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# Enhanced optical properties of luminescent solar concentrators *via* metal ion doping in carbon dots†

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Luminescent solar concentrators (LSCs) utilizing carbon dots (CDs) have emerged as promising solutions for transparent photovoltaic applications due to their high transparency and efficient light-to-electricity conversion. This study investigates the synthesis and optical enhancement of CDs doped with transition metal ions—cobalt, nickel, copper, and zinc—to improve LSC performance. Using a microwave synthesis method, we produced CDs with a high quantum yield of 81%, a substantial Stokes shift of 0.71 eV, and excellent stability. Doping CDs with metal ions at molar concentrations of 1%, 3%, and 5% revealed that 1 mol% copper-doped CDs exhibited superior optical properties, enhancing light absorption and emission through effective metal-ion interactions. LSCs, fabricated with dimensions of 15  $\times$  15  $\times$  0.6 cm<sup>3</sup> using glass and PMMA waveguides, achieved notable photovoltaic performance with an optical efficiency of 3.99% and a photoconversion efficiency (PCE) of 1.45% for PMMA-based devices. The introduction of copper at 1% concentration resulted in a 22% increase in both optical efficiency and PCE. Stability assessments over 90 days indicated minimal performance degradation, underscoring the robustness of the synthesized materials. This research highlights the potential of metal-doped CDs to optimize LSC technology, facilitating integration into urban environments and advancing the commercialization of transparent photovoltaic systems.

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## 1. Introduction

Luminescent solar concentrators (LSCs) have emerged as a promising technology for transparent photovoltaic windows. In recent years, these LSCs have attracted significant attention from researchers due to their numerous advantages including high transparency, cost-effective fabrication, independence from solar trackers, the ability to generate electricity from both

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direct and scattered light, controllable transparency, and compatibility with building and urban spaces.<sup>1,2</sup> LSCs can be applied in various settings like building windows, car glass, agricultural greenhouses, and portable electronic devices, making them efficient sources of electrical energy.<sup>3-6</sup> An LSC typically consists of a waveguide, luminophore molecules doped inside or coated on the waveguide, and narrow strip solar cells positioned at the waveguide's edges.<sup>2</sup> In operation, luminophores absorb a portion of the incoming light and emit it at longer wavelengths. This emitted light is then guided through the waveguide to the edges, where it is absorbed by the solar cells and converted into electrical power (Fig. 1a). Among the essential components of LSCs are the luminophores, which must exhibit minimal losses during light absorption and emission. Ideally, a suitable luminophore should possess high quantum yield, a large Stokes shift, and superior optical and chemical stability.1,2

In recent years, carbon dots (CDs) have emerged as promising luminescent materials for LSC development due to their easy and cost-effective synthesis, abundant production resources, high quantum yield, large Stokes shift, and extraordinary stability.<sup>7-10</sup> However, research on LSCs utilizing CDs has predominantly focused on CDs synthesis and their application in LSCs, with limited attention given to exploring structural modifications to enhance optical properties.<sup>7-12</sup> Notably,

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**Fig. 1** (a) Schematic of a LSC, including the waveguide, luminophore, and solar cell installed at the edge of the waveguide. In this schematic, (1) represents the loss of light reflected from the surface of the waveguide, (2) is the loss of light passing through the waveguide, (3) is the loss related to the escape cone, (4) is the loss related to the quantum yield, (5) is the loss related to the absorption of light by the waveguide, and (6) is the light reaching the edge of waveguide, where and the solar cells produce electric power. (b) Structure of CDs doped with copper metal ions.

adopting doping techniques involving metal ions from transition metals is an effective method for altering the optical properties of CDs.

While sporadic attempts at doping CDs with transition metal ions have been made across various research fields,13-19 comprehensive studies specifically aimed at improving the optical characteristics of CDs and their application in LSCs are lacking. Doping CDs with transition metal ions can enhance light absorption and, subsequently, the overall efficiency of LSCs through the creation of semiconductor-metal hybrid structures.13,14,20 Experimental results have shown that the introduction of metal ions into CDs can significantly improve their optical characteristics, such as light absorption and emission intensity, Stokes shift, and most metal ions, especially those belonging to transition metals, exhibit a greater abundance of unfilled orbitals and free electrons in comparison to non-metallic structures. This property enables them to readily interact with amino and carboxyl groups present on the surface of CDs.<sup>21,22</sup> Therefore, this study aims to improve the light absorption characteristics of CDs by doping them with several important and widely used metal ions, including cobalt, nickel, copper, and zinc. The investigation will focus on examining the influence of metal ion concentration and type on the optical properties of CDs for use in LSCs.

## 2. Materials and methods

#### 2.1 Materials

The materials used in this work consist of polyvinyl pyrrolidine (PVP-K30) (molecular weight: 50 000) and polyvinyl pyrrolidine (PVP-K90) (molecular weight: 1 000 000), ethanol and methanol, rhodamine 6G, citric acid, urea, sodium hydroxide, metal salts (cobalt acetate, nickel acetate, copper acetate, and zinc acetate), all sourced from Merck and used without purification.

#### 2.2 Synthesis of CDs

To synthesize the CDs, we employed the cost-effective, fast, and scalable microwave synthesis method.<sup>23</sup> In this method, 0.0052 mol of citric acid, 0.0333 mol of urea, 20 ml of deionized water and 0.02 mol of NaOH were mixed. For better homogenization, the mixture was subjected to ultrasonic bath for 10 minutes. Subsequently, the mixture was exposed to microwave irradiation at 1000 watts for 3 minutes. The resulting spongy structure was then rinsed with ethanol and centrifuged to eliminate any surplus impurities. Finally, the washed powder was dried in a vacuum oven at 60  $^{\circ}$ C for 24 h to achieve complete dehydration of the CDs powder.

For the synthesis of CDs doped with cobalt, nickel, copper, and zinc metal ions at concentrations of 1, 3, and 5 mol%, the same procedure as described above was followed. For doping, metal ion acetate salts at 1, 3, and 5 mol% was initially dissolved in 20 ml deionized water with citric acid, urea, and NaOH, after which the process continued as previously outlined. Fig. S1† illustrates the synthesized samples of CDs doped with metal ions in powder form and soluble in water under ambient light and UV light.

#### 2.3 LSCs fabrication

In the fabrication of LSCs, initially, a mixture of 10 ml methanol solution, 1 g of PVP K30, and 1 g of PVP K90 was prepared. The mixture was sonicated for 10 min obtain a clear solution. Subsequently, the CDs powder was dissolved in 3% by weight and treated with ultrasonic bath for 10 min. Following this, the solution containing the CDs was applied onto the surfaces of glass and polymethyl methacrylate (PMMA) substrate as a waveguide with dimensions of  $15 \times 15 \times 0.6$  cm<sup>3</sup> using Doctor Blade's method. Finally, LSCs were dried in ambient conditions for 2 hours in an isolated environment. The thickness was measured using a digital micrometer and it was 5 micrometers.

#### 2.4 Characterization

2.4.1 Structural and optical properties of CDs. The morphology of the CDs was examined using a transmission electron microscope (TEM) with a Philips EM 208S TEM equipped with an EDS spectrometer and high-resolution TEM (HRTEM) using the FEI model TEC9G20 at 200 kV. X-Ray diffraction (XRD) analysis was recorded using an Explorer model X-ray diffraction machine from Panalytical CO. X-Ray photoelectron spectroscopy (XPS) spectra were recorded using a BESTEC spectrometer (EA 10) equipped with an Al Ka X-ray source (15 kV, 50 W). The Fourier-transform infrared (FT-IR) spectrum was obtained using a Thermo Nicolet model AVATAR 370 FT-IR spectrometer. The photoluminescence (PL) spectrum of the CDs was prepared using a PerkinElmer ls45 device. UV-visible absorption and transmission spectra were recorded using a Hitachi UH-4150 spectrophotometer. The PL spectroscopy of the fabricated LSCs was measured using a reflection spectrometer connected to an optical fiber and a solar simulator with an optical spectral range of 200 to 900 nm. Quantum yield (QY) was measured by a relative comparison method using the following equation:<sup>24</sup>

$$Q_{\rm s} = Q_{\rm R} \times \frac{I_{\rm s}}{I_{\rm R}} \times \frac{A_{\rm R}}{A_{\rm s}} \tag{1}$$

where, *Q*, *I* and *A* are quantum efficiency, the measured fluorescence intensity (integrated area of photoluminescence spectra of CDs and rhodamine 6G) and the absorbance at the excitation wavelength (400 nm). The subscripts "S" and "R" stand for CDs samples and reference (rhodamine 6G) respectively.

2.4.2 PCE and optical efficiency. The LSC functions fundamentally as a solar concentrator, making it essential to report the optical efficiency to ascertain the percentage of incident radiation that reaches its edges, where the solar cells reside as the active area responsible for generating electrical current. The LSCs' overall photoconversion efficiency (PCE) and optical efficiency were measured using a solar simulator under standard conditions (AM 1.5 at 25 °C and irradiance intensity 1000 W m<sup>-2</sup>). The *I–V* characteristics were recorded using an *I–V* measuring device (IRASOL) connected to the solar simulator. Parameters such as short circuit current, open circuit voltage, fill factor, and PCE were derived from the I-V characteristics. A silicon photovoltaic cell (Zolix QE-B1) was directly installed on one edge of the LSC (active area:  $9 \text{ cm}^2$ ). The results were scaled by a factor of 4 to account for all four edges of the LSC, based on standard LSC measurements.25 The remaining edges were completely covered with black electrical tape to absorb incident light and prevent interference. Eqn (2)-(4) (ref. 24 and 26) were utilized to determine the PCE, optical efficiency, and geometric factor, respectively:

$$\eta = \frac{J_{\rm SC} V_{\rm OC} \rm FF}{P_0} \tag{2}$$

$$G = \frac{A_{\rm top}}{A_{\rm edge}} \tag{3}$$

$$\eta_{\rm opt} = \frac{I_{\rm LSC}}{I_{\rm SC}G} \times 100 \tag{4}$$

where,  $J_{SC}$  is the current density,  $V_{OC}$  is the open circuit voltage and FF is the LSC fill factor,  $P_0$  is the input power,  $A_{top}$  is the top area of the LSC and  $A_{edge}$  is the area of the LSC edges. Also, in eqn (S7),†  $I_{LSC}$  is the short circuit current of LSC and  $I_{SC}$  is the short circuit current of the solar cell connected to the waveguide. The dependence of emission from the edge was measured to investigate reabsorption losses. In this analysis, the entire surface of the LSC was covered with a black coating, and only at the desired point with a certain distance from the edge (L), a 25 mm square hole was created for light radiation to the LSC. The details of other parts of the characterization were included in the ESI.†

### 3. Results and discussion

#### 3.1 Optical properties of CDs

The optical properties of CDs were investigated, as depicted in Fig. 2a. The absorption spectrum indicates that CDs absorb light within the 250 to 500 nm range, with two prominent peaks: the first peak at 330 nm, attributed to the  $\pi \rightarrow \pi^*$  transition associated with sp<sup>2</sup> aromatic carbon, and the second peak at 400 nm, resulting from the  $n \rightarrow \pi^*$  transition due to C=O and C=N groups.<sup>7,23,27-30</sup> The photoluminescence spectrum of metal-doped CDs reveals emission in the visible region from 410 nm to 600 nm, with a peak emission at 518 nm when excited at 400 nm (Fig. 2b–f). Fig. S2† shows that the emission of CDs is independent of the excitation wavelength, indicating a stable emission center in the synthesized CDs.

Further investigation into the absorption and emission of metal-doped CDs reveals that all structures doped with these ions exhibit lower absorption and emission compared to those doped with copper (Fig. 2b-f). During the doping process, metal ions interact with functional groups on the surface of CDs, forming metal complex. In these complexes, the metal ion is at the core, surrounded by ligands composed of various functional groups, including those containing oxygen and nitrogen (Fig. 1b). This interaction results in electron transfer from the excited state of CDs to the 3d orbital of the metal ion, leading to reduced radiative recombination and decreased emitted intensity.31-34 Notably, this complex formation does not occur in Cu-doped and Zn-doped CDs. In the case of Cu doped CDs and Zn doped CDs, the fullness of their d orbitals prevents these orbitals from participating in electron transfer from the excited state of carbon to the metal ion. This results in enhanced performance of Cu doped CDs and Zn doped CDs in terms of light absorption and emission. Cu-doped CDs exhibits higher light absorption compared to Zn-doped CDs, attributable to its distinct optical properties that facilitate both absorption and emission of light. Copper's electronic configuration includes a fully occupied 3d subshell and a single electron in the 4s subshell, allowing various electronic transitions when exposed to light. In contrast, zinc has a fully filled 3d subshell and a completely filled 4s subshell, resulting in a lack of free electrons available for transitions. This configuration significantly



Fig. 2 Absorption and emission spectrum of (a) CDs, (b) cobalt doped CDs, (c) nickel doped CDs, (d) copper doped CDs, (e) zinc doped CDs and (f) maximum absorption and emission of metal ion-doped CDs with the best optical properties.

limits zinc's ability to absorb light effectively. The filled 4s subshell in zinc makes electronic transitions to unoccupied states less favorable than in copper.<sup>35–37</sup>

A notable decrease in absorption and emission intensity was observed as the molar percentage of metal ions increased from 1% to 5% (Fig. 1b–e). This trend can be attributed to the formation of insoluble complexes within the structure, which increases with higher molar percentages of metal ions. A comprehensive discussion of this phenomenon, especially regarding Cu-doped CDs, is presented in the following section. Given the superior optical properties exhibited by copper-doped CDs, they were selected for subsequent investigations.

#### 3.2 Synthesis and structure of CDs

CDs doped with metal ions were synthesized using a scalable, cheap and rapid method.<sup>23</sup> A common issue in CDs synthesis is photoluminescence quenching due to particle aggregation after synthesis. This problem occurs due to the large surface area in CDs. To solve this challenge, some structures have been used to prevent particle aggregation.<sup>23,38-41</sup> The purpose of using such structures is to create spongy forms and place quantum dots during synthesis in this spongy and foam-shaped structure, which, like a shell and a wall around the quantum dots, prevents the creation of the aggregation induced quenching (AIQ) phenomenon, and in addition, it also leads to the scalable synthesis of CDs.<sup>23,39</sup> Such an approach was also used in this research. The morphology, structure and size of the CDs were

high-resolution transmission electron microscope (HRTEM) and X-ray diffraction (XRD). The TEM image shows a good dispersion of CDs with a spherical structure averaging of 3.21  $\pm$  0.78 nm (Fig. 3a and c). HRTEM image shows a lattice distance of 0.23 nm, which is attributed to the distance d in the (100) plane of graphene (Fig. 3b).<sup>23,24,39,42</sup> The peak at 17.6°, 31°, 37.3°, 41.7° and 50.7° correspond to the (200), (400), (111), (311) and (020) lattice planes of the monoclinic NaOH crystal structure.23 Comparing the XRD curve of the CDs doped with copper and the CDs shows that the peak at 46.9° is related to the (111) plane of copper, which appeared after copper doping in the structure of CDs (Fig. 3d).<sup>17,43,44</sup> The chemical structure of CDs and metal ions doped CDs were characterized by Fourier-transform infrared spectroscopy (FT-IR) (Fig. 3e). The band at 3466.6  $\text{cm}^{-1}$  is related to -OH stretching vibrations, which is the presence of -OH functional group on the surface of CDs<sup>23</sup> and also on the surface of structures confirms doped with copper. The band at 2.1672 cm<sup>-1</sup> is attributed to the stretching of C=O and C=N functional groups, respectively.28 Also, the bands at 1599.196 cm<sup>-1</sup> and 1398.64 cm<sup>-1</sup> are related to C=C and C-N bond.<sup>24,45</sup> A detailed investigation of the FTIR curve of the CDs and the CDs doped with copper shows that two new bands have appeared in the FTIR curve of CD doped with copper, and the band at 1100 cm<sup>-1</sup> corresponds to the stretching vibration of Cu-N-Cu, which indicates the formation of coordination complexes in the structure of CDs doped with copper.<sup>44</sup> Also, the band at 590/

characterized using transmission electron microscope (TEM),



Fig. 3 (a) TEM and (b) HRTEM image of CDs and (c) particle size distribution histogram of synthesized CDs (d) XRD spectrum and (e) FTIR spectrum of synthesized CDs and Cu doped CDs.

467 cm<sup>-1</sup> can be attributed to the formation of Cu–O functional groups after the presence of copper in the structure of CDs.<sup>46</sup> The comparison of FTIR curves of three structures doped with copper shows that with increasing amount of copper, the Cu-O peak in the structure becomes sharper and the band corresponding to N-Cu-N becomes smaller. This observation signifies that the augmentation of metal complexes containing oxygenated functional groups like hydroxyl and carbonyl, leading to the formation of insoluble complexes, results in a reduction in the absorption and emission intensities of the doped structure due to losses associated with non-radiative recombination.32,47,48 Conversely, the amplification of the N-Cu-N band in the structure doped with 1% copper, associated with the formation of metal complexes incorporating nitrogen groups, enhances the absorption and emission intensities. It appears that due to the excitation of the electron in the Cu doped CDs structure after light absorption, the carrier is transferred through the metal complex N-Cu-N to the graphitic structure of CDs. This transfer, coupled with radiation recombination, fortifies the absorption and emission in the structure doped with 1% copper.44

X-Ray photoelectron spectroscopy (XPS) analysis was employed to investigate the elemental composition and chemical bonding states of copper-doped CDs. Fig. 4 revealed the presence of carbon (C 1s), nitrogen (N 1s), oxygen (O 1s), sodium (Na 1s) and copper (Cu 2p). These constituents account for 51.35%, 15.46%, 25.44%, 5.11%, and 2.64% of the structure, respectively. Upon scrutinizing the high-resolution XPS spectrum of C 1s carbon, three distinct peaks emerged at energy levels of 284.4 eV, 286.2 eV, and 287.7 eV, corresponding to C-C/C=C, C-N/C-O, and C=O bonding groups, respectively. The high-resolution XPS spectrum of nitrogen N 1s delineated four peaks at energy levels of 398.02 eV, 399 eV, 401.02 eV, and 402.9 eV, representing pyridinic, pyrrolic, graphitic, and oxidized nitrogen functionalities, respectively. The presence of different nitrogen groups enhances the interaction of CQDs with copper metal ions,49 as evidenced by the N-Cu-N peak in FTIR analyses (Fig. 3e). This augmented interaction resulting from the nitrogen functional groups' presence facilitates the incorporation of copper metal ions into the CDs' structure through nitrogen bonding, thereby enhancing the optical characteristics of copper-doped CDs.

The high-resolution XPS spectrum of O 1s carbon revealed two decomposition peaks associated with C=O and C-O at 531.3 eV and 534.7 eV, respectively. The relatively elevated C=O value in the O 1s spectrum may be influenced by its higher value in the C 1s spectrum. Furthermore, the detection of sodium Na 1s at 1063/33 eV, signifies the presence of sodium within the



Fig. 4 (a) XPS survey spectrum of CDs and Cu doped CDs. (b) Deconvolution of XPS spectrum of C1s, (c) N1s, (d) O1s and (e) Cu 2p.

structure, constituting approximately 11.5% of the composition. Notably, a key disparity between the XPS spectra of pure CDs and copper-doped CDs lies in the appearance of two peaks corresponding to Cu  $2p_{3/2}$  (931.61 eV) and Cu  $2p_{1/2}$  (952.21 eV), indicating the incorporation of copper metal ions into the structure as a dopant.<sup>11,17,23,24,50</sup>

The quantum yield of synthesized CDs was measured to be 75%, indicating minimal non-radiative recombination rate losses.<sup>24,41</sup> Doping the CDs with copper (1 mol%) further increased the quantum yield to 81% (Fig. S3 and Table S1†). The Stokes shift of both the control and copper-doped CDs remained constant at 0.71 eV (Fig. 2a). A higher Stokes shift typically implies a lower reabsorption loss rate. The favorable Stokes shift and high quantum yield can be attributed to the effective surface passivation of CDs and the presence of copper ions within the doped structure, promoting efficient radiative recombination. Also, the excitation of surface states induced by the  $n \rightarrow \pi^*$  transition of surface functional groups can enhance the radiative transfer rate, thereby leading to a high quantum yield and significant Stokes shift in CDs.

#### 3.3 Optical and photovoltaic investigation of LSCs

The experimental results demonstrated that CDs doped with copper ions (1 mol%) exhibited superior optical properties

compared to undoped CDs and CDs doped with other metal ions. Therefore, the optical and photovoltaic characteristics of LSCs fabricated using Cu-CDs (1 mol%) were investigated and compared with LSCs made with CDs as a reference sample. Four LSCs, with dimensions of  $15 \times 15 \times 0.6$  cm<sup>3</sup>, were fabricated using two types of waveguides (glass and PMMA) based on CDs and Cu-CDs (1 mol%) (Fig. 5a-d). The LSCs exhibited high transparency in ambient light and emitted bright green light from the edges and surface of LSC under UV light. As shown in Fig. 5e and f a significant difference in the absorption and emission intensity between Cu-CDs (1 mol%) and CDs was clearly observed in both the PVP solution and the LSCs. These results are consistent with the findings related to the absorption and emission spectra of CDs doped with metal ions, as presented in Fig. 2. Increased absorption intensity is observed in the absorption and emission spectra of Cu-CDs (1 mol%) and LSCs fabricated using this type of CDs. Additionally, the position and shape of the absorption and emission peaks remain unaltered after dispersing the CDs in a PVP and methanol mixture, suggesting the high stability of the synthesized CDs. This stability was also maintained when the CD layer was coated on waveguides, demonstrating the enduring nature of the synthesized CDs.

The absorption and emission spectra of the LSC fabricated with a PMMA waveguide exhibit significantly higher intensity



**Fig. 5** LSCs fabricated in the size of  $15 \times 15 \times 0.6$  cm<sup>3</sup>. The high transparency of LSCs can be seen well in natural light (a) in the environment of FUM university and (b) on the color test screen. (c) Light emission under UV light from the edge of LSCs and comparison of light intensity between LSC made with copper-doped CDs (top image) and CDs (bottom image) and (d) surface emission of fabricated LSCs. Absorption and emission spectrum of (e) mixture of CDs and CDs doped with copper (1% mol) with PVP and (f) LSCs made with CDs and CDs doped with copper (1% mol) based on Glass and PMMA.

compared to the LSC with a glass. This difference can be attributed to the disparity in the refractive indices of glass and PMMA. Refractive index measurements revealed that the refractive index of glass is 1.32, while that of PMMA is 1.46. By analyzing the major optical losses, often in the form of light escaping the waveguide, and using eqn (S2)–(S4) (see ESI†), it can be observed that the optical losses are approximately 35% in the glass waveguide and around 27% in the PMMA waveguide. Since the predominant share of optical losses is associated with escape cone losses,<sup>51,52</sup> this difference can be attributed to this phenomenon. As a result, less light reaching the edges in the LSC based on glass waveguide.

Comprehensive photovoltaic analyses were conducted, including the assessment of the current–voltage characteristics, optical efficiency, overall efficiency, and fill factor of LSCs. The results, presented in Fig. 6 and Table 1 demonstrate that LSCs fabricated with 1 mol% Cu-doped CDs based on PMMA exhibit superior photovoltaic performance compared to their counterparts. The Cu-doped CDs LSCs achieve enhanced optical efficiency due to the increased absorption and emission of light resulting from the interaction between copper ions and the nitrogen groups on the surface of the CDs. The photovoltaic evaluation revealed that the LSCs incorporating Cu-doped CDs based on PMMA demonstrated  $V_{\rm OC}$  of 0.52 V,  $J_{\rm SC}$  of 4.21 mA  $cm^{-2}$ , an optical efficiency of 3.99%, PCE of 1.45%, and geometric factor (G) of 6.25. Conversely, the LSCs fabricated with CDs serving as the reference with the PMMA waveguide manifested  $V_{OC}$  of 0.52 V,  $J_{SC}$  of 3.4 mA cm<sup>-2</sup>, optical efficiency of 3.27%, and PCE of 1.19%, with a *G* of 6.25. To enable a more rigorous analysis of the results and facilitate comparison with findings from other studies, the concentration factor (C) was employed. The concentration factor provides a standardized metric to assess and contextualize the outcomes within the broader research landscape. The concentration factor of a LSC represents the ability of the LSC to collect and concentrate incident light and is given by  $C = \eta_{\text{opt}} \times G.^{52,53}$  The results demonstrate that LSCs incorporating copper-doped CDs exhibit an increase in concentration factor exceeding 22% (Fig. 6d). Given the constant geometric factor, this enhancement can be attributed to the improved optical efficiency, indicating enhanced absorption and emission of light within the Cudoped CDs. This finding is significant because it demonstrates that by maintaining the geometric dimensions of the waveguide constant, it is possible to achieve an enhanced concentration factor through the optimization of the optical properties of the fluorophores. This approach offers



**Fig. 6** (a) J-V curves of LSCs made in dimensions of  $15 \times 15 \times 0.6$  cm<sup>3</sup> with CDs and CDs doped with copper with glass and PMMA waveguides (b) PL spectra and (c) normalized PL spectra collected at the edge of LSC at different optical paths (*L* is the distance between the radiation location and the edge of the LSC in the direction of the optical fiber detector). (d) Concentration factor curve *versus* PCE and optical efficiency of fabricated LSCs. (e) Mechanism of carrier generation in the structure of copper-doped CDs. The process of light absorption (hv<sub>1</sub>, hv<sub>2</sub>) and electron excitation by CDs (e<sub>1</sub><sup>-</sup>) and copper ion (e<sub>2</sub><sup>-</sup>) which causes the emission of em<sub>1</sub> and em<sub>2</sub>. In this fig, CB and VB are the conduction band and valence band of CDs, *E*<sub>F</sub> and *E*<sub>SP</sub> are the Fermi level and surface plasmon state of copper, respectively. (f) The stability curve and optical efficiency losses of the fabricated LSCs during 90 days.

a promising strategy for improving the efficiency of LSCs in large-scale LSCs. The results obtained for other large-scale LSCs are summarized in Table 1. To understand the enhanced photovoltaic and optical efficiencies of LSCs fabricated with 1 mol% Cu-doped CDs compared to undoped CDs, it's important to consider the structural analysis of the synthesized CDs. The Cu-doped CDs, exhibit enhanced interaction and bonding with copper metal ions, due to the presence of various nitrogen groups as confirmed by XPS and FTIR analyses. This phenomenon aligns with the findings of Nguyen *et al.* (2022). This interaction, coupled with distinct optical properties, leads to significantly increased absorption. Furthermore, the detection of an N-Cu-N type metal complex, as indicated by a pronounced band in the FTIR spectrum, suggests that after light absorption, the excitation of electrons within the copper structure may be transferred to the CDs *via* the N-Cu-N metal complex, leading to radiative recombination and augmented absorption and emission within the copper-doped structure (Fig. 6e). These factors contribute to the enhancement of optical characteristics, and, consequently, the improvement of the photovoltaic performance of LSCs based on 1% copper-doped CDs.

Table 1 PCE and optical efficiency of LSCs made with CDs and copper doped CDs based on PMMA and glass waveguides

LSC type	$A_{\rm LSC} \left( {\rm cm}^2 \right)$	$J (\mathrm{mA \ cm^{-2}})$	$V\left(\mathbf{V} ight)$	FF (%)	$\eta_{\mathrm{opt}}$ (%)	PCE (%)	G	С
PMMA_CD	225	3.45	0.52	66.35	3.27	1.19	6.25	20.3
Glass_CD		1.82	0.48	65.98	1.73	0.578	6.25	10.81
PMMA_Cu_Doped_CD		4.21	0.52	66.35	3.99	1.45	6.25	24.93
Glass_Cu_Doped_CD		2.22	0.48	65.98	2.11	0.705	6.25	13.18

To investigate the optical losses in LSCs with the dimensions of 225 cm<sup>2</sup>, light emission was measured at the edges of the LSC at varying distances from the edge (Fig. 6b and c). The results indicate light emission intensity decreases as the distance from the edge increases, as expected for isotropic light diffusion. However, the PL peak position and peak shape remains stable and at different distances revealed no discernible peak shift. This suggests the absence of energy loss due to light reabsorption. This indicates that the emitted light can be stably diffused in the waveguide.<sup>52,54</sup>

The stability of LSCs was evaluated over 90 days under natural sunlight irradiation conditions (Summer, Mashhad, Iran, the average daily light intensity:  $\sim$ 875 W m<sup>-2</sup>). PCE and optical efficiency were measured every 15 days. The measurements revealed no significant differences over the 90 days. This remarkable stability can be attributed to the extraordinary stability of the synthesized CDs used in the LSCs, which did not suffer from a drop in optical performance under real conditions. This highlights the high capability and importance of using CDs in LSCs. Photovoltaic studies further demonstrated that after 90 days, the photovoltaic and optical efficiency in the LSCs had dropped by approximately 2% (Fig. 6f and S4†).

Compared to existing research in the field of LSCs based on CDs, the results obtained in this work are outstanding (Table S1†). The key findings include: (1) the synthesis of Cu-doped CDs using a simple and cost-effective method, resulting in a high quantum yield (81%), a large Stokes shift (0.71 eV), and excellent stability; (2) the fabrication of large-dimension (225 cm<sup>2</sup>) LSCs based on glass and PMMA waveguides, which demonstrate higher optical and photovoltaic efficiency and (3) the innovative approach of doping CDs with metal ions, which can serve as a starting point for improving and engineering the optical properties of CDs, ultimately leading to the commercialization of CDs-based LSCs.

## 4. Conclusions

This study demonstrates the significant advancements in luminescent solar concentrators (LSCs) utilizing carbon dots (CDs) doped with transition metal ions. The synthesis of these metal-doped CDs via a microwave method resulted in materials with a high quantum yield of 81%, a substantial Stokes shift of 0.71 eV, and excellent stability, positioning them as promising candidates for transparent photovoltaic applications. The investigation revealed that doping with 1 mol% copper significantly enhanced the optical properties of the CDs, leading to improved light absorption and emission. The LSC fabricated from these Cu-doped CDs exhibited remarkable photovoltaic performance, achieving an optical efficiency of 3.99% and a photoconversion efficiency (PCE) of 1.45%. The 22% increase in both optical efficiency and PCE underscores the effectiveness of transition metal doping in optimizing LSC technology. Furthermore, stability assessments over a 90 days period indicated minimal degradation in performance, highlighting the robustness of the synthesized materials under real-world conditions. This research not only highlights the potential for integrating metal-doped CDs into urban environments but also

paves the way for the commercialization of transparent photovoltaic systems, contributing to the advancement of renewable energy technologies.

## Data availability

The authors declare that the data that support the findings of this study are available from the corresponding author upon reasonable request.

## Author contributions

Kambiz Hosseinpanahi: conceptualization (equal); data curation (lead); formal analysis (lead); investigation (equal); methodology (lead); writing—original draft (lead). Mohammad Hossein Abbaspour-Fard: conceptualization (supporting); resources (equal); funding acquisition (equal); writing—review &editing (equal). Mahmoud Reza Golzarian: formal analysis (lead); writing—review & editing (equal). Elaheh K. Goharshadi: formal analysis (equal); supervision (supporting); writing original draft (supporting). Setayesh Sajadi: formal analysis (equal); writing—review & editing (equal). Alberto Vomiero: conceptualization (equal); funding acquisition (equal); writing—review & editing (lead).

## Conflicts of interest

The authors declare no conflict of interest.

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