Internal versus external quantum efficiency of luminescent materials, photovoltaic cells, photodetectors and photoelectrocatalysis

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Internal and external quantum yield/efficiency is of paramount importance for luminescent materials, photovoltaic cells, photodetectors and photoelectrocatalysis. We aim to provide a relation between internal and external quantum yield/efficiency and correlation among the material/device properties. We also aim to understand this relation through a common example we experience in our lives.

Keywords: Internal and external quantum efficiency, luminescent materials, photovoltaic cells, photodetectors, photoelectrocatalysis.

INTRODUCTION of photons of energy equal to or greater than the band gap of a semiconductor results in photon absorption, charge separation and extraction/recombination. Preference of charge separation or recombination decides the application of solar/photon conversion devices like photovoltaic cells, photodetectors, photoelectrocatalysis and luminescent materials. It is realized that they share a concept in common, i.e. quantum efficiency (QE)/quantum yield (QY) which can further be classified into external and internal. External quantum efficiency (EQE) is of interest for photodetection, photovoltaic and photoelectrochemical cells[1–3]. For luminescent materials, the internal quantum efficiency (IQE)/internal quantum yield (QY_i), is generally quoted, which is sometimes, misleading[4]. For example, IQE/QY_i may be high and the overall brightness of the material is low. This happens if the light absorption capability of the material is low and wavelength conversion is efficient. In this article we aim to provide a relation between IQE and EQE and correlation among the material/device properties.

Discussion

Internal versus external quantum efficiency/yield for luminescent materials

QE/QY is a measure of the figure of merit of luminescent materials. Materials with high absorption and high QE are a pre-requisite for applications discussed in the introduction. QE is defined as the ratio of the number of photons emitted to those absorbed and corresponds to IQE. Another definition of QE is the ratio of the number of photons emitted to the total number of incident photons and corresponds to EQE. IQE is related to EQE as follows

$$\mathrm{IQE} = \frac{\mathrm{EQE}}{(1-T-R)}, \tag{1}$$

where T is the transmittance and R is the reflectance. This indicates that IQE is always greater than EQE. As an example, we consider YAG phosphor that is being used for the conversion of blue LED into white. QY of YAG phosphor is 97% and is used for the conversion purpose[4]. This indicates that it can convert blue light completely into yellow. However, white light is realized, which suggests a strong blue component along with yellow light. Therefore, it is considered that QE of 97% is IQE and EQE is expected to be much lower than IQE. A low IQE indicates that the phosphor is unable to make good use of the photons.

Figure 1 shows the absorbance (A), EQE and IQE of $\mathrm{La}_{3(1-y)}\mathrm{Si}_{6.5}\mathrm{Al}_{1.5}\mathrm{N}_{9.5}\mathrm{O}_{5.5}:3y\mathrm{Ce}$, where y varies from 0.005 to 0.50 (ref. 5). The highest IQE of 84% is achieved when $y = 0.01$ (1% doped) and highest EQE of 60% at $y = 0.05$ at room temperature[5]. We have considered 1% Ce-doped sample as efficient blue-emitting phosphor. We reckon that 0.05% Ce-doped sample should have been considered for this purpose, as EQE is highest for it.

Photovoltaic cells

Like the case of QE/QY in luminescent materials, two types of quantum efficiency of a solar cell are often considered.

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- EQE is the ratio of the number of charge carriers collected by the solar cell to the number of incident photons.

$$\mathrm{EQE} = \frac{\text{Electrons/sec}}{\text{Incident photons/sec}}.$$

- IQE is the ratio of the number of charge carriers collected by the solar cell to the number of photons absorbed by the cell and is related to EQE by

$$\mathrm{IQE} = \frac{\text{Electrons/sec}}{\text{Adsorbed photons/sec}} = \frac{\mathrm{EQE}}{1-R-T}.$$

It can also be written as[6]

$$\mathrm{IQE} = \frac{\mathrm{EQE}}{(1-L)}, \tag{2}$$

where L is the absorption and reflection loss.

EQE, therefore, depends on both the collection of charges and the absorption of light. EQE gives the efficiency of the overall photovoltaic device. As is the case of luminescent materials, EQE is always lower than IQE for a photovoltaic device. IQE can be evaluated using the (eq. (2)) if transmission and reflection are known. A low IQE indicates that the active layer of the solar cell is unable to make good use of the photons. Figure 2 provides a comparison of IQE and EQE for a Si solar cell[7].

Photodetectors

Similar to solar cells, two types of quantum efficiency are also considered for a photodetector.

- EQE is defined as the ratio of the number of photogenerated charge carriers to the number of incident photons.

For any detector, EQE is lower than IQE, and is given by[8]

$$\mathrm{EQE} = \frac{hc}{qn\lambda}\left(\frac{i_{\mathrm{ph}}}{P}\right) = \frac{Rhc}{q\lambda}, \tag{3}$$

where h is the Planck's constant, c the speed of light in vacuum, q the elementary charge, n the refractive index in air, λ the wavelength of the incident radiation, i_{ph} the photocurrent, P the power and R is the responsivity of a photodiode which is given by

$$R = \frac{i_{\mathrm{ph}}}{nP}. \tag{4}$$

- IQE is defined as the ratio of the number of photogenerated charge carriers to the number of photons absorbed within the active layer(s) of the device. Some portion of the light beam generally gets reflected from the photodiode surface, and IQE can be written as

$$\mathrm{IQE} = \frac{Rhc}{q\lambda\,(1-L)} = \mathrm{EQE}/(1-L), \tag{5}$$

where L is the reflectance of the photodiode.

Figure 3 presents the EQE and IQE of nanostructured black-Si photodiode measured at zero bias. Identical IQE and EQE were observed due to very low reflectance loss[9]. For photodetection, EQE determines the performance of the real device.

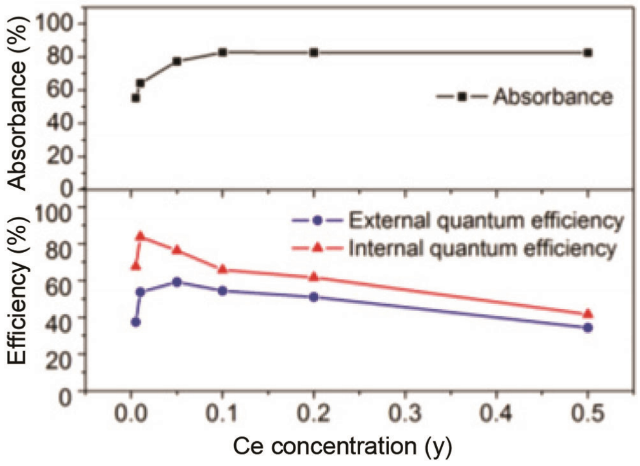

Figure 1. Variation in absorbance (A), internal quantum efficiency (IQE) and external quantum efficiency (EQE) for $La_{3(1-y)}Si_{6.5}Al_{1.5}N_{9.5}O_{5.5}$: 3yCe (y = 0.005–0.50) phosphors. Adapted with permission from ref. 5. © 2017 American Chemical Society.

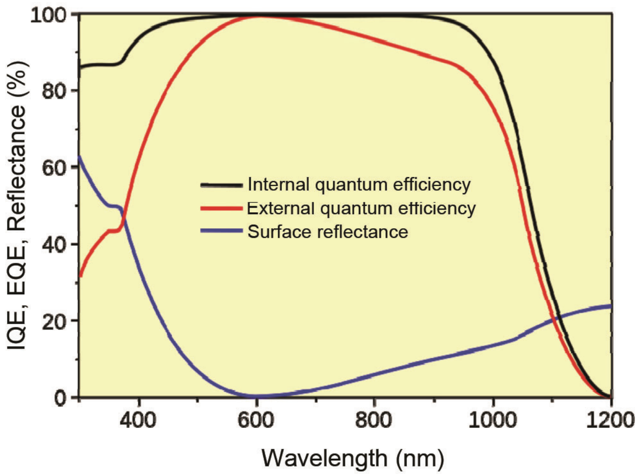

Figure 2. Variation of IQE, EQE and reflectance (R) with wavelength of a crystalline Si solar cell[7]. Adapted from https://en.wikipedia.org/wiki/Quantum efficiency

Photoelectrochemical solar fuel production (photoelectrocatalysis)

Similar to luminescent materials, photovoltaics and photodetectors, quantum efficiencies exist in solar fuel producing devices as well.

- Incident photon to current conversion efficiency (IPCE) measures the total number of electrons converted from all of the incident photons, which is also the EQE.

$$\mathrm{IPCE} = \frac{\text{Electron flux}\left(\frac{\text{mol}}{s}\right)}{\text{Photon flux}\left(\frac{\text{mol}}{s}\right)},$$

$$\mathrm{IPCE} = (J_{\mathrm{ph}} * hc)/P_{\lambda} * \lambda), \tag{6}$$

where J_{ph} is the photocurrent density, h the Planck's constant, c the speed of light in vacuum, P_{λ} the power of light at a particular wavelength and λ is the wavelength of irradiation.

- Absorbed photon to current conversion efficiency (APCE) or IQE takes into account the total number of electrons converted from the absorbed photon[10].

$$\mathrm{APCE} = \frac{\mathrm{IPCE}}{A_{\lambda}},$$

$$\mathrm{APCE} = (J_{\mathrm{ph}} * hc)/(P_{\lambda} * \lambda * A_{\lambda})$$

$$= (J_{\mathrm{ph}} * hc)/\ [P_{\lambda} * \lambda * (1 - L_{\lambda})], \tag{7}$$

where A_{λ} is the absorptance as a function of wavelength.

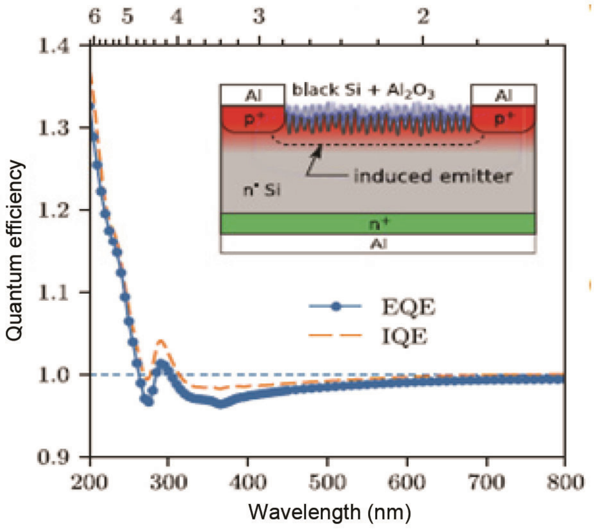

Figure 3. EQE and IQE of black-silicon ultraviolet photodiodes at zero bias. Adapted with permission from ref. 9. © 2020 American Physical Society.

As an example, we have taken IPCE and APCE of bare and surfactant-modified In_2O_3 for water oxidation reaction (Figure 4 *a*)[11]. It is observed that at a particular wavelength, APCE is greater than IPCE. The highest IPCE and APCE values were 28% and 40% respectively, for the 0.01 M surfactant-modified In_2O_3 (ref. 11). We have taken another example that compares IPCE and APCE of CoPi decorated hematite grown on 3D and planar FTO substrate (Figure 4 *b*). The APCE values of 3D and planar FTO substrate in the long-wavelength region are close (>550 nm), revealing that the improved light trapping effect by 3D substrate is responsible for the improved IPCE value. The IPCE value at 380 nm for Ti-doped Fe_2O_3 grown on 3D FTO substrate is 42% higher than that on the planar FTO substrate[12].

Figure 4 *c* and *d* shows the IPCE and APCE values of Fe–V-oxide films with different compositions of Fe and V respectively. FeV_2O_4 shows the highest photoconversion efficiency of 60% APCE and 22% IPCE compared to the other Fe–V-oxides due to its high carrier concentration, low charge transfer resistance and higher double-layer capacitance[13]. Though APCE helps in understanding the system better, obtaining high IPCE values is of greater importance for practical applications.

Approaches to improve IQE

It can be concluded that the efficiency of photon conversion devices can be enhanced by maximizing the light-harvesting

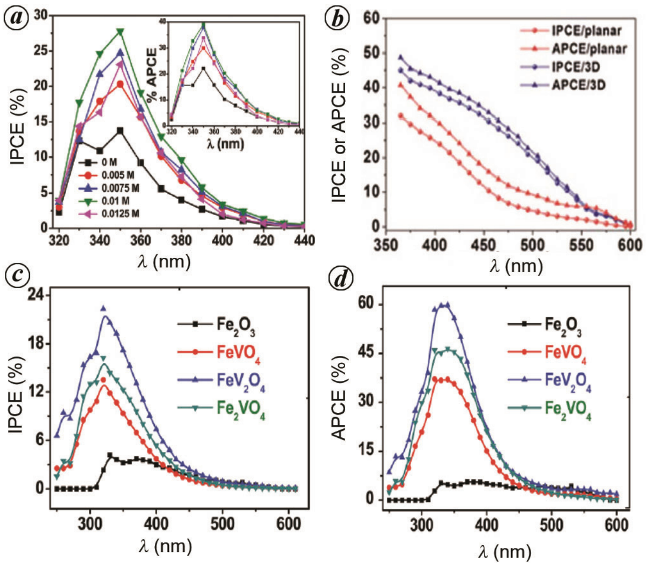

Figure 4. Incident photon to current conversion efficiency (IPCE) and absorbed photon to current conversion efficiency (APCE) of (***a***) modified In_2O_3 for oxygen evolution reaction at 0.1 M SO_4^{2-} solution. Adapted with permission from ref. 11. © 2018 Royal Society of India. (***b***) 3D and planar fluorine doped tin oxide substrate. Adapted with permission from ref. 12. © 2014 Royal Society of Chemistry. (***c***) IPCE and (***d***) APCE of Fe–V-oxide semiconductors in 0.1 M Na_2SO_4 at applied potential 1.0 V versus Ag/AgCl reference electrode. Adapted with permission from ref. 13. © 2016 Royal Society of Chemistry.

capacity or minimizing reflection loss. Strategies adopted to improve light absorption or reflection loss include anti-reflection coating, band engineering, dual absorber and back reflector[14].

Anti-reflection (AR) coating: The reflectance at normal incidence for single layer on substrate is expressed as follows[15]

$$r = \frac{(n_{\text{air}} n_{\text{s}} - n^2)}{(n_{\text{air}} n_{\text{s}} + n^2)}. \tag{8}$$

For zero reflectance, $n = \sqrt{(n_{\text{air}} n_{\text{s}})}$, where, n, n_{air} and n_{s} are the refractive index of the film, air and substrate respectively.

Therefore, choosing the right material coating can minimize reflectance loss[16]. Multiple layers of AR coating have been explored for broadband and omnidirectional AR characteristics[17].

Band-gap engineering: Semiconductor with small band gap can absorb more photons compared to large band gap materials and therefore, can improve the light-capturing capacity. Intrinsic or doping of foreign atoms is generally adopted to reduce the band gap of a semiconductor[14].

Dual absorber: Two materials of different band gaps can be coupled so that the photon transmitted by the higher band-gap material is further absorbed by the smaller band-gap material. This helps in efficient utilization of the incoming photons[18], and is generally adopted in photoelectrochemical solar to fuel conversion devices.

Back reflector: Use of a back reflector is a potential strategy to enhance light-trapping effect[19]. The photons that are transmitted through the thin semiconductor layer are reflected back to the semiconductor by the reflector that improves the optical path length without optical loss[20,21].

The properties of absorbing material, antireflection coating and back reflector can be modulated by various methods. The absorption probability of a given absorbing material is given by[22]

$$P = \frac{f_{\text{A}} * \propto L}{(f_{\text{A}} * \propto L) + 1},$$

where L is the thickness of the material, α the absorption coefficient of material and f_{A} is the absorption enhancement factor defined by the optical designing of photonics devices. To enhance the absorption probability, either f_{A} or L must be enhanced. An arbitrary increase in L is not acceptable as photogenerated carriers in a thick film will recombine before being collected by the contacts. The other approach is to enhance the f_{A} by patterning the absorbing material, back reflector or anti-reflection coating. The photons incident on the semiconductor get internally reflected between the patterned absorbing materials/back reflector/anti-reflection coating allowing multiple absorption which overall leads to enhancement in absorbed photons[22,23].

Correlation and understanding through a common example

Overall, QY/QE of luminescent materials and QE of solar cells/photodiodes/photoelectrochemical solar fuel-production devices share similar relations as evident from eqs (1), (2), (5) and (7).

For a better understanding of QY/QE, we take the following example. Two persons *A* and *B*, are given US$ 1000 to invest. At the end of the day, *A* invests only US$ 50 and makes a profit of US 50, whereas *B* invests the full amount and makes a profit of US$ 600. If the amount invested and the profit made are taken into consideration (similar to IQE), *A* seems to be highly efficient. However, if one considers the amount available and the profit made (similar to EQE), *B* is more efficient.

Conclusion

In conclusion, we have considered QY of luminescent materials and QE of solar cells/photodiodes and understood their relation through a common example we experience in our life. We have shown that QY of luminescent materials and QE of solar cells/photodiodes/photoelectrochemical solar fuel-production devices share similar relations. We also outline different strategies to improve QE. This work is expected to motivate teachers/researchers to develop approaches for a better understanding of the subject matter.

Conflict of interest: The authors declare no competing financial interest.

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