatment the mixtures are converted into PPV nanocomposites. These PPV nanocomposites are then spin-coated onto glass substrates during PLED fabrication.

The CdS nanoparticles are prepared by first introducing H₂S gas into an argon-purged solution of *N,N*-dimethylformamide (DMF) and Cd(CH₃COO)₂·2H₂O. Unreacted H₂S is removed from the CdS-DMF solution by nitrogen purging for 1.5 h. The surface of the CdS nanoparticles is then modified by introducing a solution of pentafluorothiophenol (C₆F₅SH)-DMF into the CdS-DMF solution. The final result is pentafluorophenyl-capped CdS nanocrystals. The purpose of the CdS capping agent is to inhibit agglomeration^[7-8].

Nanoparticle Improvement Mechanisms

The mechanisms explaining the enhanced current density and radiance in PLEDs using nanoparticle composites as the active emitting layer are not particularly clear. Initially, optical scattering from the nanoparticle surfaces was believed to be a factor but was excluded since the observed radiance enhancement is independent from the refractive index which would be altered upon scattering effects^[9]. A possible explanation of the current enhancement was an increase of the recombination at the polymer/nanoparticle interfaces. However, this was also quickly discounted because an increase in recombination would result in increased efficiency of the PLED, which was not being observed.

Nanoparticle Morphology

A more plausible mechanism has been developed, which suggests that the change in morphology leads to both the enhanced current density and radiance in polymer/nanoparticle LEDs^[9,10]. When nanoparticles are spun and mixed into solution with the active polymer layer (i.e. MEH-PPV) strong electrostatic forces attract the nanoparticles to the anode and to themselves. The MEH-PPV solution is then drawn around the nanoparticles into cavities, which result in rough surfaces on which the cathode is evaporated. Thus producing a rough interface between the cathode and the composite film leads to a significant increase in surface area and also electron injection. Additionally, higher current densities and device radiances can result from effective thin spots which are formed from the capillary forces in the nanoparticle incorporation process. These spots allow extra pathways for current flow^[10]. Typically, these “spots” would lead to small electrical shorts in electric devices but the presence of the nanoparticles serve as physical barriers to electrical shorts by creating in essence a “tortuous path” in the MEH-PPV composite^[10].

Effective Film Thickness Improvement with Nanoparticles

Optimal electro-optic properties are obtained in thin film devices rather than the “bulk” film due to higher chain mobility, structural order and a faster response time to an electric field. Thus thinner films are more desirable in electro-optic devices such as PLEDs. However, mechanical strength and substrate coverage are superior in thicker films. Blom *et al* investigated the current density (J) and voltage bias (V) characteristics as a function of the effective length (L_{eff}) of the active emitting layer

with and without SiO₂ nanoparticles^[9]. A plot of J (A/m²) vs. V (V) for the active emitting PPV layer with and without SiO₂ nanoparticles for different film thicknesses is given in Figure 3. The magnitude and voltage dependence for the SiO₂ composite film with an effective length L_{eff} = 200 nm was nearly identical to the film without the SiO₂ nanoparticles with an effective length L_{eff} = 80 nm. Nanoparticle composites have the ability to thus utilize the mechanical strength and substrate coverage of thicker films while maintaining the desired electro-optic properties of thin films.

Driving Voltage Effects

From Figure 3 it is still difficult to see the effect nanoparticle composites have on driving voltage in PLEDs. It appears that the PPV+SiO₂ composite device exhibits a slightly lower driving voltage than the plain PPV device. More efficient and cost-effective PLEDs could be fabricated if the driving voltage (operating voltage) of PLEDs was lowered. As you raise the voltage, it is clear the current increases as well, but the idea is to achieve the same effect at lower voltages and utilize the charge carriers more efficiently. Lowering driving voltage of PLED devices leads to improved quantum and power efficiency^[10]. More convincing results by Carter *et al* show in Figure 4 the radiance-voltage and current-voltage curves for 1:1 TiO₂ (anatase)/MEH-PPV, 1:1 TiO₂ (rutile)/MEH/PPV, 1:1 SiO₂/MEH-PPV and for MEH-PPV film without nanoparticles. From Figure 4 it is evident that a lower driving voltage (~1.8 V) can be achieved using TiO₂ or SiO₂ nanoparticles, which is lower than the plain MEH-PPV film. The improvement of nanoparticle composite films on the external quantum and power efficiency can be seen in Figure 5. Nanoparticles increased light output in these devices and exhibited higher quantum and power efficiency. Nanoparticles do not decrease the external quantum efficiency because of inclusions of impurities as was originally believed^[10].

Temperature Dependence of Polymer Composite Devices

In addition to increasing the effective layer thickness and lowering the driving voltage, polymer/nanoparticle composites can be thermally controlled to improve the quantum and recombination efficiency of electro-optic devices^[11]. Experimentally it has been shown by Carter *et al* that decreasing the temperature in MEH-PPV/ SiO₂ active layers increases the quantum efficiency of the composite devices. The mechanism for this temperature dependency starts with the saturation of charge carriers by nanoparticle charge traps. Nanoparticles such as SiO₂ and TiO₂ will take electrons from the active polymer (MEH-PPV) because the nanoparticles act as an electron acceptor. Therefore device quantum efficiencies begin low due to these charge traps, which cause an imbalance in the charge injection carriers. The nanoparticles continue this process of extracting electrons until a surface charge density optimization or charge balance is reached, at which point remaining charges will be repelled by Coulomb forces. Finally, the external quantum efficiency increases rapidly with subsequent current increase. As the quantum efficiency rises as seen in Figure 6, the required current needed to obtain this charge balance of injected carriers drops with lowering of the temperature. A lower temperature leads to lower mobilities, which requires fewer charges since the charges can now diffuse longer into the active region. Therefore at lower temperatures lower currents are needed to obtain recombination saturation and thus incorporation of nanoparticles can be used as trap centers to improve the external quantum efficiency^[11].

Refractive index tuning from nanoparticles

Nanoparticles can also be used to tune the refractive index of the active emitting layer^[5] to create photonic structures with sufficient optical contrast to support a higher current density^[6]. A large refractive index contrast between surfaces is crucial in reflectivity devices since light reflected at each interface constructively interferes with light reflected from other interfaces. The amplified reflection offsets losses due to absorption. Therefore manipulating refractive indices can lead to fabrication of microcavity LEDs (MCLEDs), with improved properties in terms of efficiency, brightness, directionality, spectral linewidth, and speed of response. MCLEDs allow radiative decay of electron-hole pairs to be coupled to the cavity modes which enhances device luminance. The optical transition of the injected electrons and holes is confined and modified inside the microcavity. The microcavity consists of a wavelength size active region surrounded top and bottom by distributed Bragg reflector (DBR). A general schematic of a MCLED is given in Figure 7. The DBR is comprised of alternating layers of PPV and composite PPV +SiO₂ nanoparticles. The large contrast in refractive index at 550 nm ($n_{550,PPV} = 2.5$ to $n_{550,PPV+SiO_2} = 1.45$) between the PPV and SiO₂ provides the mechanism for enhanced performance in the device. The refractive index of the PPV and SiO₂ layer can be tuned via SiO₂ volume loading from 2.35 at 0% (SiO₂) to 1.7 at 50% (SiO₂). Refractive index tuning demonstrates a definite advantage of SiO₂ nanoparticle incorporation.

The well dispersed SiO₂ nanoparticles combined with PPV lower the effective refractive index of the composite. Voids and chain alignment disruption due to the nanoparticle density are further explanations for the decrease in the effective refractive index of the composite. MCLEDs have also been demonstrated using other matrix polymers and inorganic nanoparticles such as polyfluorenes and ZrO₂, respectively.

Nanoparticles in Photovoltaic Devices

In addition to PLEDs, CdS nanoparticles can be used to improve the performance of polymer photovoltaic devices. Photovoltaic or “solar cells” are LEDs in reverse. Radiation is absorbed and an electrical voltage results. It is important in photovoltaic devices for electrons and holes to travel *without* radiative recombination. These charge carriers need to travel along separate pathways in the materials to their respective anodes. CdS nanoparticles can be incorporated to assist in the charge separation of these photoexcited carriers^[12] by providing a separate “pathway” for the electrons to travel. Charge separation is known to be enhanced at interfaces with materials of higher electron affinity, where it is energetically favorable for electron transfer to the second material.

Upon radiation in a polymer/nanoparticle photovoltaic device, electron-hole pairs are dissociated with the electron transferring to the nanocrystal (CdS) and the hole transferring to the polymer (MEH-PPV). Raising the concentration of CdS nanoparticles in the MEH-PPV polymer matrix forms a connected network, which makes it easier for the electrons to travel through the whole material to the electrode. Similarly at lower concentration of nanoparticles fewer electrons will be able to travel all the way to the electrode since the nanoparticles are isolated. In fact only those electrons closest to the electrodes will make it completely^[12]. Even in highly concentrated and well connected polymer/nanoparticle composites the quantum efficiency is below 100% because some

electrons will come upon dead ends in the network and be forced to jump to the neighboring polymer and thus recombine, lowering the quantum efficiency^[12].

Nanocrystals in these devices are typically capped by an organic ligand (triethylphosphineoxide (TOPO)) of ~11 Å, which ensures solubility and creates a barrier between the polymer matrix. TOPO has been shown to be significant in suppressing luminance quenching, which occurs due to an annihilation of positive space charge and an increase in the threshold voltage. Removal of this layer leads to free electron transfer which results in separated electron-hole pairs that can recombine to give off light, which is undesirable in photovoltaic devices. This also confirms that charge transfer occurs at the polymer/nanocrystal interface, since^[12].

Polymer/Nanoparticle Laser Diodes

Lasing has been previously demonstrated in polymer diodes^[13]. The concept of lasing uses the fundamental principle of stimulated emission. Stimulated emission occurs when a photon of energy ($h\nu$) strikes an electron already in a higher energy level. The photon forces the electron to decay to the lower energy state producing two photons with identical energy ($h\nu$). This phenomenon has been historically limited to solid-state semiconducting materials. However, using conductive polymer with sufficient gain and pumping, stimulated emission can also be obtained in polymeric devices. Pumping refers to the external energy source which is used to promote the initial photons to the higher energy state (population inversion) and gain indicates the exiting beams net increase in photons as a result of stimulated emission. The whole idea is to narrow the emission of the excited beam to obtain maximum intensity, which is referred to as *gain or spectral narrowing*.

TiO₂ nanoparticles can be incorporated into a polymer (MEH-PPV) composite matrix to significantly narrow the emission spectrum. These TiO₂ particles scatter emitted photons in the active polymer matrix which creates a gain that exceeds loss, which is a fundamental requirement in lasing^[14]. This scattering of the titania nanoparticles increases the path length traveled by the emitted light, which creates stimulated emission if the scattering length increase is greater than the original gain length of the photons when pumped above a certain threshold. Increasing the scattering length of the photons improves the probability of a photon striking another photon which increases the amplification of the stimulated emission. (look back in notes on this)

Figure 8a indicates that gain narrowing occurred in the presence of 10^{10} cm^{-3} TiO₂ particles. The solid line in Figure 8a indicates the broad luminescence emission from a plain MEH-PPV polymer and the dashed line represents the narrowed luminescence of a MEH-PPV solution with 10^{10} cm^{-3} TiO₂ particles added. Figure 8b displays a similar relation between luminescence emission and excitation energy. The excitation energy is the energy need to pump the polymer/nanoparticle device above the lasing threshold.

This review has shown a number of different applications for nanoparticles in electro-optic devices. The primary use is still in PLEDs and different mechanisms have been proposed and supported to explain the improvement seen in these devices by incorporating nanoparticles into the conjugated polymer matrix. Nanoparticle applications in other electro-optic devices such as photovoltaic and polymer diode lasers have also been realized. AS the science of polymeric electro-optic devices

advances, more potential applications could be discovered by incorporating nanoparticles into the active polymer matrix.

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