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CHAPTER 1

Bridging Electrochemistry and Solar Energy: Cyclic Voltammetry as a Tool for Innovation

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Abstract: Cyclic voltammetry (CV) has emerged as innovative electrochemical technique for probing the electronic properties of semiconducting nanomaterials, playing a crucial role in the design and optimization of high-efficiency optoelectronic devices. This book chapter delivers a comprehensive overview of the application of CV in determining key band structure parameters, such as the valence band maximum (VBM) and conduction band minimum (CBM), through the analysis of oxidation and reduction potentials. Unlike ultraviolet photoelectron spectroscopy (UVPES), CV enables real-time measurements with greater accuracy and accessibility, offering a cost-effective alternative for band structure investigations. In addition to band edge determination, we discuss the role of CV in analyzing charge transfer mechanisms, essential for understanding interfacial processes in solar cell architectures. The chapter also explores the significance of hole transport layers (HTL) and electron transport layers (ETL) in solar cells and provides an in-depth discussion of voltammetric data interpretation, including why specific features appear in voltammograms and how they correlate with electronic properties. The

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Brus model is introduced to establish a connection between voltammetric findings and quantum confinement effects. Furthermore, a major challenge for researchers is differentiating between optical and electrochemical band gaps. This chapter addresses this issue by presenting a detailed theoretical model that clarifies the correlation between these two fundamental parameters. By bridging the gap between optical and electrochemical characterizations, this work provides valuable insights into band engineering strategies for next-generation photovoltaic devices. Overall, this chapter serves as a guide for researchers in electrochemistry and semiconductor science, aiding in the development of advanced solar energy technologies through interface optimization and the strategic design of semiconducting nanomaterials for energy conversion applications.

Keywords: Electrochemistry; Cyclic Voltammetry; Solar cell; Band structure parameters

1. Introduction

Cyclic voltammetry (CV) has established itself as a pivotal technique in the engineering of advanced solar cell devices, providing detailed insights into the electrochemical properties essential for optimizing material performance.[1–3] This chapter highlights how CV is used to probe the energy levels, band structures, and charge transport mechanisms within photovoltaic materials like perovskites, quantum dots, and organic photovoltaics.[1,3,4] By cycling potential and analysing redox peaks, CV enables researchers to map conduction and valence band edges accurately, which is essential for designing materials with efficient energy alignment. The use of non-aqueous media, such as organic solvents and ionic liquids, further enhances CV's effectiveness by providing a stable environment for measuring band edge positions without interference from water-based side reactions, thereby giving a clearer picture of how materials will behave in real-world solar cells.[4]

In addition to characterizing individual materials, CV is invaluable for analysing charge transfer processes at key interfaces, such as between electrode and electrolyte layers or semiconductor materials. This interface analysis reveals how passivation layers and interfacial modifications can reduce unwanted charge recombination, directly improving solar cell efficiency.[3,5,6] Non-aqueous media play a significant role here as well, allowing for more accurate and reproducible electrochemical measurements that are crucial for understanding and optimizing multi-layer architectures in solar cells. CV also offers a unique advantage over other techniques like electrochemical impedance spectroscopy (EIS), as it provides direct insights into redox behaviours and band structure dynamics that are essential for fine-tuning energy levels, while EIS focuses more on overall impedance profiles and can complement CV for a fuller picture.[4]

Looking forward, CV's versatility and ability to conduct in-situ measurements show promise for real-time solar cell analysis under operational conditions. This capability, combined with emerging applications in ionic liquids and other non-aqueous solvents, offers exciting possibilities for advancing solar cell stability and scalability.[1,3] However, challenges remain in standardizing CV results for commercial applications, particularly regarding reproducibility across different materials and electrode setups. As this chapter outlines, CV stands self-assured to continue pushing the boundaries of solar cell

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efficiency, stability, and sustainability, making it a cornerstone technique in the journey toward more effective and commercially viable solar energy solutions.

2. Secret of high efficiency solar cells

The efficiency and performance of a solar cell are complexly tied to the band alignment of its key components: the electron transport layer (ETL), the semiconducting (absorber) material, and the hole transport layer (HTL).[5,7] Each of these layers serves a pivotal function in the process of converting sunlight into electricity, and their optimal alignment is crucial for maximizing charge transfer, minimizing energy loss, and improving overall cell efficiency.

2.1 Electron Transport Layer (ETL)

The ETL is responsible for efficiently extracting and transporting electrons from the absorber layer to the electrode. For this layer to function effectively, it must have a conduction band edge that aligns closely with the conduction band of the semiconducting material, enabling a seamless flow of electrons. A well-aligned ETL reduces energy barriers, enhancing electron extraction and reducing recombination losses at the interface. Additionally, the ETL should be able to block holes to prevent charge recombination, which would otherwise decrease efficiency. Common materials used for electron transport layers (ETLs) include metal oxides such as TiO_2, ZnO, and SnO_2; fullerene derivatives like C_{60} and PCBM; perovskites such as $BaSnO_3$ and $SrTiO_3$, as these materials possess appropriate energy levels and good electron mobility.[5,7]

Key Functions of ETL

Electron Extraction and Transport: The ETL collects electrons generated in the semiconductor and transfers them to the external circuit.

Hole Blocking: It prevents holes from reaching the cathode, minimizing recombination.

Energy Level Matching: The ETL's conduction band must align well with the conduction band of the semiconductor for effective electron transfer.

2.2 Semiconducting (Absorber) Layer

The semiconducting layer, also known as the absorber layer, is the core of the solar cell where photons are absorbed and electron-hole pairs are generated. This material should have a suitable band gap that enables it to absorb a broad spectrum of sunlight, especially in the visible range. For efficient operation, the conduction band minimum (CBM) should be aligned closely with the ETL's CBM, while the valence band maximum (VBM) should align with the VBM of the HTL. The ideal band gap for a single-junction solar cell is around 1.3 to 1.5 eV, balancing the ability to absorb light across a wide spectrum and minimize thermal losses. Common materials for the absorber layer include silicon (Si), cadmium telluride (CdTe), and perovskite materials like methylammonium lead iodide ($MAPbI_3$), which have tunable band gaps and high absorption coefficients.[2,3,5,7–10]

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Key Functions of the Absorber Layer

Photon Absorption and Exciton Generation: It absorbs sunlight, generating electron-hole pairs that can be separated for electricity.

Energy Level Matching: The band edges of the absorber should align with those of the ETL and HTL for efficient charge transfer.

Charge Transport: It should support the transport of electrons to the ETL and holes to the HTL with minimal recombination losses.

2.3 Hole Transport Layer (HTL)

The HTL facilitates the extraction and transport of holes from the absorber to the anode while blocking electron transfer, thereby reducing recombination losses.[5,7] The valence band of the HTL must align with the valence band of the absorber layer to ensure efficient hole transfer.[5,7,11] This alignment reduces energy losses and allows for the effective collection of photo generated holes. Common materials used for HTLs include organic semiconductors like spiro-OMeTAD, poly(triarylamine) (PTAA), and inorganic materials like nickel oxide (NiO) and copper thiocyanate (CuSCN). These materials are chosen for their suitable energy levels, high hole mobility, and ability to block electron backflow.

Key Functions of HTL

Hole Extraction and Transport: The HTL collects holes generated in the semiconductor and transfers them to the external circuit.

Electron Blocking: It prevents electrons from reaching the anode, thereby minimizing recombination.

Energy Level Matching: The HTL’s valence band should align well with the valence band of the semiconductor to ensure efficient hole transfer.

2.4 Importance of Band Alignment in Solar Cells

The alignment of the ETL, absorber, and HTL energy levels is critical for reducing energy losses and optimizing charge carrier transport. Misalignment can create energy barriers that slow down or prevent charge transfer, resulting in increased recombination and lower overall efficiency. Here’s why each interface matters: **ETL/Absorber Interface:** A well-matched conduction band between the ETL and the absorber ensures that electrons can flow easily from the absorber to the ETL, minimizing electron-hole recombination at this junction. **Absorber/HTL Interface:** Proper alignment of the valence band at the absorber/HTL interface facilitates the efficient extraction of holes from the absorber, allowing them to flow freely into the HTL without significant energy loss. **Reducing Recombination:** Effective band alignment at both interfaces is essential to minimize charge carrier recombination, a key factor that impacts efficiency.

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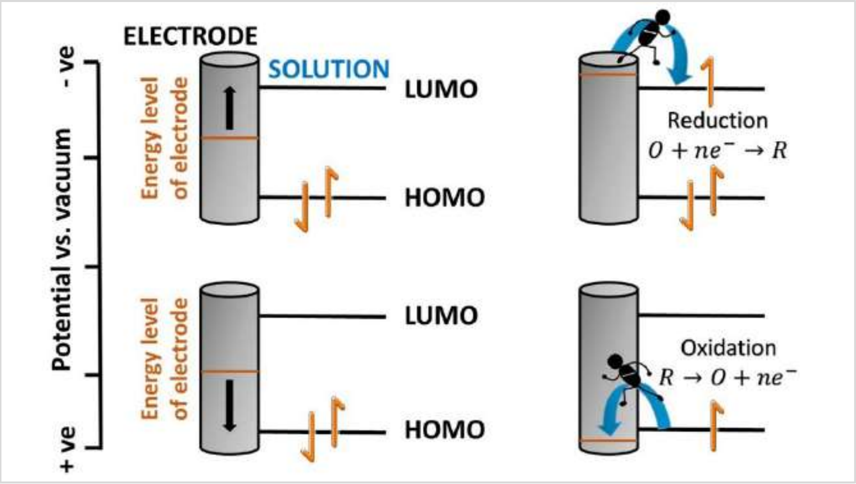
2.5 Band Alignment Optimization Strategies

Optimizing band alignment in solar cells involves adjusting the energy levels of each layer to ensure smooth charge transfer. This can be achieved by tuning the chemical composition or doping levels of the ETL, absorber, and HTL materials. Additionally, using interfacial layers or modifying the surface chemistry can help to improve alignment, reduce defect density, and further enhance charge transport properties. Properly aligned layers help to maximize open-circuit voltage, short-circuit current, and overall power conversion efficiency of the solar cell. In summary, the performance of a solar cell depends critically on the band alignment among the ETL, absorber layer, and HTL. Each layer must have well-matched energy levels to facilitate efficient charge separation and transport while minimizing recombination. Through careful material selection and engineering, the band alignment can be optimized to absorb high-energy photons, achieve effective charge transport, and ultimately enhance solar cell efficiency.

3. Cyclic Voltammetry to Analyse Charge Transfer and Band Alignment in Semiconductors



Scheme 1: A schematic illustration of the cyclic voltammetry process, depicting the charge transfer dynamics between the electrode and analyte species in solution. The diagram highlights oxidation and reduction events at the electrode interface, visualized through an analogy of energy barriers and electron movement, ultimately correlating with characteristic cyclic voltammograms.

Cyclic voltammetry (CV) is a powerful electrochemical technique that provides valuable insights into charge transfer processes and band alignment in semiconducting materials.[1–3,8,12,13] By analysing the redox behaviour of materials, CV can help determine the energy levels of the conduction band (CB) and valence band (VB) in semiconductors, as well as study how charges move between different layers, which is crucial for optimizing solar cells, transistors, and other devices.[3]

In CV, the applied potential is swept in a cyclic manner, which can cause the semiconductor to either donate or accept electrons at specific potentials. These potentials correspond to the energy levels of the CB and VB. By measuring the onset of oxidation (positive potential) and reduction (negative

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potential) during the cyclic sweep, we can estimate the highest occupied molecular orbital (HOMO, related to VB) and the lowest unoccupied molecular orbital (LUMO, related to CB) energy levels. These values provide a direct estimate of the semiconductor's band edge positions, which is essential for understanding its electronic structure and compatibility with other layers in a device.[1]

CV is a powerful electrochemical technique where the applied potential is linearly swept over time between two predefined limits, enabling the investigation of electron transfer processes in quantum dots (QDs) systems. When the Fermi level of the electrode aligns with the electronic energy levels of the QDs—whether dispersed in solution or adsorbed onto the electrode surface—electron transfer occurs, leading to a measurable current response. This phenomenon forms the basis for electrochemical band structure analysis (see Scheme 1).

In the reduction process, applying a negative potential raises the Fermi level of the electrode. When this level coincides with an available unoccupied state in the QDs (conduction band minimum), electrons are injected from the electrode into the QDs, generating a cathodic current. Conversely, during oxidation, a positive potential lowers the Fermi level of the electrode. When this level matches the highest filled state in the QDs (valence band maximum), electrons are extracted from the QDs into the electrode, producing an anodic current. Since these electrons transfer events correspond to the conduction and valence band edges, the peak positions in the CV curve directly indicate these fundamental energy levels. The energy separation between the reduction and oxidation peaks is defined as the electrochemical band gap, a crucial parameter for understanding QDs electronic properties.[1–4,8,12–14]

For freely diffusing QDs in solution, electron transfer occurs at isolated particles, ensuring that the measured electrochemical band gap coincides with the quasi-particle gap. However, interpreting these results requires attentiveness, particularly in QDs adsorbed on the electrode surface and forming thin film.[4] Due to the limited density of QDs on the electrode, only the anodic peak (valence band edge) is typically observed, while the conduction band edge is inferred by adding the optical band gap obtained from spectroscopic measurements. Additionally, in solution-based systems, current peaks in CV arise from mass transport-controlled processes.[1] For single-electron transfer systems with reversible kinetics, the peak potential shifts by 28.5 mV from the formal redox potential, introducing only minor errors in band gap estimation.[4] However, in quasi-reversible and irreversible systems, such as semiconductor QDs, these shifts can exceed hundreds of millivolts, depending on the activation over potential and scan rate.[1,4] This highlights the necessity of careful analysis and calibration when using CV for band structure determination.

4. Electrochemical Dynamics of Semiconductors

Brus[15] theoretically predicted that the redox potential of semiconducting QDs depends on particle size, using the particle-in-a-box model, where the bandgap energy (E_g) follows an inverse square relationship with the quantum dot radius ($E_g \propto 1/_{r^2}$).[3] While this model was experimentally

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validated by the size-dependent shift in optical absorption spectra, direct measurements of conduction and valence band-edge shifts remained unexplored.

Electrochemical techniques, particularly cyclic voltammetry (CV), provide a precise method for determining the energy difference between HOMO and LUMO levels in redox-active molecules. Based on this principle, Haram and co-workers[1] were the first to establish a direct correlation between electrochemically determined bandgap energies and UV-Vis absorption spectra of CdS QDs in dimethylformamide (DMF), thus offering experimental validation of the Brus model.[1]

An essential consideration in CV measurements of quantum dots (QDs) is distinguishing the mode of electron transfer—whether it occurs via freely diffusing QDs in solution or through an adsorbed QD film on the electrode surface. This distinction is crucial, as adsorbed QD films introduce several limitations[4], including:

Chemical degradation, diffusion limitations, and theoretical inconsistencies are key challenges associated with cyclic voltammetry (CV) measurements of adsorbed quantum dot (QD) films:

- Chemical Degradation: Charge transfer (electron or hole injection) can initiate chemical reactions that gradually degrade QDs.
- Diffusion-Controlled Limitations: In particulate films, charge transport is not governed by diffusion, complicating data interpretation.
- Theoretical Constraints: Computational models, such as the semi-empirical pseudopotential method (SEPM), assume charge transfer occurs in isolated QDs. However, in adsorbed films, the close packing of QDs disrupts this assumption, leading to deviations from theoretical predictions.

Using diffusing QDs in electrochemical measurements mitigates these challenges by ensuring charge transfer occurs in isolated QDs, aligning more closely with theoretical boundary conditions. This approach enables a more accurate comparison between experimental and theoretical data, particularly in determining the quasi-particle gap of QDs.[1,3,4] However, while QDs dispersed in an electrolyte medium are commonly used for electrochemical analysis, their charge transfer kinetics may not always follow classical diffusion-controlled behaviour.[3,4] During CV experiments, QDs from the dispersion can adsorb onto the electrode surface, potentially altering the expected electrochemical response and adding complexity to data interpretation.

To differentiate between diffusion-controlled and surface-adsorbed electron transfer processes, the peak current for oxidation and reduction should be examined as a function of the square root of the scan rate.[1–4,8,12–14] A linear relationship indicates a diffusion-controlled process, while deviations from this trend suggest significant adsorption effects, necessitating further analytical considerations.

The peak current in cyclic voltammetry is governed by the Randles–Sevcik equation:

$$i_p = 0.4463nFAC\left(\frac{nF\upsilon D}{RT}\right)^{\frac{1}{2}}$$

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Or if the solution is at 25 °C

$$i_p = (2.69 \times 10^5) n^{3/2} A D^{1/2} C \upsilon^{1/2}$$

where:

i_p = peak current (A)
D = diffusion coefficient (cm^2/s)
A = electrode surface area (cm^2)
C = analyte concentration (mol/cm^3)
n = number of electrons transferred
υ = scan rate (V/s)
F = Faraday constant in C mol^{-1}
R = Gas constant in J K^{-1} mol^{-1}

A linear relationship between the peak current and the square root of the scan rate for peaks oxidation and reduction confirms a diffusion-controlled electrochemical process.[1] This indicates that the QDs in solution undergo redox reactions at the electrode surface without significant interference from an adsorbed QD film.[1,3] Such behaviour aligns with classical diffusion-controlled kinetics, ensuring that charge transfer occurs between freely diffusing QDs and the electrode rather than being constrained by surface interactions or aggregation effects.[4]

5. Correlation Between Optical Band Gap and Electrochemical Band Gap: A Comparative Analysis

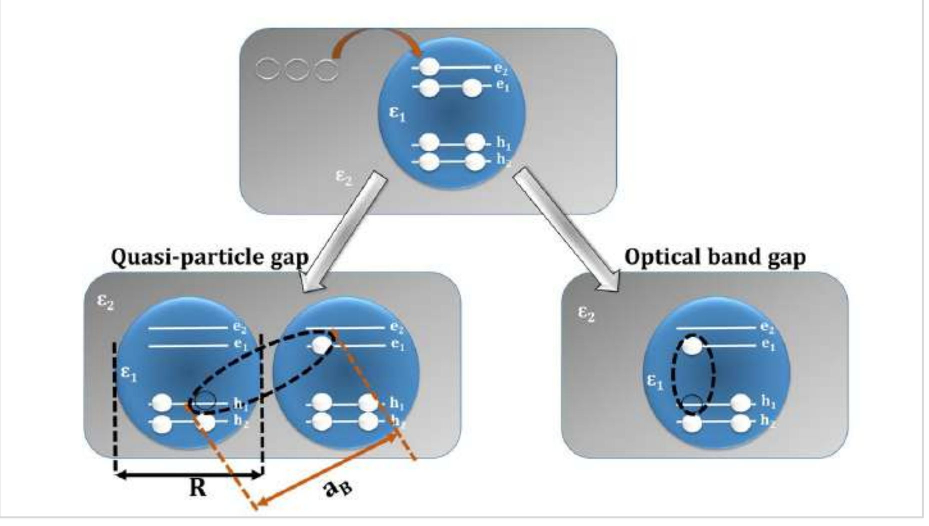

Figure 1. (A) Electron loading into semiconductor quantum dots (QDs). (B) Addition of an electron to a QD leads to charge redistribution, resulting in the formation of a spatially separated electron-hole pair, characterized by the quasi-particle gap. (C) The formation of an interacting electron-hole pair within a QDs, induced by excitonic effects, defines the optical band gap.

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Consider a spherical quantum dot of radius R and dielectric constant ε_1 encapsulated by an organic medium such as oleic acid with a dielectric constant ε_2. Initially, electron addition occurs to the neutral quantum dot with an intrinsic energy E_0. The introduction of three electrons follows the Pauli exclusion principle, dictating their spatial and spin arrangements.[15]

When a single electron is incorporated into the conduction level e_1, an energy perturbation occurs, leading to the following energy conservation relation:

$$E_1[e_1] = E_\circ + \varepsilon_{q1}$$

Where ε_{q1} represents the quasiparticle energy, incorporating contributions from quantum confinement effects and polarization due to its image charge at the quantum dot surface. The chemical potential associated with the addition of the first electron is given by:

$$\mu_1 = E_1[e_1] - E_\circ$$

Subsequently, when a second electron is introduced into the conduction level e_1, the total energy of the quantum dot system is modified as:

$$E_2 = E_\circ + 2\varepsilon_{q1} + J_{e_1,e_1}$$

Where J_{e_1} accounts for the Coulombic repulsion between the two electrons occupying the same conduction level. Consequently, the energy required for the second electron addition is:

$$\mu_2 = E_2[e_1^2] - E_1[e_1]$$

Upon introducing a third electron into a higher conduction level e_2, the total energy of the quantum dot is:

$$E_3[e_1^2 e_2] = E_\circ + 2\varepsilon_{q1} + J_{e_1 e_2} + 2J_{e_1 e_2} - K_{e_1 e_2}$$

Here, $K_{e_1 e_2}$ represents the exchange energy associated with parallel spin electrons occupying distinct conduction levels. The energy required for the third electron addition is thus:

$$\mu_3 = E_3[e_1^2 e_2] - E_2[e_1^2]$$

Following this, the formation of a Wannier exciton occurs, characterized by a bound state of an electron-hole pair, driven by Coulombic interactions. The spatial separation between the electron and hole is defined by the exciton Bohr radius:

$$a_B = \frac{4\pi\varepsilon_1\varepsilon_2\hbar^2}{e^2}\left(\frac{1}{m_e^*} + \frac{1}{m_h^*}\right)$$

where m_e^* and m_h^* are the effective masses of the electron and hole, respectively, ε_1 and ε_2 is the relative dielectric constant of the quantum dot and surrounding medium.

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Using the Brus[15] and Franceschetti model[10], the excitonic behavior manifests in two distinct regimes:

a) Quasiparticle Energy Regime (Non-Interacting Electron-Hole Pair)

In this scenario, an electron transitions from the valence band of one quantum dot to the conduction band of another quantum dot, positioned at an infinitely large separation. Mathematically, this condition is expressed as $R \ll a_B$, indicating that the electron and hole do not form a bound state and are thus deprived of any Coulombic interaction. The energy required to create this non-interacting electron-hole pair corresponds to the quasiparticle energy.[3,10,15]

This energy is model by treating the charge carriers as independent particles confined within a spherically symmetric potential well with infinite potential barriers.[3] The quantized energy levels for such a system can be expressed as:

$$E = E_g + E_{nl} = \varepsilon_g^{qp}$$

$$E_{nl} = \frac{\chi_{nl}^2 \hbar^2}{2R^2}\left(\frac{1}{m_e^*} + \frac{1}{m_h^*}\right)$$

Where R is the QDs radius and χ_{nl} are the roots of spherical Bessel function with n and l representing the principal and orbital quantum numbers respectively.

For the lowest state (n=1, l = 0) $\chi_{nl} = \pi n$, energy can be expressed as

$$E_{nl} = \frac{\pi^2 \hbar^2}{2R^2}\left(\frac{1}{m_e^*} + \frac{1}{m_h^*}\right)$$

b) Conversely, an electron can undergo optical excitation from the highest occupied state in the valence band to the lowest unoccupied state in the conduction band within the same quantum dot. This regime is characterized by $R \gg a_B$, where the quantum dot radius significantly exceeds the exciton Bohr radius. Under this condition, the electron and hole are spatially confined within a region comparable to the excitonic ground state in an ideal infinite crystal.

Unlike the quasiparticle energy regime, where charge carriers are treated as independent particles, this scenario necessitates a more comprehensive quantum mechanical treatment. The system cannot be approximated as a single free particle; instead, it requires a Hamiltonian that incorporates both quantum confinement effects and the Coulombic interaction between the electron and hole. The total energy of the excitonic state is thus given by:

$$H = \frac{\hbar^2}{2m_e}\nabla_e^2 - \frac{\hbar^2}{2m_h}\nabla_h^2 - \frac{e^2}{\varepsilon|r_e - r_h|} + U\,(r)$$

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This Hamiltonian describes the coupled electron-hole dynamics, incorporating both spatial confinement effects and the electrostatic interaction between charge carriers, which ultimately defines the excitonic energy states in semiconductor quantum dots.

Brus[15] employed a vibrational approach to solve this system, incorporating the Coulombic interactions between the electron and hole into the total excitonic energy. The resulting expression for the optical excitation energy, which accounts for both quantum confinement and electron-hole interaction, is given by:

$$E = E_g + \frac{\pi^2\hbar^2}{2mR^2}\left(\frac{1}{m_e^*} + \frac{1}{m_h^*}\right) - \frac{Ae^2}{4\pi\varepsilon_0\varepsilon_\infty R} = \varepsilon_g^{op}$$

Where, E_g is the bulk bandgap energy of the material, R is the radius of QDs, $\hbar$ is the Planck's constant, m is the reduced effective mass of the electron-hole pair, m_e^* and m_h^* are the effective masses of the electron and hole respectively, e is the elementary charge, ε_0 is the permittivity of free space, ε_∞ is the dielectric constant of the surrounding medium, A is a coefficient determined from numerical calculations, typically around 1.786 for a spherical quantum dot system.

This equation explicitly accounts for the quantum confinement energy (the second term) and the Coulombic interaction (the third term), leading to a reduction in the optical band gap compared to the quasiparticle band gap observed in cyclic voltammetry.[3,10,15]

6. Summary and Conclusions

In this book chapter, we have highlighted the immense potential of cyclic voltammetry (CV) as a powerful and accessible tool for investigating band structure parameters critical to the design of high-efficiency solar cells. While Ultraviolet Photoelectron Spectroscopy (UVPES) remains a valuable technique for probing electronic structures, its inherent limitations—such as surface sensitivity, the requirement for ultra-high vacuum (UHV) conditions, and the need for complementary techniques to determine the conduction band minimum (CBM)—make it less practical for comprehensive band structure analysis.

In contrast, CV offers a cost-effective and straightforward approach to estimating the valence band maximum (VBM) and CBM by analyzing oxidation and reduction potentials. Its ability to probe deeper electronic states provides more representative bulk energy levels, making it highly relevant for solar cell applications. Furthermore, we have clarified the fundamental distinction between the optical band gap and the quasi-particle band gap, demonstrating why the quasi-particle band gap is always greater than the optical band gap through an appropriate theoretical model.

Overall, this chapter underscores the significance of electrochemical techniques like CV in semiconductor research, offering a practical alternative to traditional spectroscopic methods. By integrating CV-based band structure analysis into solar cell design, researchers can better understand material properties, optimize energy level alignments, and ultimately enhance the performance of next-generation photovoltaic devices.

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8. References

(1) Haram, S. K.; Quinn, B. M.; Bard, A. J. Electrochemistry of CdS Nanoparticles: A Correlation between Optical and Electrochemical Band Gaps [5]. *J. Am. Chem. Soc.* **2001**, *123* (36), 8860–8861. https://doi.org/10.1021/ja0158206.

(2) Inamdar, S. N.; Ingole, P. P.; Haram, S. K. Determination of Band Structure Parameters and the Quasi-Particle Gap of CdSe Quantum Dots by Cyclic Voltammetry. *ChemPhysChem* **2008**, *9* (17), 2574–2579. https://doi.org/10.1002/cphc.200800482.

(3) Mane, S. S.; Sinha, A.; Haram, S. K. Composition-Dependent Band Structure Parameters and Band-Gap Bowing Effect in a Caesium Lead Mixed Halide System: A Cyclic Voltammetry Investigation. *Phys. Chem. Chem. Phys.* **2024**. https://doi.org/10.1039/D3CP05956A.

(4) Ingole, P. P. A Consolidated Account of Electrochemical Determination of Band Structure Parameters in II – VI Semiconductor Quantum Dots : A Tutorial Review. **2019**, 4695–4716. https://doi.org/10.1039/c8cp06847j.

(5) Kaushika, N. D.; Mishra, A.; Rai, A. K. *Solar Photovoltaics*; **2018**. https://doi.org/10.1007/978-3-319-72404-1.

(6) Bhattacharya, P.; Ghosh, S.; Stiff-Roberts, A. D. *Quantum Dot Opto-Electronic Devices*; **2004**; Vol. 34. https://doi.org/10.1146/annurev.matsci.34.040203.111535.

(7) Apostoleris, H.; Stefancich, M.; Chiesa, M. *High-Efficiency Solar Cells*; **2018**; Vol. 0. https://doi.org/10.1007/978-3-319-62980-3_3.

(8) Li, Y.; Zhong, H.; Li, R.; Zhou, Y.; Yang, C.; Li, Y. High-Yield Fabrication and Electrochemical Characterization of Tetrapodal CdSe, CdTe, and CdSexTe1-x Nanocrystals. *Adv. Funct. Mater.* **2006**, *16* (13), 1705–1716. https://doi.org/10.1002/adfm.200500678.

(9) Rondiya, S.; Rokade, A.; Sharma, P.; Chaudhary, M.; Funde, A.; Jadhav, Y.; Haram, S.; Pathan, H.; Jadkar, S. CZTS/CdS: Interface Properties and Band Alignment Study towards Photovoltaic Applications. *J. Mater. Sci. Mater. Electron.* **2018**, *29* (5), 4201–4210. https://doi.org/10.1007/s10854-017-8365-5.

(10) Franceschetti, A.; Zunger, A. Pseudopotential Calculations of Electron and Hole Addition Spectra of InAs, InP, and Si Quantum Dots. *Phys. Rev. B - Condens. Matter Mater. Phys.* **2000**, *62* (4), 2614–2623. https://doi.org/10.1103/PhysRevB.62.2614.

ISBN: 978-93-95369-49-7 (electronic) 978-93-95369-48-0 (paperback) |

(11) In, S. B. *Lioz Etgar Hole Conductor Free Perovskite-Based Solar Cells*.

(12) Haram, S. K.; Kshirsagar, A.; Gujarathi, Y. D.; Ingole, P. P.; Nene, O. A.; Markad, G. B.; Nanavati, S. P. Quantum Confinement in CdTe Quantum Dots: Investigation through Cyclic Voltammetry Supported by Density Functional Theory (DFT). *J. Phys. Chem. C* **2011**, *115* (14), 6243–6249. https://doi.org/10.1021/jp111463f.

(13) Jasieniak, J.; Califano, M.; Watkins, S. E. Size-Dependent Valence and Conduction Band-Edge Energies of Semiconductor Nanocrystals. *ACS Nano* **2011**, *5* (7), 5888–5902. https://doi.org/10.1021/nn201681s.

(14) Jiang, F.; Li, Y.; Ye, M.; Fan, L.; Ding, Y.; Li, Y. Ligand-Tuned Shape Control , Oriented Assembly , and Electrochemical Characterization of Colloidal ZnTe Nanocrystals. **2010**, No. d, 4632–4641. https://doi.org/10.1021/cm101225b.

(15) Brus, L. E. Electron-Electron and Electron-Hole Interactions in Small Semiconductor Crystallites: The Size Dependence of the Lowest Excited Electronic State. *J. Chem. Phys.* **1984**, *80* (9), 4403–4409. https://doi.org/10.1063/1.447218.

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