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Blue Organic-Inorganic Light Emitting Diode Based on Electroluminescence CdS Nanoparticle

Asama N. Naje, Omar A. Ibrahim and Estabraq T. Abdullah
Department of Physics, College of Science, University of Baghdad, Baghdad, Iraq

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Abstract

A hybrid cadmium sulfide nanoparticles (CdSNPs) electroluminescence (EL) device was fabricated by Phase – Segregated Method and characterized. It was fabricated as layers of (ITO/poly-TPD:CdS) and (ITO/poly-TPD:CdS /Alq_3). Poly-TPD is an excellent Hole Transport Layer (HTL), CdSNPs is an emitting layer and Alq_3 as electron transport layer (ETL). The EL of Organic-Inorganic Light Emitting Diode (OILED) was studied at room temperature at 26V. This was achieved according to band-to-band transition in CdSNPs. From the I-V curve behavior, the addition of Alq_3 layer decreased the transfer of electrons by about 250 times. The I-V behavior for (poly-TPD/CdS) is exponential with a maximum current of 4500 µA. While, the current is constant for (poly-TPD:CdS /Alq_3) and the maximum current was 16.5 µA. Semiconductor nanoparticles like CdS are attractive for fabricating hybrid LEDs with spectrally pure color, low operating voltage values, and short-wavelength electro-luminescence, needed for the RGB devices. The correlated color temperature (CCT) was equal to (1700 ^{o}K) for the emitted blue light.

Keywords: CdSNPs, Alq3, Electroluminescence device, light emitting diode.

الصمام الثنائي الباعث للضوء الازرق العضوي والغير عضوي المعتمد على الجسيمات النانوية لكبريتيد الكادميوم ذات التلألؤ الكهربائي

اسامه ناطق ناجي*,عمر عدنان ابراهيم , استبرق طالب عبدالله
قسم الفيزياء, كلية العلوم جامعة بغداد, بغداد, العراق

الخلاصة

تم تصنيع وتوصيف جهاز هجين من جسيمات كبريتيد الكادميوم النانويه . تم تصنيع الجهاز من عدة طبقات وهي طبقه ناقله للفجوات (ITO/poly–TPD:CdS) و (poly–TPD:CdS /Alq3) وجسيمات كبريتيد الكادميوم النانوية كطبقة انبعاث وثلاثي(8–هيدروكسي كينوليناتو) الألومنيوم (Alq3) كطبقة ناقله للالكترونات. تمت دراسة التلألؤ الكهربائي (EL) للديود العضوي غير العضوي الباعث عند 26 فولت وبدرجة حرارة الغرفة. تم تحقيق ذلك وفقًا للانتقال من النطاق إلى النطاق لكبريتيد الكادميوم من خلال تصرف منحني التيار– فولتية أدت إضافة طبقة ثلاثي(8–هيدروكسي كينوليناتو) الألومنيوم إلى قلة انتقال الإلكترونات بنحو 250 مرة. لوحظ ان تيار– فولتية لـ (poly–TPD / CdS) يسلك سلوكا اسيًا بحد أقصى للتيار يبلغ 4500 مايكرو امبير. بينما التيار ثابت لـ (poly–TPD: CdS / Alq3) وكان الحد الأقصى للتيار 16.5 مايكرو

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*Email: asama.naje@sc.uobaghdad.edu.iq

امبير. تعتبر الجسيمات النانوية شبه الموصلة مثل CdS جذابة لتصنيع المصابيح الهجينة ذات الفولتية التشغيلية المنخفضة واللون النقي الطيفي والتلألؤ الكهربائي ذي الطول الموجي القصير. اخيرا من خلال دراسة درجة حرارة اللون المرتبطة (CCT) وجد ان قيمتها تقريبا 1700 كلفن للضوء الازرق الباعث.

1. INTRODUCTION

Light emitted diodes hybrid device consisting of organic/inorganic components have been developed during the last years from a single layer which is sandwiched to complex multilayered by adding hole and electron transporting/injecting layers. The injection of hole-electron can enhance the balance of the device [1] [2]. Hybrid opto-electronic devices combine nanoparticles, which have unique optical and electrical properties, with an organic material designed to transit charges towards the diffusion layer in light emitting devices (LEDs) or from the diffusion layer to electrode in photodiodes [3]–[5]. Hybrid Organic-Inorganic NP LEDs (OILED) benefits are manifested in controlled charge transport through amorphous organic thin films and narrow NPs emission, yielding efficiencies approaching the Organic Light Emitting Diode (OLED) and LED. This property of OILEDs allows for the universal design of multicolor OILEDs by simply changing the NPs emission layer without altering the transport layers (i.e. the organic layers) [6] [8].

The nanoparticles have been considered as an attractive option for opto-electronic devices of the next generation, as a result of their good physical characteristics of the size-tunable band gaps, good photostability, photo or electro luminescence efficiency, and compatibility with the approaches of solution processing [9][11]. The NPs semiconductor have many extrinsic as well as intrinsic deep-level defects emitting various light colors, which include green, violet, blue, yellow, red and orange, in other words, all white light constituents [12] [14].

Cadmium sulfide nanoparticles (CdSNPs) are (II-VI) semiconductor materials, which have direct energy gap of (2.42 eV). It is of quite a small size, so quantum dots show opto-electronic behavior that differs from the bulk semi-conductors of identical compositions [15-17]. The electroluminescence (EL) of CdS bulk is at 515 nm in the green zone, but it is around 450 nm in the blue zone for CdSNPs, which is used to make NPsLED or organic-inorganic LED (OILED) in the blue zone by material emission in the green zone by taking advantage of nanoparticle properties and defect conditions[18] [19].

Song et al. [20] reported white EL from CdS/Si heterojunctions LED observed under forward bias of ∼4.0 V, which is attributed to several characteristics including: the nanocrystal silicon, the band gap emission and the defect levels emissions of nanocrystal CdS. Mohammed and Ibrahim [21] demonstrated that organic-inorganic hybrid composites ITO/TPD:PMMA/ Eu_2O_3/Alq3/Al, emit green and white light by controlling the bias voltage from the transition through the deep levels in energy gap of Eu_2O_3 NPs (5D0-3 and 5L6 to 7F0-6) and through the defect states of these NPs. Bansal et al. [22] reported the formation of highly luminescent organic capped colloidal cadmium sulfide (CdS) nanoparticles having highest photoluminescence quantum yield of 69% in solutions and 34% in neat thin films in the near infrared range.

The aim of this work is to fabricate organic hybrid organic-inorganic NPs LEDs (OILED) to generate blue light by EL phenomenon using CdSNPs.

2. EXPERIMENTAL WORK

The Tris (8-hydroxyquinolinato) aluminum (Alq_3) and poly N,N’-Bis(3-methyl-phenyl)-N,N’-bis(phenyl)benzidine (poly-TPD) (supplied from Ossila company (UK)) were used as an "Electron" Transport Layer (ETL) and "Hole" Transport Layer material (HTL), respectively. Cadmium Sulphide nanoparticles (CdSNPs) were produced in accordance with the procedures of an earlier study that has been conducted by Suhail et al. [7] showed that the UV-Vis absorption spectrum have a peak at 350 nm and absorption edge at 480 nm which indicated a blue shift of about 32 nm due to the quantum confinement effect. The particle size determined from Atomic Force Microscopic (AFM) was about 8 nm while, the size of the formed CdSNPs was found to be about 5 nm from X-ray diffraction.

The preparation of OILED can be briefed as follows:

Poly-TPD solution was prepared by adding 0.07 g of poly-TPD to 1ml of the chloroform with magnetic stirring to complete the dissolving. The colour change of the solution from pink to purple is an indication of complete dissolving. The ratio of (poly-TPD:CdSNPs) was (1ml:0.5wt%). The composite between organic material (poly-TPD) and inorganic material (CdSNPs) is called hybrid composite. Alq_3 was dissolved in ethanol at a ratio of 70mg:3ml. The hybrid junction was prepared through spin-coating composite at 3000rpm for 1min on indium tin oxide (ITO) substrate and then placed in an oven below 80°C for 1h for complete dryness. Using the phase-segregation method [21], the poly-TPD and CdSNPs were redistributed to form two layers, with the CdSNPs layer over the poly-TPD layer, which means that the CdSNPs layer is implanted in the Poly-TPD layer. This allows energy transfer and generation of exciplex between poly-TPD and CdSNPs. The poly-TPD:CdSNPs hybrid composite turns into poly-TPD /CdSNPs hybrid junction. The Alq3 layer was prepared by dropping 0.25 ml of Alq3 solution onto the poly-TPD/CdSNPs layers, spinning at 2500rpm for 1min and then were placed in an oven to dry the samples. The thickness of poly-TPD layer was 800nm, of CdSNPs layer was 400nm and of Alq3 layer was 300nm. Finally, aluminum was deposited by thermal evaporation, on the Alq_3 to serve as the cathode electrode. The emission layers are thus sandwiched between the two electrodes indium tin oxide (ITO) and aluminum (Al) to produce OILED. The structure of OILED is depicted in Figure 1.

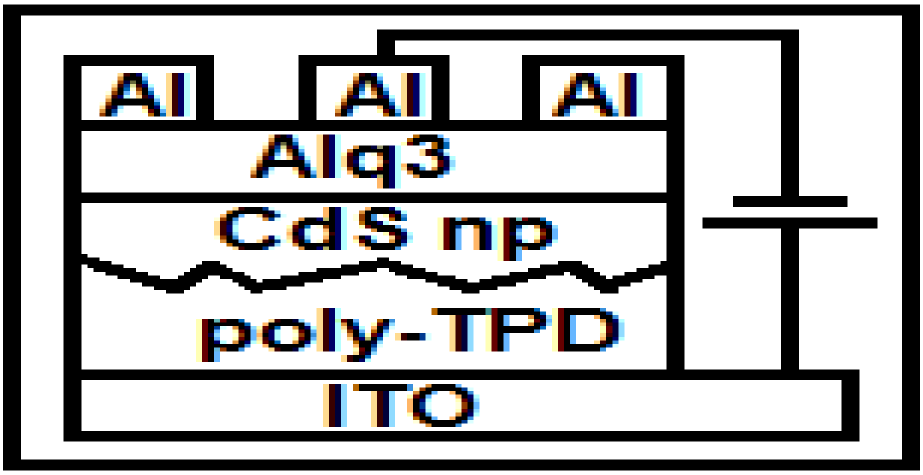

Figure 1: Structure of organic-inorganic light emitting diode.

3. RESULT AND DISCUSSION

3.1(I–V) CHARACTERISTICS

The I–V behavior of (poly-TPD/CdSNPs) and (poly-TPD/CdSNPs/Alq_3) are composed of three regions, as shown in Figure 2. The first region is below 4.5V for poly-TPD/CdSNPs/Alq_3 and at 8.6V poly-TPD/CdSNPs; the behavior in this region was linear which is an indication that the current transport is dominated by tunneling at low voltages. The second region below 21.5V for poly-TPD/CdSNPs and below 11.5V for poly-TPD/CdSNPs/Alq_3, where the current increases exponentially, the carriers injected into the dielectric are generated from the thermionic process occurring across the barrier. As a result, the number of free charges is much lower than the number of trapped charges and the current shows an exponential relationship to the voltage. With further increase of the applied voltage, the injected carriers increased rapidly and the traps filled in 21.5V for poly-TPD/CdSNPs and 11.5V for poly-TPD/CdSNPs/Alq_3.This region is named Traps-Filled-Limit Voltage (V_{TFL}) which is the third region above V_{TFL}. In this region, the current follows a power law ($I\alpha V^2$), because the transport through the OILED is governed by trapped–charge-limited current (TCLC) in CdSNPs' band gap, which indicates that the injected free charge carrier density is considerably higher than the thermally generated free carriers; the conduction is by space-charge limited current (SCLC) is dominant. This is consistent with Ahmad and Sayyad results [23]. Finally, the third region, which is the saturated current region, for poly-TPD/CdSNPs/Alq_3 was at a voltage higher than 21.5V, where the current was constant at a maximum value of 16.5μA. The current has decreased around 100 times with the addition of Alq_3 because Alq_3 is an electron transport layer, which prevents the confinement of electrons between Al electrode and CdSNPs.

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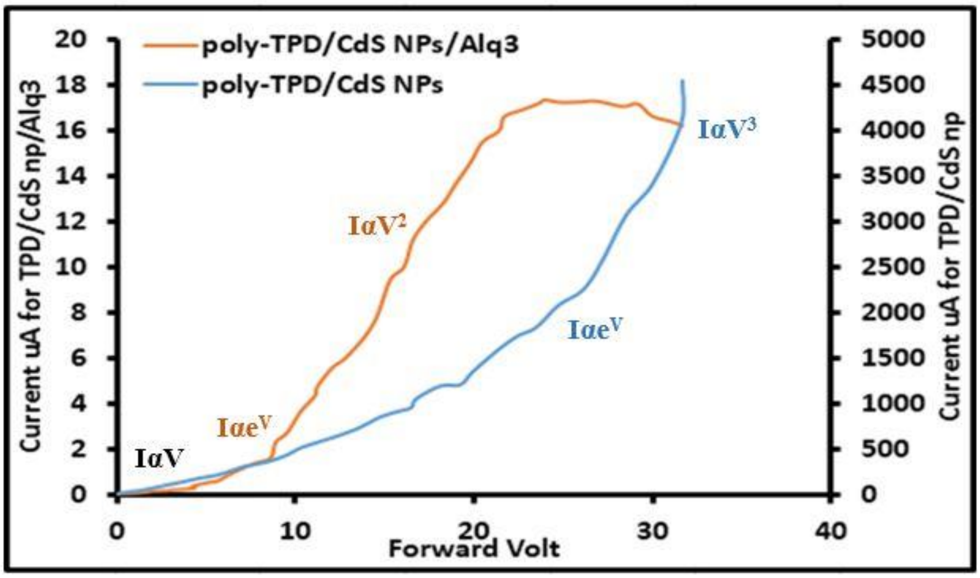

Figure 2: I-V forward characteristics of the OILED.

3.2 ELECTROLUMINESCES (EL) MEASUREMENT

EL measurements in the saturation current region at a forward voltage of 26V for the samples (poly-TPD/CdSNPs) and (poly-TPD/CdSNPs/Alq_3) OILED were carried out with a fiber optic spectrometer (CCS Series, THORLABS Company, Germany). The EL spectra are depicted in Figure 3.

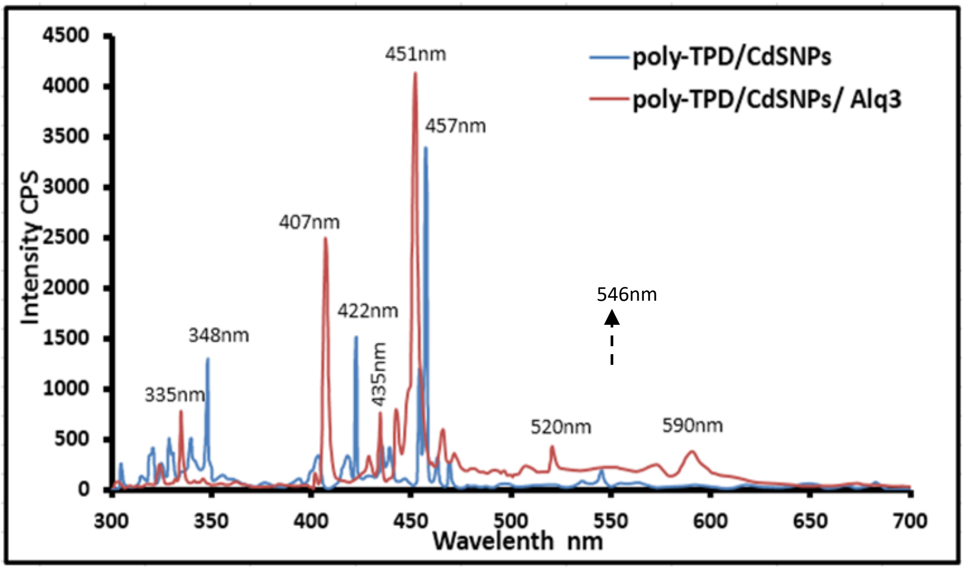

Figure 3: EL spectrum under forward bias voltage of 26V for the (poly-TPD/CdSNPs) and (poly-TPD/CdSNPs/Alq_3).

The spectrum of poly-TPD/CdSNPs shows peaks at 348, 422, 457nm, and 546nm.The last peak (546nm) disappeared when Alq_3 was added. This means that the transition from CB for CdS to HOMO for poly-TPD does not happen because of the increase of the diffusion current for poly-TPD but the exciplex generation increases [24]. The peak 407nm of the poly-TPD/CdSNPs/Alq_3 spectrum corresponds to TPD emission due to the fact that those peaks' energy equals TPD's band gap which is 3eV; this energy gap value was calculated using the EL wavelength peak ($E = 1240/\lambda$) [25]. The 407nm peak appears when using NPs where Auger-assisted energy that results from the nano-sized materials results in causing high Auger recombination cross section. In the case of the decrease of the TPD, injected holes across TPD/CdSNPs interface is decreased, as a result of energy offset (approximately 2eV) between HOMO level of the TPD and VB of CdSNPs, whereas electrons are injected efficiently into CB of CdSNPs. On the other hand, energy offset of (approximately 1.8eV) between CdSNPs results in the accumulation of the electron at the interface of TPD/CdSNPs. Upon the accumulation of charges at the interface of heterojunctions, holes and electrons form the interfacial charge transfer (CT) excitons, or exciplex states. Energy that is released from recombination of those CT excitons is transferred resonantly to proximal electrons in CB of CdSNPs via Auger process for the purpose of producing electrons that have sufficiently high energy to be injected to TPD's LUMO. Those electrons are then recombined with holes in the polymer's HOMO, leading to emissions of the photons with an energy that equals TPD's HOMO-LUMO gap. Those processes are depicted in Figure 4. This analysis is in good agreement with that of Khan [15] and Cerdan-Pasaran et al. [16]. The excitations are through the energy transfer from TPD to CdSNPs due to the fact that the EL device structures are with sub-10 nm separation between the TPD and CdSNPs [17].

The blue emission at around 451 and 457nm is a result of the transition between CB and VB for CdSNPs, which is called the band-to-band transition[3]. The emissions in the red zone (520 and 590nm) correspond to interstitials cadmium defect (Cd) to vacancy cadmium defect (V_{Cd}) transitions [7] or produced from surface state in nanostructure effect [3]. Vacancy defects are created when Cd atoms are missing in one of the lattice sites. While, interstitials cadmium defect is created if the cadmium atom occupies a position where there is usually no atom [7]. The mechanism transport of the charge and emission energy is illustrated in Figure 4.

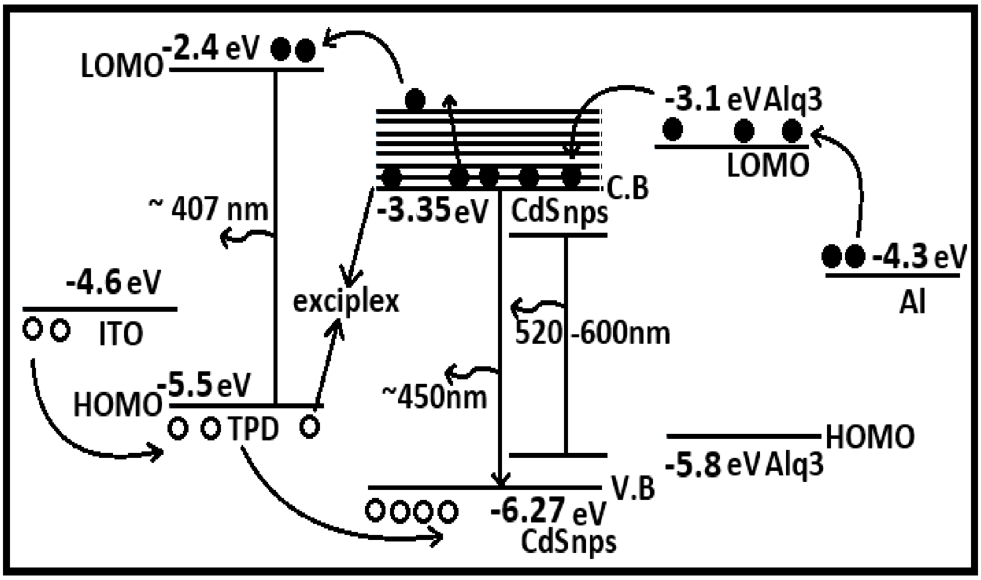

Figure 4: Energy diagram of poly-TPD/CdS NPs/Alq3 hybrid device [8-10].

Figure 5 shows the electroluminescence spectra that were analyzed according to the CIE1976 chromaticity diagram [25][26]. The blue light generated was calculated according to the following equations:

$$u' = \frac{4X}{X + 15Y + 3Z} \dots \dots \dots .1$$

$$v' = \frac{9Y}{X + 15Y + 3Z} \dots \dots \dots .2$$

Where the X, Y and Z represent the area under the curve for the blue, green and red zones, respectively, and u' and v' are coordinates of chromaticity.

Chromaticity coordinates (u',v') can describe any color of light. Substituting the values of (u', v') from the diagram chromaticity (Figure 5) into Eqs. 1 and 2 gave the chromaticity coordinates for (poly-TPD/CdSNPs) and (poly-TPD/CdSNPs/Alq_3) which were (0.21, 0.13) and (0.19, 0.15), respectively. The color of the emitted light was blue for both samples (with and without Alq_3), but according to for Figure 2 when the Alq_3 was added, the electrical current was very little.

Correlated color temperature (CCT) was computed by McCamy's algorithm of approximation and CCT was calculated from u' v' chromaticity using the following equations:

$$\mathrm{CCT} = -449\mathrm{n}^3 + 3525\mathrm{n}^2 - 6823.3\mathrm{n} + 5520.33 \dots \dots \dots \dots .3$$

$$n = \frac{x - 0.332}{y - 0.1858} \dots \dots \dots \dots .4$$

$$x = \frac{9u'}{6u' - 16v' + 12} \dots \dots \dots .5$$

$$y = \frac{4v'}{6u' - 16v' + 12} \dots \dots \dots .6$$

The value obtained was equal to (1700K) for the emitted blue light.

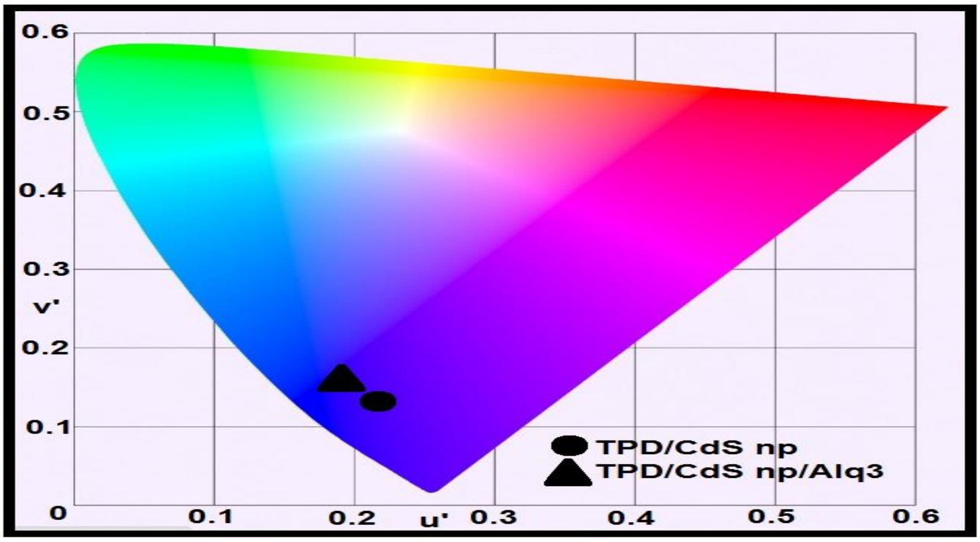

Figure 5: The CIE 1976 chromaticity diagram for OILED.

4. CONCLUSION

Nowadays, due to the fact that 25% of electricity consumption worldwide is utilized for lighting, light generation had drawn much interest for saving consumption of electrical energy for the purpose of reducing operating expenses and safety in comparison with traditional light sources. In this work, hybrid organic-inorganic NPs LEDs (OILED) from CdSNPs with hole injection organic (TPD) was fabricated. It proved to be effective in blue light generation. The color of the emitted light can be controlled by the defect state in the energy gap of CdSNPs. Blue light was also generated, but with much less current. The addition of Alq_3 layer increased the transfer of electrons by about 250 times.

References

[1] S. Bhaumik and A. J. Pal, “All-inorganic light-emitting diodes based on solution-processed nontoxic and earth-abundant nanocrystals,” *IEEE J. Quantum Electron.*, vol. 49, no. 3, pp. 325–330, 2013. doi: 10.1109/JQE.2013.2245404.

[2] H. Zhang, Q. Su, and S. Chen, “Quantum-dot and organic hybrid tandem light-emitting diodes with multi-functionality of full-color-tunability and white-light-emission,” *Nat. Commun.*, vol. 11, no. 1, pp. 1–8, 2020. doi: 10.1038/s41467-020-16659-x.

[3] A. G. Vitukhnovsky, V. S. Lebedev, A. S. Selyukov, A. A. Vashchenko, R. B. Vasiliev, and M. S. Sokolikova, “Electroluminescence from colloidal semiconductor CdSe nanoplatelets in hybrid organic-inorganic light emitting diode,” *Chem. Phys. Lett.*, vol. 619, pp. 185–188, 2015. doi: 10.1016/j.cplett.2014.12.002.

[4] D. A. Tonpe, K. P. Gattu, V. V. Kutwade, M. E. Sonawane, A. S. Dive, and R. Sharma, “Development of organic/inorganic PANI/ZnO 1D nanostructured hybrid thin film solar cell by soft chemical route,” *J. Mater. Sci. Mater. Electron.*, vol. 30, no. 17, pp. 16056–16064, 2019. doi: 10.1007/s10854-019-01976-9.

[5] R. Kandulna, R. B. Choudhary, R. Singh, and B. Purty, “PMMA–TiO_2 based polymeric nanocomposite material for electron transport layer in OLED application,” *J. Mater. Sci. Mater. Electron.*, vol. 29, no. 7, pp. 5893–5907, 2018. doi: 10.1007/s10854-018-8562-x.

[6] M. Sessolo and H. J. Bolink, “Hybrid organic-inorganic light-emitting diodes,” *Adv. Mater.*, vol. 23, no. 16, pp. 1829–1845, 2011. doi: 10.1002/adma.201004324.

[7] A. M. Suhail, M. J. Khalifa, N. M. Saeed, and O. A. Ibrahim, “White light generation from CdS nanoparticles illuminated by UV-LED,” *EPJ Appl. Phys.*, vol. 49, no. 3, pp. 1–5, 2010. doi: 10.1051/epjap/2010005.

[8] A. M. Suhail, A. N. Naje, R. R. Mohammed, G. S. Muhammed, and O. Adnan, “Enhancement of solar cell efficiency by adding cds nanoparticles,” *Int. J. Theor. Appl. Phys.(IJTAP)*, vol. 2, no. November, pp. 155–162, 2012.

[9] C. Zang, M. Xu, L. Zhang, S. Liu, and W. Xie, “Organic-inorganic hybrid thin film light-emitting devices: interfacial engineering and device physics,” *J. Mater. Chem. C,* vol. 9, no. 5, pp. 1484–1519, 2021. doi: 10.1039/d0tc05059h.

[10] I. G. Subramani, V. Perumal, S. C. B. Gopinath, K. S. Fhan, and N. M. Mohamed, “Organic-Inorganic Hybrid Nanoflower Production and Analytical Utilization: Fundamental to Cutting-Edge Technologies,” *Crit. Rev. Anal. Chem.*, vol. 52, no. 7, pp. 1–23, 2021. doi: 10.1080/10408347.2021.1889962.

[11] F. Chen, Q. Lin, H. Shen, and A. Tang, “Blue quantum dot-based electroluminescent light-emitting diodes,” *Mater. Chem. Front.*, vol. 4, no. 5, pp. 1340–1365, 2020. doi: 10.1039/d0qm00029a.

[12] G. Lozano, S. R. K. Rodriguez, M. A. Verschuuren, and J. G. Rivas, “Metallic nanostructures for efficient LED lighting,” *Light Sci. Appl.*, vol. 5, no. 6, pp. 1–10, 2016. doi: 10.1038/lsa.2016.80.

[13] H. S. Chen, P. Yang, Z. H. Khan, J. M. Wu, G. Li, and A. R. Kamali, “Quantum dots and nanoparticles in light emitting diodes, displays, and optoelectronic devices,” *J. Nanomater.*, vol. 2015, pp. 2–4, 2015. doi: 10.1155/2015/371679.

[14] J. B. Varley and V. Lordi, “Electrical properties of point defects in CdS and ZnS,” *Appl. Phys. Lett.*, vol. 103, no. 10, pp. 1–5, 2013. doi: 10.1063/1.4819492.

[15] A. Khan, “CdS nanoparticles with a thermoresponsive polymer: Synthesis and properties,” *J. Nanomater.*, vol. 2012, pp. 1–8, 2012. doi: 10.1155/2012/451506.

[16] A. Cerdán-Pasarán, T. López Luke, D. Esparza, and I. Zarazua, “Photovoltaic properties of multilayered quantum dot/quantum rod-sensitized TiO2 solar cells fabricated by SILAR and electrophoresis,” *Phys. Chem. Chem. Phys.*, vol. 17, no. 28, pp. 18590–18599, 2015. doi: 10.1039/c5cp02541a.

[17] A. M.Suhail, W. R. Saleh, O. A. Ibrahim, and R. K. Ibrahim, “White Light Generation by Electroluminescence for ZnO Nanoparticle –Organic Hybrid Junction Device,” *Int. J. Eng. Innov. Technol.*, vol. 4, no. 9, pp. 196–202, 2015.

[18] D. H. Alman, R. S. Berns, G. D. Snyder, and W. A. Larsen, “Performance testing of color-difference metrics using a color tolerance dataset,” *Color Res. Appl.*, vol. 14, no. 3, pp. 139–151, 1989. doi: 10.1002/col.5080140308.

[19] A. M. Suhail and O. A. Ibrahim, “Characterization of CdS quantum dots prepared by a Chemical Method,” *Iraqi J. Phys.*, vol. 7, no. 8, pp. 53–58, 2009.

[20] Y. L. Song, Y.L. Feng, Q.Z.Peng, F.J.Xiao, J.S.Ming, L.Wan and M. L. Tian., “White electroluminescence from a prototypical light-emitting diode based on CdS/Si heterojunctions,” *Mater. Lett.*, vol. 196, pp. 8–11, 2017. doi: 10.1016/j.matlet.2017.02.117.

[21] H. R. Mohammed and O. A. Ibrahim, “Electroluminescence of light- Emitting organic semiconductor / Europium oxide nanoparticle hybrid junction,” *Iraqi J. Sci.*, vol. 61, no. 8, pp. 1952–1959, 2020. doi: 10.24996/ijs.2020.61.8.12.

[22] A. K. Bansal, F. Antolini, S. Zhang, L. Stroea, L. Ortolani, M. Lanzi, E. Serra, S. Allard, U. Scherf, and I. D. W. Samuel, “Highly luminescent colloidal CdS quantum dots with efficient near-infrared electroluminescence in light-emitting diodes,” *J. Phys. Chem. C*, vol. 120, no. 3, pp. 1871–1880, 2016. doi: 10.1021/acs.jpcc.5b09109.

[23] Z. Ahmad and M. H. Sayyad, “Extraction of electronic parameters of Schottky diode based on an organic semiconductor methyl-red,” *Physica E: Low-dimensional Systems and Nanostructures*, vol. 41, no. 4, pp. 631–634, 2009. doi: 10.1016/j.physe.2008.08.068.

[24] L. Qian, Y. Zheng, K. R. Choudhury, D. Bera, F. So, J. Xue & P. H. Hollway, “Electroluminescence from light-emitting polymer / ZnO nanoparticle heterojunctions at sub-bandgap voltages,” *Nano Today*, vol. 5, no. 5, pp. 384–389, 2010. doi: 10.1016/j. nantod. 2010. 08.010.

[25] S. Ananthakumar, J. Ramkumar, and S. M. Babu, “Facile synthesis and transformation of Te nanorods to CdTe nanoparticles,” *Mater. Sci. Semicond. Process.*, vol. 27, pp. 12–18, 2014. doi: 10.1016/j.mssp.2014.06.008.

[26] O. Kopylov, “Hybrid Light-Emitting Diode Enhanced with Emissive Nanocrystals,” Ph.D. thesis, Technical University of Denmark, 2014.