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Research on Surface Functionalization Modification and Photoelectric Properties of Single-Walled Carbon Nanotubes

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Abstract: Single-walled carbon nanotubes (SWCNTs) are regarded as the primary candidate materials for optoelectronic devices in the post-Moore era due to their unique two-dimensional quantum confinement effect, high carrier mobility, and tunable bandgap structure. However, the intrinsic SWCNTs feature strong chemical inertness, easy agglomeration, and fixed band structure, which greatly restrict their performance in complex optoelectronic systems. Therefore, this paper focuses on bandgap renormalization induced by sp^3 hybridization, Fermi level shift caused by charge-transfer doping, exciton binding energy modification via dielectric environment screening, and the influence of chiral-selective modification on circular dichroism. Based on the established Hamiltonian perturbation model and many-body Green's function theory framework, the physical picture of macroscopic reconstruction of the photoelectric response of SWCNTs by functional groups as artificial defects or dielectric coating layers is revealed from a microscopic perspective, providing a theoretical basis for the design of high-performance and multifunctional carbon nanotube optoelectronic devices.

Keywords: Single-walled carbon nanotubes; Surface; Functionalization modification; Photoelectric properties

1. Topological reconstruction of electronic structure by covalent functionalization

1.1. Bandgap renormalization induced by sp^3 defects

The bandgap (Eg) of intrinsic semiconducting SWCNTs is mainly determined by the curvature effect and chirality. When carbon atoms undergo sp^3 hybridization, their pz orbitals no longer participate in the formation of π bonds, leading to the interruption of the π electron cloud at these sites. The tight-binding approximation is equivalent to introducing a strong scattering potential well into the lattice and removing the hopping integral of the lattice point. According to the generalization of Anderson localization theory, high-concentration sp^3 defects cause tailing of the density of states at the band edges and even convert the original extended states into localized states [1–4].

More importantly, appropriate covalent modification can open or tune the bandgap in specific SWCNTs. Theoretical calculations show that when functional groups are arranged in a periodic pattern, a bandgap can be opened in metallic armchair nanotubes, i.e., new Brillouin zone folding occurs. This phenomenon is called "bandgap engineering". Hydrogenation or fluorination can convert metallic SWCNTs into wide-bandgap semiconductors [5]. The physical mechanism originates from the charge redistribution caused by the different electronegativities of functional groups, which breaks the symmetry between sublattices, generates a mass term near the Dirac point, and thus opens the bandgap.

The content of sp^3 defects directly affects the carrier transport and bandgap characteristics of SWCNTs. The photoelectric properties of SWCNTs show obvious regular changes under different sp^3 defect coverage rates, as shown in Table 1.

In addition, sp^3 defects generate deep or shallow impurity states in the bandgap. These impurity states act as traps for electrons or holes, greatly affecting the carrier recombination rate. In photodetector applications, these trap states lead to persistent photoconductivity, i.e., the current remains for a period after light cessation, which can be theoretically described by the Shockley-Read-Hall (SRH) recombination model combined with defect energy level distribution [6]. However, excessive disordered sp^3 sites cause a sharp drop in carrier mobility, as carriers undergo strong elastic scattering during transport, the mean free path (le) is significantly shortened, and the transport mechanism changes from ballistic transport to diffusive transport.

Table 1. Photoelectric property changes of SWCNTs under different sp^3 defect coverage rates

sp^3 defect coverage	Bandgap variation characteristics	Carrier mobility variation	Carrier transport mechanism	Photoconductivity performance
< 5%	Slight bandgap broadening, no obvious impurity states	Slight decrease (<10%)	Dominated by ballistic transport	No obvious persistent photoconductivity, fast photocurrent decay
5%–10%	Moderate bandgap tuning, shallow-level impurity states appear	Decrease by 30%–50%	Mixed ballistic-diffusive transport	Obvious persistent photoconductivity, slow photocurrent decay
10%–20%	Significant bandgap modification, coexistence of deep/shallow impurity states	Decrease by 70%–90%	Dominated by diffusive transport	Enhanced persistent photoconductivity, significantly reduced response speed
> 20%	Bandgap distortion, localized state-dominated band structure	Sharp drop, nearly lost carrier transport ability	Diffusive transport with strong scattering	Weak photoconductive signal, persistent effect has no practical value

1.2. Chemical doping and fermi level regulation

In addition to structural distortion, the electronegativity difference of covalent groups also induces charge-transfer doping. Grafting strong electron-withdrawing groups results in p-type doping of SWCNTs, with the Fermi level (EF) shifting toward the valence band maximum; grafting electron-donating groups results in n-type doping, with EF shifting toward the conduction band minimum [7]. In first-principles calculations, this is manifested as a rigid shift of the entire band structure and a change in work function.

The regulation of the Fermi level directly determines the operating point of SWCNTs in photodiodes or field-effect transistors. Theoretically, precisely controlling the degree of functionalization to pin EF near a van Hove singularity can greatly enhance the photon absorption cross-section for a specific energy. In addition, heavy doping causes the Burstein-Moss effect, i.e., the optical absorption edge blue-shifts due to the filling of low energy levels. Under extreme doping conditions, SWCNTs exhibit metallic-like plasmon resonance characteristics, whose frequency range can be accurately tuned by carrier concentration using the Drude model.

2. Non-covalent functionalization and dielectric screening effect

2.1. Dielectric regulation of exciton binding Energy

In one-dimensional systems, the Coulomb interaction between electrons and holes cannot be effectively screened as in three-dimensional bulk materials due to geometric confinement. According to the Rytova-Keldysh potential model, the binding energy (Eb) of one-dimensional excitons is remarkably high, typically ranging from 0.3 eV to 1.0 eV, far exceeding the thermal energy kBT at room temperature. Therefore, photogenerated carriers in SWCNTs are mainly excitons rather than free electron-hole pairs.

Non-covalent coating layers use dielectrics with different dielectric constants (εenv). Theoretically, an increase in the effective dielectric constant (εeff) significantly weakens the Coulomb attractive potential between electrons and holes: $V(r) \propto -e^2/(\varepsilon_{eff} r)$. Solving the one-dimensional Schrödinger equation via the variational method shows a strong nonlinear relationship between exciton binding energy Eb and the environmental dielectric constant. The exciton binding energy and optical spectral characteristics of SWCNTs under different dielectric environments are shown in Table 2, directly reflecting the regulation law of dielectric constant on their photoelectric properties.

Table 2. Exciton binding energy and optical properties of SWCNTs under different dielectric environments

Dielectric environment	Environmental dielectric constant εenv	Exciton binding energy Eb (eV)	Optical absorption spectrum change	Fluorescence emission spectrum change	Optical regulation characteristics
Air	1.0	0.8–1.0	High absorption peak energy, narrow peak shape	Blue-shifted emission peak, low quantum yield	No dielectric screening, high exciton stability
Ethanol	24.3	0.4–0.6	Slightly red-shifted absorption peak, broadened peak shape	Moderately red-shifted emission peak, improved quantum yield	Weak dielectric screening, moderately reduced exciton binding energy
Deionized water	80.1	0.3–0.4	Significantly red-shifted absorption peak	Greatly red-shifted emission peak, increased FWHM	Moderate dielectric screening, obviously weakened Coulomb interaction
Polymer matrix (PMMA)	3.5	0.6–0.7	Slightly red-shifted absorption peak, stable peak shape	Slightly red-shifted emission peak, stable quantum yield	Weak dielectric screening, suitable for device fabrication
High-dielectric polymer (PVDF)	8.4	0.5–0.6	Moderately red-shifted absorption peak	Moderately red-shifted emission peak, moderate quantum yield	Medium-weak dielectric screening, balanced regulation and stability

When SWCNTs are transferred from air to high-dielectric polymer matrices or aqueous solutions, Eb can be reduced by hundreds of meV [8,9]. The reduced binding energy directly causes red shifts in the optical absorption and fluorescence emission spectra. Notably, since the spatial extension of the exciton wavefunction is confined, the red shift mainly reflects the shift of exciton resonance peak energy, with a relatively small change in the bandgap Eg. Thus, non-covalent modification can precisely tune the emission color and absorption threshold of SWCNTs without damaging the lattice integrity.

2.2. Exciton diffusion and dissociation kinetics

In photovoltaic applications, excitons must reach the donor-acceptor interface and dissociate into free carriers to generate photocurrent. In addition to modifying Eb, non-covalent functional layers affect the exciton diffusion length (LD). Theoretically, ordered π-π stacked polymers can act as energy transfer media, transferring exciton energy to SWCNTs via Förster resonance energy transfer (FRET) and facilitating long-range exciton migration on the tube surface. Conversely, overly disordered coatings or quenching groups introduce non-radiative recombination channels. According to Fermi's golden rule, the non-radiative transition rate (knr) is related to the electron-phonon coupling strength and density of states [10,11]. Low-frequency vibration modes of functional molecules may resonate with the electronic transition energy of SWCNTs, enhancing phonon-assisted Auger recombination or intersystem crossing and reducing fluorescence quantum yield. Evidently, the key to theoretical design is to strike a balance: using dielectric screening to reduce Eb and promote charge separation without introducing excessive non-radiative recombination centers.

3. Breaking of optical transition selection rules and chiral manipulation

The optical properties of SWCNTs are constrained by helical symmetry. In the intrinsic state, optical transitions follow strict selection rules: the strongest transition occurs only when the incident light polarization is parallel to the tube axis, and the transition probability under circularly polarized light is highly dependent on the matching degree between photon angular momentum and nanotube chirality, resulting in distinct circular dichroism. Anisotropic covalent functionalization (e.g., band-shaped modification on one side of the tube wall) breaks the cylindrical symmetry, enabling originally forbidden transverse polarization transitions. Within the perturbation theory framework, this corresponds to the introduction of angular-momentum-non-conserving terms in the Hamiltonian. Calculations show that for band-shaped hydroxyl modification with 10% coverage, the absorption coefficient of transverse polarized light can reach ~35% of the longitudinal absorption coefficient, enabling significant response of SWCNTs to non-parallel polarized light. Local strain fields induced by functionalization also alter the band structure via deformation potentials; tensile or compressive strain splits the band structure, separating van Hove singularities and generating new split peaks in the absorption spectrum. Theoretical calculations indicate that the equivalent strain caused by asymmetric functionalization can reach 1.5%, leading to a band splitting width of 30 meV. This functionalization-induced pseudo-magnetic field effect is theoretically equivalent to applying an axial magnetic field, enabling the regulation of valley degrees of freedom [12,13].

Chirality-pure SWCNTs are critical materials for spintronics and quantum information processing. Non-covalent functionalization achieves chiral separation via stereoselective interactions between chiral molecules (e.g., specific-sequence DNA or chiral polymers) and specific-chirality SWCNTs. Theoretically, this is a thermodynamic process based on free energy differences: chirality-matched systems exhibit lower adsorption energy and more stable configurations. Molecular dynamics simulations show that the binding energy of (6,5) tubes with specific chiral polymers is 0.15 eV/nm lower than that of (7,5) tubes, enabling high-purity separation under thermal fluctuations [14]. Once complexes form, the asymmetric potential field generated by chiral molecules induces strong intrinsic circular dichroism signals in SWCNTs. Even for racemic mixtures, coating with specific chiral molecules produces strong macroscopic circular dichroism signals via chiral amplification. In quantum mechanical terms, this arises from the mixing of electronic states with different angular momenta in the chiral environment, leading to large differences in absorption coefficients for left- and right-handed circularly polarized light. Theoretical predictions suggest that optimized chiral complexes can achieve an anisotropy factor g of 0.05, two orders of magnitude higher than the intrinsic value. This effect can be applied in detection and the design of circularly polarized light detectors that directly distinguish photon spin states without external polarizers.

4. Many-body interactions and nonlinear optical response

At high excitation densities or ultrafast time scales, the photoelectric behavior of SWCNTs is governed by complex many-body interactions. The regulation of these nonlinear processes by surface functionalization is a frontier of current theoretical research. In one-dimensional systems, exciton-exciton annihilation becomes the dominant non-radiative loss pathway at high exciton densities, involving the collision of two excitons: one returns to the ground state, and the other is excited to a high-energy state before relaxation. Functional layers directly influence the annihilation rate constant by tuning the spatial spread and effective mass of exciton wavefunctions. Theoretical simulations show that appropriate dielectric screening increases the exciton radius, reduces wavefunction overlap, and suppresses exciton-exciton annihilation, lowering the bimolecular recombination rate constant from 10^{-8} cm^3/s to below 10^{-9} cm^3/s and improving quantum efficiency at high light intensities.

SWCNTs possess an extremely large third-order nonlinear polarizability, making them suitable for all-optical switches and mode-locked lasers. Surface functionalization enhances this performance via resonance enhancement. When impurity states induced by functionalization satisfy multi-photon resonance conditions with incident photon energy, resonance-enhanced nonlinear absorption occurs. In particular, intra-band states introduced by covalent modification act as intermediate virtual states in multi-photon processes, greatly reducing the threshold for multi-photon transitions. From the density matrix equation, analytical relationships between functionalization parameters and nonlinear refractive index/absorption coefficient can be derived. Theoretical predictions indicate that carefully designed functional patterns can increase the real part of the third-order nonlinear polarizability of specific phenyl-modified SWCNTs from 10^{-10} esu to 10^{-9} esu at the 1550 nm communication band while maintaining low linear loss [15].

In addition, charge-transfer states at functionalized interfaces induce new nonlinear optical phenomena such as light-induced absorption saturation. Under femtosecond laser pulse excitation, the recovery time of functionalized samples is extended from picoseconds to nanoseconds due to temporary carrier trapping by trap states. Long-lived nonlinear responses are crucial for optical storage applications.

5. Conclusion

In summary, surface functionalization modification of SWCNTs represents a form of “quantum engineering”. Covalent modification reconstructs the lattice potential field via sp^3 hybridization, enabling bandgap opening, Fermi level tuning, and localized state engineering; although partial mobility is sacrificed, rich band-tunability is achieved. Non-covalent modification modulates Coulomb interactions via dielectric screening, greatly tuning exciton binding energy and optical transition energy while preserving good transport performance. Both types of modification affect the symmetry of SWCNTs, breaking inherent optical selection rules and enabling responses to chirality, polarization, and nonlinear optical fields. With the refinement of this theoretical system, research on carbon nanotubes has shifted from property discovery to property design.

Disclosure statement

The author declares no conflict of interest.

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