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Review

Development of coumarin composite with graphene oxide influence: Preparation, characterization, and application

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Abstract: The tunable conduction of coumarin-based composites has attracted considerable attention in a wide range of applications due to their unique chemical structures and fascinating properties. The incorporation of graphene oxide (GO) further enhances coumarin properties, including strong fluorescence, reversible photodimerization, and good thermal stability, expanding their potential use in advanced technological applications. This review describes the developmental evolution from GO, GO-polymer, and coumarin-based polymer to the coumarin-GO composite, concerning their synthesis, characterization, unique properties, and wide applications. We especially highlight the outstanding progress in the synthesis and structural characteristics along with their physical and chemical properties. Therefore, understanding their structure-property relations is very important to acquire scientific and technological information for developing the advanced materials with interesting performance in optoelectronic and energy applications as well as in the biomedical field. Given the expertise of influenced factors (e.g., dispersion quality, functionalization, and loading level) on the overall extent of enhancement, future research directions include optimizing coumarin-GO composites by varying the nanofiller types and coumarin compositions, which could significantly promote the development of next-generation polymer composites for specific applications.

Keywords: coumarin-based polymer; polymeric features; coumarin-GO composites; synthesis and structural characteristics; structure-property relations; specific application

1. Introduction

The field of unique polymeric features (e.g., ease of fabrication, lightweight, exceptional processability, durability and comparatively less cost) dependent technical applications has developed considerably in the past decades [1]. In a recent study, the stimuli-responsive polymers have attracted considerable attention due to their unique capacity to perform the rapid shifting of their physical and chemical properties in response to the surrounding environment [2]. These polymers, especially coumarin-based photoresponsive polymers, have garnered significant interest due to their potential applications in the ranged fields from self-healing materials to drug delivery systems [3]. According to the coumarin dimerization reaction, it is more important to understand the design principles of moieties location in the polymer matrix for making informed choices to optimize their performance for specific applications [4]. Therefore, the versatility of light-based triggers offers a promising avenue for the design and fabrication of innovative materials with enhanced functionality and responsiveness [5]. Coumarin conjugated with their derivatives has attracted significant attention in various fields of research owing to its exceptional properties and the wide range of enhancements it offers to polymer matrices [6]. The synthesis of coumarin-based polymers has evolved significantly from classical and modern methods to green synthetic methods to produce versatile materials. How to understand their synthetic mechanism with nanofiller modification is crucial for optimizing the properties and applications of coumarin-based polymers in various fields.

As an alternative nanofiller among carbon materials (e.g., carbon nanotube and graphite), graphene oxide (GO) with economic feasibility and large-scale manufacturing underscores its importance to significantly enhance the mechanical, thermal, electrical, and barrier properties of polymers [7]. Further exploration into the structural dynamics of GO has revealed its suitability for integration into nanocomposites, supercapacitors, and electrochemical sensors, attributed to the presence of various oxygen-containing groups and high surface functionality of GO [8,9]. Several factors from GO critically influence the overall extent of polymer properties (e.g., tensile strength, elastic modulus, toughness and electrical, thermal and mechanical properties), such as dispersion quality to prevent agglomeration, functionalization to disrupt the network conductivity and optimal loading to affect the electrical behavior [10]. In line with this trend, the incorporation of GO into polymer matrices significantly improves their thermal stability, thermal conductivity, and overall thermal performance, making these composites suitable for various advanced applications [11–13]. Recently, the functionalized GO as a nanofiller, especially doped coumarin-based polymers, could perform a unique combination of mechanical, thermal, electrical, and chemical properties for meeting the specific application requirements [14–16].

In this review, advancements from GO, GO-composites and coumarin-based polymers to coumarin-GO composites are presented, as well as highlighting the various methods, typical characterizations and specific properties. Especially, the contribution of GO introduction on property enhancement is summarized dependent on the manufacturing strategy. Moreover, the scope of the fabrication of coumarin-GO composites in demanded applications has been overviewed. To the end, the challenges encountered related to the accomplishment of coumarin-GO composite systems for achieving the desired features have been deliberated.

2. Structure and property of graphene oxide

As a crucial material in nanotechnology, graphene oxide (GO) is known for its unique properties and wide range of applications. Universal strategies have been developed for GO-based material synthesis and property tailoring to address various technological applications in photonics, electronics and optoelectronics [17]. It is always synthesized by subjecting pristine graphite to strong oxidizers and acids to alter the structural functionalities and maintain the layered configuration. During this process, various oxygen-containing functional groups of epoxy (C–O–C), hydroxyl (–OH), and carboxyl (–COOH) groups were introduced to attach both the basal planes and side edges of host graphene layers, resulting in a combination of sp^2 and sp^3 hybridized carbons within the formation (**Figure 1**) [18]. While characterized by the presence of oxygen-containing functional groups from various synthetic methods, structures significantly influence their intrinsic properties to explore as an excellent candidate for a wide range of applications.

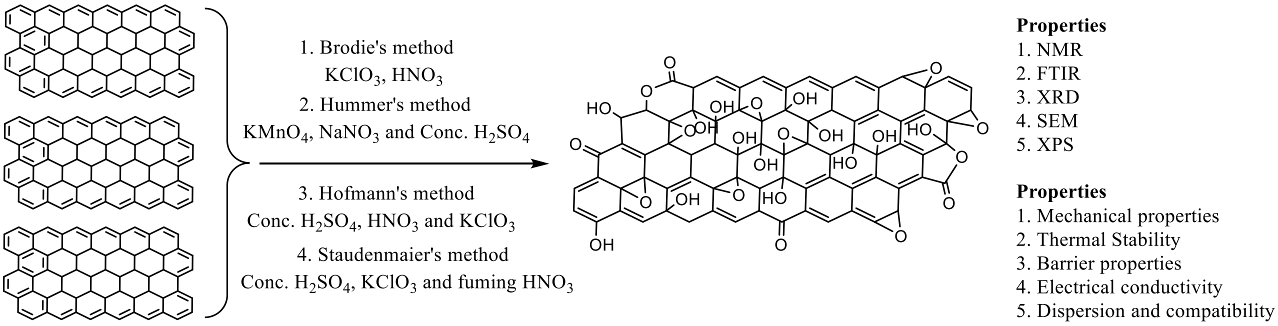

Figure 1. Summary of synthetic methods, characterization techniques and tunable properties for GO.

2.1. Synthetic methods

The synthesis of GO has evolved over time, as well as several methods developed to optimize its production [19]. The primary synthetic methods were summarized as follows.

2.1.1. Brodie method

The Brodie method introduced by Benjamin C. Brodie in 1859 (**Figure 1**), was the original technique for GO synthesis via graphite oxidation involving potassium chlorate ($KClO_3$) in fuming nitric acid (HNO_3) [20]. Despite its historical significance, this reaction is highly exothermic and requires careful control to prevent explosive hazards from violent reactions [21].

2.1.2. Hofmann method

The Hofmann method is a modified Brodie method that employs a mixture of concentrated sulfuric acid (H_2SO_4) and HNO_3 with $KClO_3$ as the oxidizing agent in 1898 (**Figure 1**). In comparison to the Brodie method, the Hofmann method improves the safety and efficiency of the oxidation process, while it still involves handling strong acids and oxidizers to cause the significant safety risks [22].

2.1.3. Staudenmaier method

As another improvement over the Brodie method, the Staudenmaier method was developed by L. Staudenmaier in 1898 through mixing the intercalant of concentrated H_2SO_4 and H_2SO_4 with $KClO_3$ in a batch reaction (**Figure 1**) [23–25]. The Staudenmaier method is capable to produce GO with a higher degree of oxidation (i.e., a higher carbon-to-oxygen ratio) and better control over the reaction conditions than the Brodie method. However, it still involves handling strong acids and oxidizers, which require careful control to ensure safety [26].

2.1.4. Hummers method

The Hummers method was developed by William S. Hummers and Richard E. Offeman in 1958, which evolved as one of the most widely used methods for GO preparation (**Figure 1**) [27,28]. This synthesis involves the oxidation of graphite using a mixture of concentrated H_2SO_4, sodium nitrate ($NaNO_3$) and potassium permanganate (K_2MnO_4). This method is favored for its efficiency and relatively safer procedure than the Brodie and Hofmann methods, deriving from their conducted reaction at low temperatures to control the exothermic nature of the process [29]. However, it still generates toxic gases such as nitrogen dioxide (NO_2) and dinitrogen tetroxide (N_2O_4) during the reaction [30]. Therefore, several modifications have been made to the original Hummers method to enhance its efficiency and safety. For example, through the removal of $NaNO_3$ and the partial replacement of K_2MnO_4 with potassium ferrate (K_2FeO_4), this modification reduces the generation of toxic gases and improves the yield of GO [31]. Another approach includes a pre-oxidation step before the main oxidation reaction, resulting in achieving a higher degree of oxidation and better quality of the final product [32].

2.2. Characterization techniques

As a non-stoichiometric substance, the structure of GO with oxygen-containing functional groups from different preparations remains a challenge to determine [33]. Through the powerful and exact characterization of solid-state nuclear magnetic resonance (NMR), X-ray photoelectron spectroscopy (XPS), Fourier transform infrared spectroscopy (FTIR), and Raman spectroscopy, the precise structure of GO has been successively determined (**Figure 1**), such as the isotope ^{13}C labeling of C–O–C and C–OH (60.2 ppm and 71.2 ppm) from NMR, sp^3 carbon (C–C, 284.4 eV), epoxide group/hydroxyl group (C–O, 285.3 eV) and carbonyl group (C=O, 288.0 eV) from XPS, stretching vibration peaks of O–H (3420 cm^{-1}), C=O (1720–1740 cm^{-1}), unoxidized sp^2 hybridized C=C (1590–1620 cm^{-1}) and C–O (1250 cm^{-1}) from FTIR [34]. Unlike the spectral analysis, the examination of surface morphology from electron microscopy of scanning electron microscopy (SEM), transmission electron microscopy (TEM) and atomic force microscopy (AFM) provides complete information about the layered structure of GO with a variety of surface formations.

2.3. Tunable properties

GO is a versatile material with a unique combination of mechanical, thermal, electrical, and chemical properties with respect to their structures (**Figure 1**). The ability to tailor its properties through reduction and functionalization was furthered to enhance its utility in advanced materials science [35].

2.3.1. Mechanical properties

After disrupting the sp^2 hybridization of carbon atoms, the interlayer space increases to approximately 0.7 nm more than pristine graphite (0.34 nm) to cause the buckled structure [36]. While mechanical properties of GO could enhance through the facilitated strong covalent bond within the graphene layers and the interlayer interactions by the functional groups (e.g., –C–O–C– and –OH) [37], leading to render GO as a suitable nanofiller for reinforcing polymer matrices [38].

2.3.2. Thermal properties

Generally, GO performed lower thermal stability compared to pristine graphene when oxygen-containing groups decomposed at elevated temperatures [39]. From the consideration of oxidation degree and additional functional groups (e.g., –C–O–C– and –C=O) on thermal stability [40], we could still significantly enhance the thermal properties of polymer composites when GO is selected as a nanofiller [41,42].

2.3.3. Barrier properties

GO also exhibits excellent barrier properties against gases and liquids due to its layered structure and the tortuous path created by the functional groups. The functional groups in GO result in the chemical reactivity, rendering it potentially active in various chemical reactions and hence versatile for functionalization and composite formation [43]. While the presence of oxygen-containing groups (e.g., –C–O–C– and –COOH) [44] makes GO highly hydrophilic for adequate dispersion in water and other polar solvents [45], allowing for applications in packaging and coatings [46].

2.3.4. Electrical conductivity

GO with high surface area forms conductive networks within the polymer matrix. The dielectric properties of GO make it useful in applications requiring materials with high dielectric constants (40 at 100 Hz and 80 ℃) and low dielectric losses (5 at 100 Hz and 80 ℃) [47]. One of the most notable properties of GO is its ability to improve the electrical conductivity of polymers or composites for extending the applications in electronics, sensors, and energy storage devices [48].

3. Structure and properties of coumarin-based polymers

Referred to as “antenna” or “light-harvesting” polymers, coumarin-based polymers have attracted significant attention due to their unique optical, biological and photochemical properties [49].

3.1. Structural properties

The coumarin group can undergo photodimerization, a reversible [2πs + 2πs] cycloaddition reaction upon exposure to UV light. This reaction leads to the formation of cyclobutane dimers, which can be reversed by UV irradiation of higher energy photons, typically at wavelengths greater than 250 nm [50,51]. Coumarin-based polymers are recognized by the presence of coumarin units, which consist of a benzene ring fused to an α-pyrone ring (**Figure 2**, blue structure). These polymers feature coumarin moieties as pendant or terminal groups on the polymer chain, exhibiting their structure dependent on fascinating properties. These properties are summarized below:

1) Photophysical Properties: Coumarin-based polymers exhibit strong fluorescence, suitable for applications in optoelectronics [52] and photonics [53]. While the fluorescence behavior is influenced by the conjugated system of the coumarin moiety, which allows for efficient light absorption and emission [54].
2) Photochemical Properties: The ability of coumarin derivatives to undergo photo-induced cyclodimerization and subsequent photo-cleavage is a key feature [55]. This reversible reaction is utilized in photo-optical devices for information storage and management [56].
3) Thermal Stability: Coumarin-based polymers generally exhibit good thermal stability via the incorporation of nanofillers such as GO [57], leading to applications requiring high thermal resistance [58].
4) Mechanical Properties: The mechanical properties of coumarin-based polymers can be tailored by varying the composition and structure of the polymer matrix. Such incorporation of coumarin groups enhances the rigidity and strength of the polymer [59,60].

5) Biocompatibility: Coumarin derivatives such as thiazole, azetidinone and oxazole have been found to be effective against bacterial and fungal infections, highlighting their potential in biomedical applications [61].

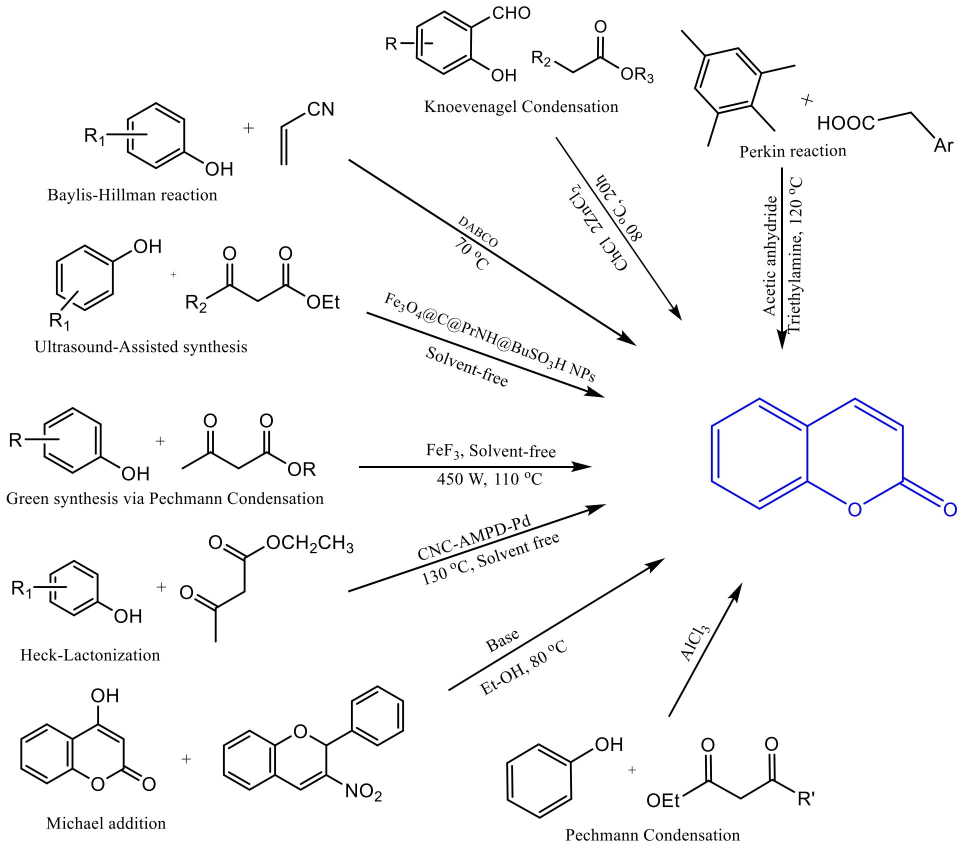

Figure 2. Illustrating the synthesis of coumarin-based polymer.

3.2. Synthetic methods

All above-mentioned properties have propelled coumarin-based polymers into the spotlight as versatile materials with wide-ranging applications. While producing these materials, various synthetic methods have evolved significantly over the past decades (**Figure 2**). All methods are summarized to highlight the pathways, mechanisms, advantages and limitations.

3.2.1. Classical synthesis

(1) Pechmann Condensation: The Pechmann condensation is one of the earliest and most widely used methods for synthesizing coumarin derivatives [62]. The process is typically carried out using H_2SO_4 or other strong acids as catalysts, involving the acid-catalyzed condensation of phenols with β-keto esters. The method is favored for its simplicity and high yield, but it requires stringent reaction conditions as well as significant amounts of by-product formation [63].

(2) Knoevenagel Condensation: The Knoevenagel condensation involves the reaction of aldehydes with active methylene compounds in the presence of a base (e.g., piperidine or pyridine) [64]. This method is particularly useful for synthesizing coumarin derivatives with various substituents on the aromatic ring. Deriving from its

mild reaction conditions and high selectivity, this method was alternatively selected as a popular choice for synthesizing coumarin-based polymers [65].

(3) Perkin Reaction: The Perkin reaction is another classical method for synthesizing coumarin derivatives. It involves the condensation of aromatic aldehydes with anhydrides in the presence of a base, such as sodium acetate. This method is advantageous for producing coumarins with specific substituents, but it often requires high temperatures and long reaction times [66].

3.2.2. Modern synthesis

(1) Heck-Lactonization Reaction: In addition to the classical synthesis, the modern synthetic methods include the Heck-Lactonization Reaction, which was particularly useful for producing coumarin-based polymers with enhanced photophysical properties [67]. This method is highly efficient and allows for designing the coumarin derivatives with complex structures through the intramolecular cyclization of aryl halides with alkenes from the palladium coupling reaction [68].

(2) Baylis-Hillman Reaction: Another important technique for coumarin production is the Baylis-Hillman Reaction**,** which involves the coupling of aldehydes with activated alkenes triggered by a tertiary amine [69,70]. This method results in coumarin derivatives with reasonable tolerance to several functional groups and bland conditions of reaction.

(3) Michael addition reaction: The nucleophilic addition reaction involving a, b-unsaturated carbonyl compounds through a Michael addition reaction is also a suitable method, widely used in the synthesis of coumarin derivatives with various substituents. The Michael addition is suitable for coumarin preparation with high efficiency and selectivity [71].

3.2.3. Green synthesis

(1) Microwave-Assisted Synthesis: This is a green chemistry approach to using microwave irradiation for accelerating chemical reactions [72]. This method is advantageous for synthesizing coumarin-based polymers with high yields (95%–99%) and purity under the reduced reaction times and energy consumption [73].

(2) Ultrasound-Assisted Synthesis: Assisted with ultrasonic waves to promote chemical reactions, coumarin-based polymers with improved properties (e.g., enhanced mechanical strength, chemical resistance, optical activity and thermal stability) and reduced environmental impact (e.g., energy consumption and waste generation) produced under mild reaction conditions with high efficiency [74].

3.3. Broad applications

Understanding these synthetic methods is crucial for optimizing the properties and applications of coumarin-based polymers in various fields of science and technology (**Figure 3**).

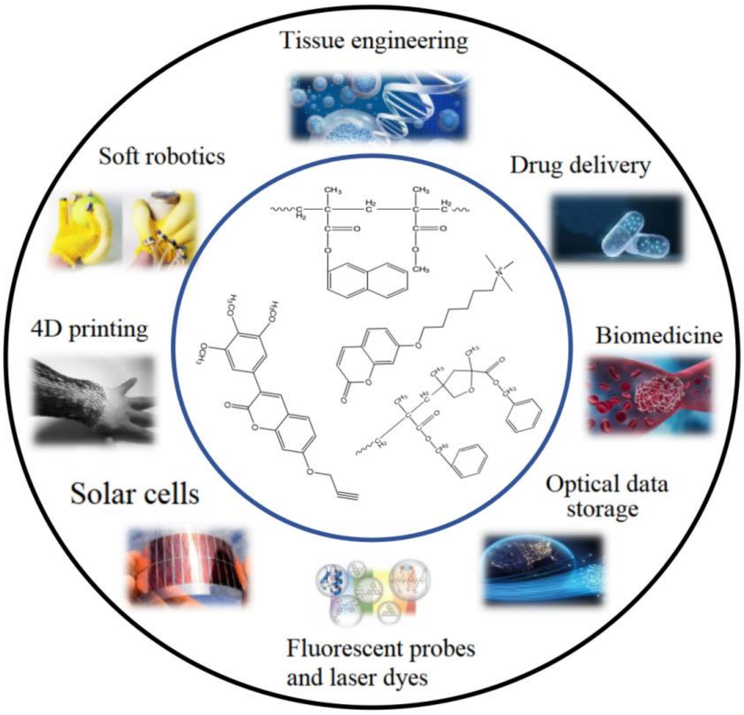

Figure 3. Illustration of various applications from coumarin-based polymers.

3.3.1. Electronics and optics

Coumarin-based polymers are increasingly applied in electronics and optics due to their unique photochemical properties. They serve as optical limiters to protect sensitive devices from high-intensity light and act as fluorescent dyes in bio-imaging and chemical sensing. Especially in organic light-emitting diodes (OLEDs), these polymers enhance light emission to be valuable for display technologies. Also they are utilized in electronic devices for efficient light guiding and modulation, while their sensitivity allows them to function as real-time sensors for various analytes. Additionally, coumarin-based polymers contribute to solar energy conversion in organic photovoltaics, which were applied as protective coatings to enhance the aesthetic and functional properties of surfaces in optics [75,76].

3.3.2. Liquid-crystal materials

Deriving from their alignment after interaction with liquid crystal phases, coumarin-based polymers are employed in the fabrication of liquid-crystal displays (LCDs) and other optical devices. In this way, they tuned liquid crystal features to enhance the responsiveness of LCDs by providing improved switching speeds and color ratios in optics. Therefore, they are applied in smart windows and adaptive optics, advanced imaging and display technologies, resulting in better flexibility and efficiency [77,78].

3.3.3. Biomedical applications

Coumarin-based polymers, possessing unique light-responsiveness, serve as effective fluorescent probes for bio-imaging, enabling the visualization of cellular processes and disease markers in biomedicine. For instance, these polymers can be utilized in imaging techniques such as fluorescence microscopy to track cancer cell migration or monitor the expression of specific proteins associated with diseases.

Additionally, they enhance the solubility of therapeutic agents, promoting drug delivery systems that improve the bioavailability of poorly soluble drugs. In photothermal therapy, coumarin-based polymers can selectively target cancer cells, generating localized heat upon light irradiation to induce cell death while minimizing damage to surrounding healthy tissues. Furthermore, these materials are being developed into biosensors for real-time monitoring of biomolecules, such as glucose or cancer biomarkers, facilitating advancements in diagnostics and personalized medicine [79].

3.3.4. Organic-inorganic hybrid materials

Coumarin-based polymers integrated into hybrid materials (e.g., polymer nanocomposites, polymer-ceramic composites, polymer-metal composites, and polymer-organic hybrid materials) achieve outstanding photochemical properties and excellent mechanical strength, enhancing their performance in diverse applications, e.g., in optoelectronics for organic light-emitting diodes (OLEDs) and solar cells, in coatings for enhanced durability and self-healing capabilities [80]. In the field of optoelectronics, these hybrids are utilized in OLEDs for displays and lighting, where their tunable emission properties improve color purity and efficiency. They also contribute to solar cells by enhancing light absorption and charge transport, leading to higher energy conversion efficiencies. In coatings, coumarin-based polymers provide enhanced durability and self-healing capabilities, making them suitable for protective coatings in the automotive and aerospace industries. Additionally, they play a vital role in nanotechnology for packaging applications, where they can provide barrier properties and antimicrobial effects, as well as in sensors for environmental monitoring, detecting pollutants or hazardous substances. In energy storage, these materials are being explored for use in batteries and supercapacitors, where their unique properties can enhance charge capacity and cycling stability [81,82].

4. Property and application of GO-coumarin composites

The synthesis of coumarin-based polymers has evolved significantly, while the incorporation of GO nanofiller into the polymer matrix further enhances their properties as well as expands potential applications in various fields. Therefore, how to understand the structure-property relations of coumarin-based polymers, along with the advantages of using GO as a nanofiller, is very important for developing the advanced materials with interesting performance.

4.1. GO-polymer composites

As the hot topics, nanofiller-based polymer composites have been presented with special emphasis on significant industrial potential [83]. The various polymer composites with high performance were widely constructed through the controllable interfacial interaction between the filler and the matrix [84]. Among other nanofillers (e.g., carbon, silica and clay minerals), GO with the favorable functional properties has been extensively explored as the appropriate candidate in polymer composites [85]. Due to π–π stacking and Van der Waals forces, reactive oxygen moieties on the basal plane and edges of GO could contact with the polymer matrix through the covalent bond and hybrid approach. Therefore, most of the important polymers commercially (e.g., polymethyl methacrylate, polyacrylamide, polyethylene terephthalate and polyvinyl alcohol) have been used in the production of GO-filled polymer composites [86].

4.2. GO-Coumarin composites

In comparison to the structural regulation of photoresponsive coumarin by inorganic nanoparticles (e.g., Au, Pt, Pd and SiO_2), a new set of emerging GO-coumarin composites with novel structure-dependent functional properties has been developed, which was interesting both for fundamental research and advanced applications [87].

4.2.1. Synthetic methods

Through the electrostatic self-assembly of positively charged nitrogenous coumarin and negatively charged GO, GO-coumarin composite could be obtained as well as improved morphological structure and adsorption capacity [88]. It is speculated that the structure of GO-coumarin composite can also be controlled by coumarin-based polymer, although there is little research in the field. This review especially highlighted the development of GO incorporation with lactone-ended poly (benzyl methacrylate) (LE-PBMA/GO) and random copolymers of 4-methyl-2-oxo-2H-chromen-7-yl methacrylate (COUMA) and methyl methacrylate (MMA) (COMCOP/GO) along with others (**Figure 4**) [89].

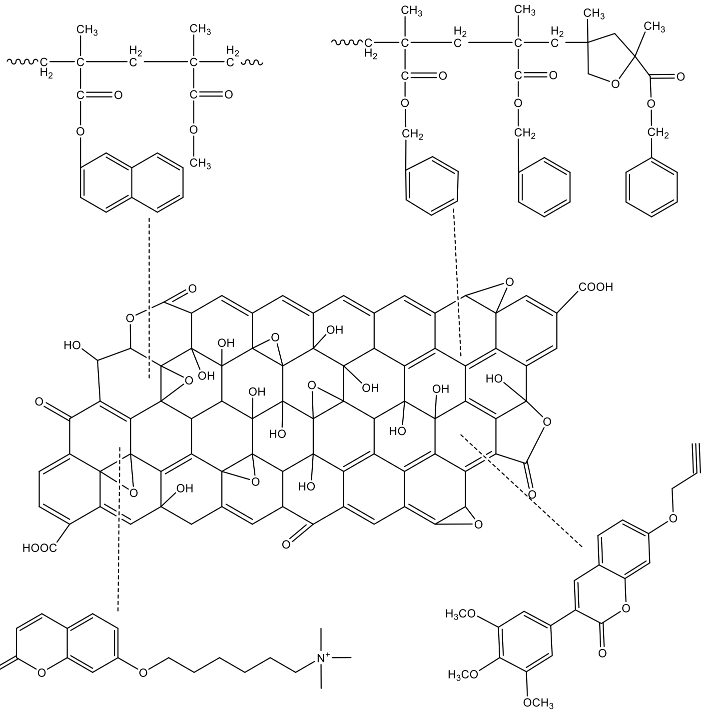

Figure 4. Schematic representation of the formation of GO-coumarin composites.

4.2.2. Characterization technologies

After synthesis, the products were detailedly analyzed using various characterization techniques.

(1) NMR, FTIR and XPS were utilized for structural characterization to confirm the presence and functionality of various chemical groups within the polymer. From the ^{1}H-NMR spectrum (in $CDCl_3$), the resonance signals of =CH next to the C=O group in the COUMA unit and the OCH_3 groups of MMA at 6.23 and 3.61 ppm were observed (**Figure 5a**). Most characteristic bands of COUMA and MMA units are at 1730 cm^{-1} (C=O stretching) and 1624–1572 cm^{-1} (C=C stretching), respectively. While the amount of benzyl methacrylate and benzyl alcohol was less produced from LE-PBMA/GO degradation, implying that GO has decreased depolymerization of LE-PBMA. For identifying the electronic states of composites, the signals of C 1s (C-C, C-N, C-O and C=O) and O 1s (N-O and O-C) are assigned to the GO, while a new peak at approximately 400 eV corresponding to N 1s is observed to prove the successful introduction of coumarin for the coumarin-GO [88].

(2) Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were carried out for detailed analysis of thermal behavior, including stability, melting points and decomposition kinetics (**Figure 5b**). With an incorporation of COUMA content, the glass transition temperature (T_g) of COMCOP increased to 166 °C, which was higher than that of the control PMMA (109.5 °C). Consistent with the literature, it has been recorded that the T_g value of copolymers with increasing ratios of COUMA units containing butoxyethyl methacrylate has increased [90]. When GO content in COMCOP increased from 10% to 16%, the T_g value increased from 162 to 173 °C due to the synergic contribution of the coumarin group and GO on movement ability.

(3) UV-Vis spectroscopy was employed to investigate the photophysical properties and photodimerization behavior of the coumarin units (**Figure 5c**), which are integral to the polymer backbone or exist as side chains. It was found that the UV absorption peak of coumarin appears at around 320 nm and a broad peak of GO locates between 220 nm and 240 nm, while coumarin-GO displays a maximum absorption at 320 nm. From another study, it can be seen that the values of the refractive index of LE-PBMA increased with increasing wavelength to 590 nm and subsequently decreased due to disperse property with increasing wavelength. While the strong band absorption of LE-PBMA/GO in the UV range (between 400 and 800 nm) leads to a drastic decrease in refractive index, indicating the restricted movement of polymer chains from interaction between GO and polymer matrix [91].

(4) The crystal structures are normally characterized by X-ray diffraction (XRD) analysis. In comparison to the sharp characteristic diffraction (001) peak of GO at 2θ =11.29° and a shoulder peak of coumarin at around 21°, the composite shows characteristic peaks of both GO and coumarin (**Figure 5d**) to demonstrate their successful synthesis through the electrostatic self-assembly [92]. According to the XRD pattern, the (001) peak of coumarin-GO with broadening diffraction appears at 10.05°, evidently revealing the coumarin introduction changes the crystal structure of the GO and increases their interlayer spacing from 0.79 nm to 0.88 nm.

(5) SEM and TEM are carried out to investigate the structural morphology. As shown from SEM images (**Figure 5e**), coumarin-GO shows a three-dimensional (3D) close-packed structure similar to a squished multi-porous structure instead of a two-dimensional (2D) planar structure of pure GO. Meanwhile, the 3D close-packed structure of the composite was verified from the TEM image (**Figure 5f**), along with

observation of small pores distributed on the surface. The pore size distribution would be characterized based on the Barrett-Joyner-Halenda method, in which the composite displays pore sizes ranging from 1.8 to 2.5 nm to be in line with the specific surface area increment from 56 $m^2 g^{-1}$ to 89 $m^2 g^{-1}$ via the typical type-IV isotherms with H_3-type hysteresis loops. Additionally, from the analysis of TEM equipped with energy-dispersive X-ray spectroscopy, it proved that C, O and N elements uniformly distributed on all material, further clearly demonstrating the successful introduction of coumarin groups in the coumarin-GO composite.

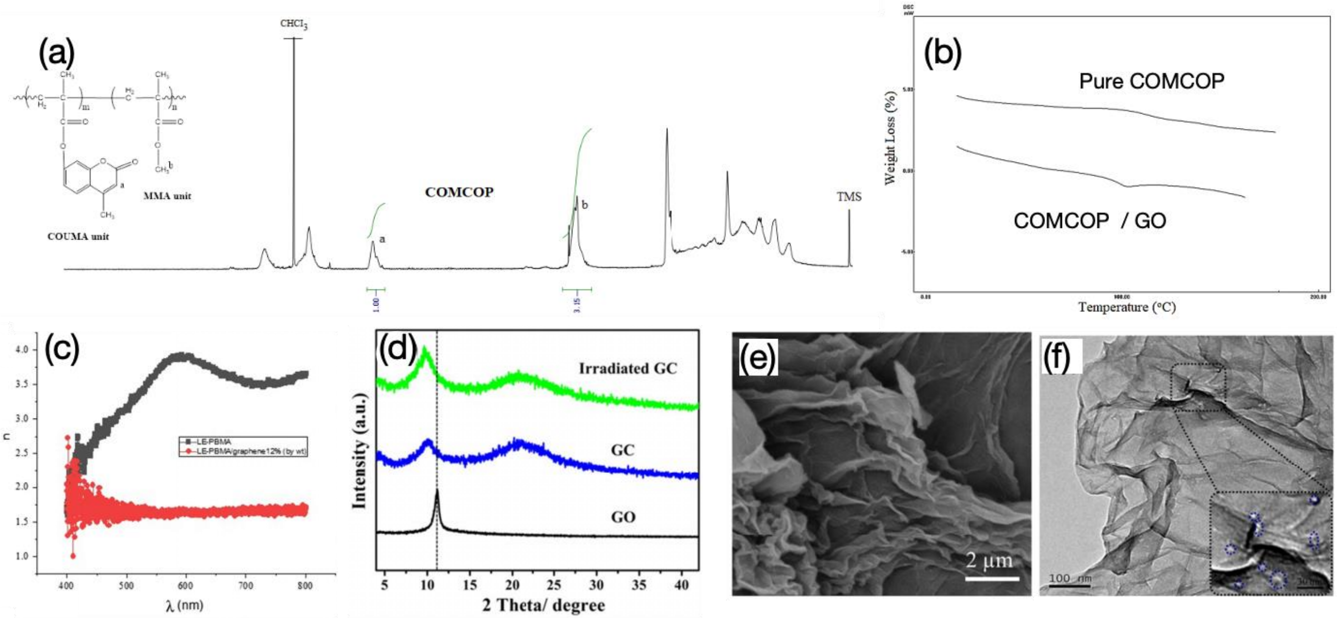

Figure 5. Materials characterization of **(a)** NMR; **(b)** DSC; **(c)** UV-vis absorption; **(d)** XRD; **(e)** SEM; **(f)** TEM.

4.3. Unique property

Stemming from the unique properties (e.g., mechanical, thermal, electrical, and barrier enhancements) of GO along with its chemical reactivity and biocompatibility, it is always selected as an exceptional nanofiller for doping coumarin-based polymers with improved properties.

4.3.1. Electrical conductivity

When GO are well dispersed in the polymer medium, they create pathways in the form of a hole or empty space in the conduction band of the material, rendering it ready for electron or charge carrier gain from the valence band of the material to achieve the crucial conductivity [93]. Functionalized GO normally gives better performance of composites in terms of electrical properties as well as the loading levels related to agglomeration [94]. The electrical properties with respect to the maximum current values increase significantly with the concentration of GO loading, demonstrating the strong interfacial interactions between GO and the copolymer [94]. While the dielectric constant and loss factor also increase with GO contents attributed to the polar functional groups in both GO and the copolymer (**Figure 6a**), which further enhanced the dipolar and interfacial polarizations [95]. Dielectric analysis of the COMCOP/GO further supports these findings, showing the magnitude of conductivity changes with increasing amounts of GO. Also, the polymer with GO attachment showed a linear variation between I-V, especially the maximum current values for COMCOP/GO estimated at 8.53×10^{-4} A (**Figure 6b**). Similarly, a study conducted by GO incorporated into polyvinylpyrrolidone (PVP) created nanocomposites with enhanced dielectric properties [96].

4.3.2. Thermal stability

Several studies have shown that GO can increase the degradation temperature of polymers via a mechanism of barrier creation, which slows down the release of volatile degradation products [65–67]. For instance, the inclusion of GO nanosheets in polypropylene (PP) composites has been reported to increase the thermal stability [97]. The superior nanofiller of GO-doped coumarin-based polymers significantly improves the mechanical properties of polymers by enhancing tensile strength, elastic modulus, and toughness through strong interfacial interactions [98]. Additionally, GO enhances the thermal stability of polymer matrices by increasing the activation energy required for thermal decomposition. According to the thermal degradation kinetics, it revealed that decomposition temperatures of LE-PBMA [99], poly (BMA) and LE-PBMA/GO at 10% weight loss were 265 ℃, 273 ℃ and 288 ℃, respectively, while thermal stability of the composite between 308 ℃ and 363 ℃ has increased. Also, the decreased activation energy values were consistent with enhanced stability in the presence of GO nanofiller (**Figure 6c**), due to the higher T_g of the copolymers (COMCOP/GO). Another study found that the thermal reduction of graphite oxide in the presence of polymers to produce reduced graphite oxide (rGO) led to decreased thermal stability of the polymer. In line with a study on poly (ethylene oxide) (PEO) intercalated in GO (PEO/GO) composites demonstrated a significant decrease in thermal stability [100,101]. Similarly, it found that PVA/PEO composite with GO incorporation significantly influences the optical, thermal, electrical, and dielectric properties. The optical bandgap of composites decreased with increasing GO concentrations, indicating enhanced charge transport, while thermal stability improved due to chemical interactions between PVA and PEO [102].

4.3.3. Photochemical transition

Based on reversible photoresponses of coumarin, the coumarin-GO composites are investigated by monitoring the absorbance evolution under UV light (365 nm or 254 nm) irradiation. It found the characteristic peak of coumarin (320 nm) decreases with illumination time under 365 nm UV light due to the photodimerization of coumarin, while it increases with time under 254 nm light illumination due to the photocleavage of coumarin. Similar as COMCOP/GO, by preparing very low dilute solutions of coumarin-containing homopolymer or copolymers, when exposed to UV light at $\lambda > 350$ nm, it can be controlled by the formation of cyclobutane intramolecularly with a cyclo-addition photodimerization and photocleavage (**Figure 6d**) [103]. The maximum peak intensity for $n \rightarrow \pi^*$ transition in the coumarin group at 310 nm decreased along the period of irradiation, indicating an increase in the degree of dimerization. However, as time increases, the maximum peak intensity decreases; the peaks reflect the contribution of $\pi \rightarrow \pi^*$ transitions of conjugated benzene and pyron subunits in the coumarin chromophores within the copolymer structure. The conjugation between the double bonds and the benzene ring decreased significantly as a result of the homolytic cleavage of the C=C bond next to the C=O. Based on previous studies, four isomeric structures of coumarin dimers have been recorded [104]. This reversible process accounts for the unique behaviors of supramolecular networks and provides a useful reaction pathway in polymer science [105].

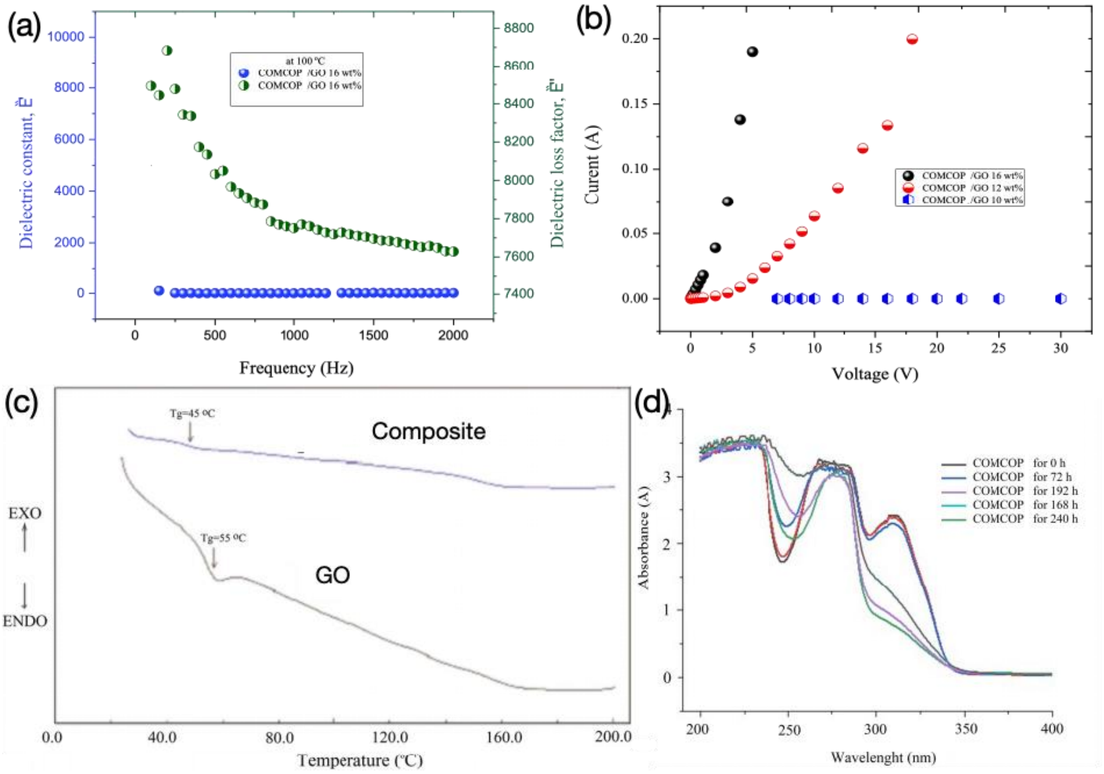

Figure 6. Dependence of E' and E" as a function of frequency: **(a)** and Current (I)-Voltage (V) characteristics; **(b)** for composites with various concentrations of GO; **(c)** DSC curves of GO and their composite; **(d)** Photodimerization recorded from UV–vis spectra after UV irradiation.

4.4. Versatile application

Proper characterization of the polymers is crucial to provide insights into their electrical, thermal and photoresponse properties, which directly helps in optimizing the material design for specific applications.

4.4.1. Intracellular imaging

The nanoprobe of the coumarin-GO composite has a fluorescence on–off response for intracellular imaging via covalently linking coumarin derivatives to GO through disulfide bonds [106]. More significantly, from in vitro cytotoxicity study, there was no obvious toxicity observed for composites even at a high concentration of 60 g mL^{-1}, indicating the resultant nanoprobe is not cytotoxic and suitable for cell imaging. According to the time-course fluorescence microscopy experiments using HeLa and NIH-3T3 cells, we found the fluorescence signal from HeLa cells after 30 min of incubation was clearly detected in the cytoplasm while weakly detected from NIH-3T3 cells. However, the nanoprobe exhibited nominal cytoplasm fluorescence in HeLa cells or NIH-3T3 cells even after 4 h of incubation. In vivo tumor imaging, subcutaneous HeLa tumors in mice were established using the proposed activatable nanoprobe. As the time expanded, the accumulation in tumors and subsequent fluorescence activation of the nanoprobe is visible as early as 1 h post-injection and even achieves maximum contrast by 4 h post-injection (**Figure 7a**). Although the fluorescence emission of the nanoprobe is weakened, the improved signal-to-noise ratio under two-photon near-infrared (NIR) excitation affords alternative detection of cancer. Also, a coumarin-GO-based turn-on fluorescence strategy is proposed for the detection of Cu^{2+} ions [107].

4.4.2. Heavy metal ions removal

Coumarin introduction produced a large amount of micropores and mesopores on the surface of the coumarin-GO composite as well as photo-regulated structure transformation to solve the separation problem through the reversible controlling of adsorption capacity (**Figure 7b,c**). After 365 nm UV light irradiation, the composite displays better adsorption capacities for Pb^{2+} (492.51 mg g^{-1}), Cd^{2+} (419.7 mg g^{-1}), Cu^{2+} (392.1 mg g^{-1}) and Zn^{2+} (375.3 mg g^{-1}) than the intrinsic one (403.97 mg g^{-1}, 340.3 mg g^{-1}, 319.9 mg g^{-1} and 280.1 mg g^{-1}). Additionally, a part of adsorbed heavy metal ions can be desorbed after illuminated by 254 nm UV light, which not only greatly reduces the amount of water or organic reagent for elution of heavy metal ions but also lowers the complexity of the desorption process. From the consideration of practical applications, the adsorption capacity of the composite and their irradiation decreases about 16.5% and 18.4%, respectively, after the consecutive adsorption desorption process (six times). The results indicate that the coumarin-GO provides an experimental basis for structurally photocontrollable materials, which can be served as photoreversible adsorbents for effective removal of Pb^{2+} ions from wastewater at low cost.

4.4.3. Organic solar cell

Ternary blends are considered an encouraging model to increase organic solar cell (OSC) performance by either increasing charge mobility or incorporating optical materials or both. The incorporation of functional materials such as GO with unique properties together with the light harvesting groups of coumarin make them promising materials for ternary blend composites (**Figure 7d**). The OSC performances of covalently bonded hybrid materials (coumarin-GO) in P3HT: PCBM blends were investigated. The reference device based on the pure P3HT: PCBM blend has displayed a power conversion efficiency (PCE) of 2.62% with a fill factor (FF) of 60% and a short-circuit current density (J_{sc}) of 7.1 mA cm^{-2}, while the PCE and J_{sc} reached 2.85% and 8.65 mA cm^{-2}, respectively, with coumarin-GO. Apart from the contribution of GO with unique properties on improved electrical conductivity, extended conjugation in coumarin to increase in the benzene ring and improve the electron transfer ability resulted in an enhancement of solar cell efficiency [108]. The increase in the J_{sc} also confirmed using internal power conversion efficiency (IPCE) measurements with respect to absorption spectra in wide ranges from around 610 nm to 300 nm.

4.4.4. Photodiodes

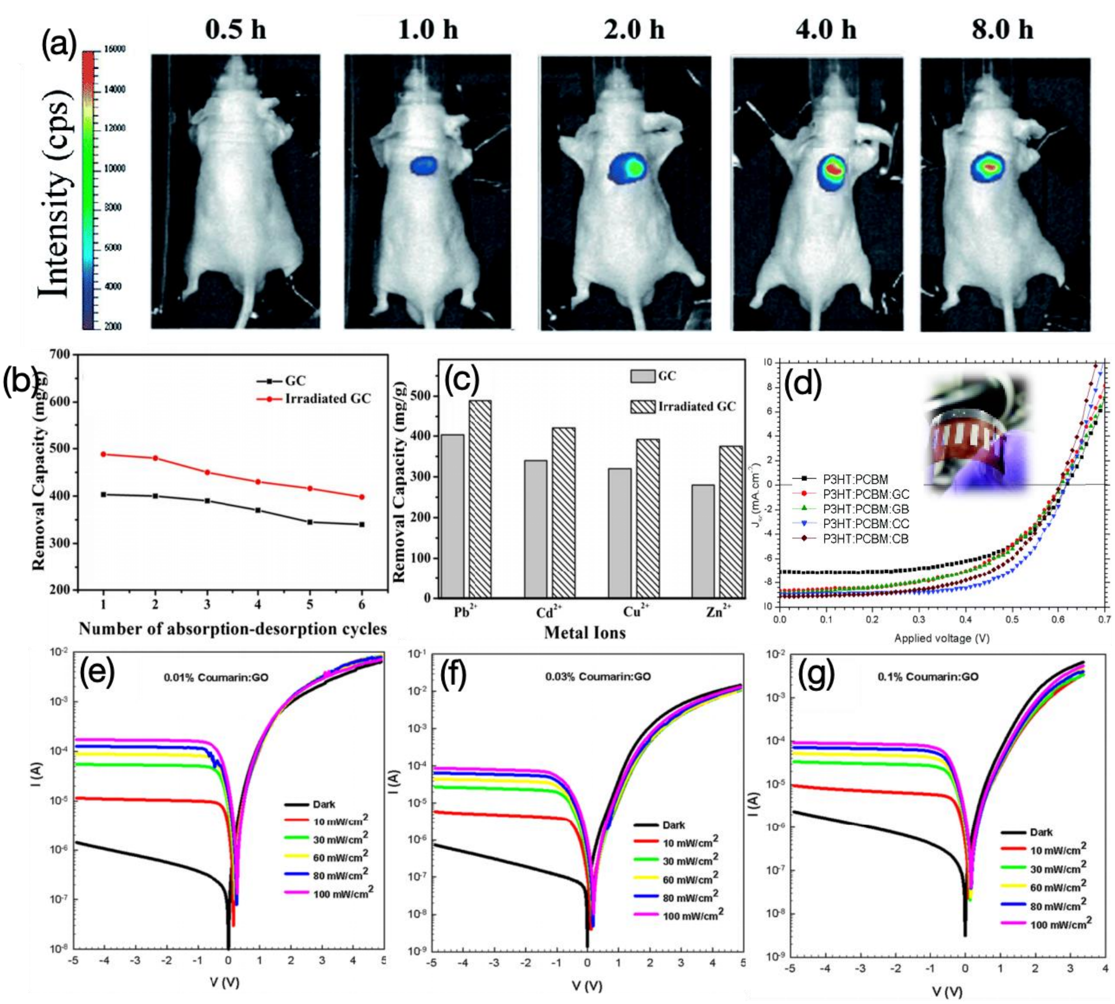

Figure 7. In vivo NIR images of HeLa tumor-bearing mice at 0.5, 1, 2, 4 and 8 h post-intratumor injection with 100 μL of the nanoprobe solution: **(a)** Adsorption recyclability of the composite along with irradiation for Pb^{2+}; **(b)** Adsorption capacities of the composite along with irradiation in relation to various heavy metal ions; **(c)** J(V) characteristics of solar cells based on pristine P3HT:PCBM blends and P3HT:PCBM hybrid ternary blends; **(d)** GO:BODIPY, GO: Coumarin, SWCNTs: BODIPY and SWCNTs: Coumarin are referred to as (GB), (GC), (CB) and (CC), respectively. Photo of a flexible OSC based on P3HT: PCBM hybrid active layer was inset in **(d)**; I–V characteristics of the diodes with various Coumarin: GO under dark and various illumination intensities: **(e)** 0.01%; **(f)** 0.03%; **(g)** 0.1%.

New photodiode-based GO-organic semiconductor hybrid materials were well developed over the past decades [109]. The current–voltage characteristics (e.g., I–V, C–V and transient characteristics) of the coumarin-GO-based diodes were investigated under dark and various illumination intensities. When the diode is illuminated by solar light, the photogenerated charges are produced to form photocurrent in the reverse bias region, revealing the typical photodiode behavior (**Figure 7e–g**). It was found that the photoconducting behavior of the diodes was also improved with Coumarin: GO doping, i.e., the diode having 0.01% coumarin: GO exhibited the highest photoresponsivity. The ideality factor (n) and barrier height (Φ_b) of the Au/Coumarin: GO-doped Bi_2O_3/p-Si diodes with various Coumarin: GO contents were determined in the range of 2.5–4.8 and 0.68–0.8 eV, respectively, suggesting the lower coumarin contents clearly improved the photoresponsivity properties. The transient photocurrent measurements indicate that Au/GO: coumarin/p-Si/Al diodes are very sensitive to illumination and the precise responsivity of the diodes is tunable by adjusting the GO: coumarin fraction. Additionally, the capacitance–voltage–frequency (C–V–f) measurements indicate that the capacitance of the diodes depends on voltage and frequency. The ability to tune the photosensitivity in the photoconductive mode through the GO: coumarin weight ratio has been shown to lead to a near-constant sensitivity to illumination for an optimal weight ratio. Thus, this interlayer of coumarin-GO in diodes is a preferable alternative to traditional insulator layers regarding the enhancements in device parameters. Furthermore, the diodes exhibited a photocapacitance and photoconductance behavior under solar light illumination to be used as a photocapacitor or photodiode in electro-optic applications.

5. Comparative analysis of coumarin-GO composites with other similar composites

Coumarin-GO composites boast distinct advantages compared to other types of polymer-graphene oxide composites, such as polythiophene-GO and polyaniline-GO composites. Here’s a detailed comparison focusing on several key aspects:

5.1. Photostability

The successful photodimerization of coumarin groups in Coumarin-GO composites enhances their stability under UV exposure [110]. This characteristic is crucial for long-term applications in light-sensitive devices, such as sensors and photonic systems, where prolonged exposure to light is common. Even polythiophene-based materials (i.e., polythiophene-GO) also exhibit good conductivity; they can degrade under extended UV light exposure, limiting their effectiveness in certain applications [111]. Similar to polythiophene, polyaniline composites (i.e., polyaniline-GO) may experience photodegradation, which could compromise their optical properties over time [112].

5.2. Conductivity and charge carrier mobility

Coumarin-GO composites show enhanced electrical and thermal conductivity due to the effective integration of GO, which facilitates improved charge transport [113]. The design of coumarin structures can be tailored to optimize these properties further. Known for their excellent electrochemical performance, polythiophene-GO typically exhibit high conductivity but may require additional doping to reach optimal levels [114]. While polyaniline offers good conductivity in polyaniline-GO composites, its inherent instability and the requirement for oxidation can complicate application processes [115].

5.3. Functional versatility

The incorporation of coumarin groups not only enhances conductivity but also introduces unique photochemical characteristics, allowing coumarin-GO composites to be used in applications such as targeted drug delivery and bioimaging [116]. The ability to modify functional groups easily enables tailored responses to specific stimuli. For polythiophene-GO composites, they are primarily limited to applications in organic electronics and sensors, with less versatility regarding functional modifications [117]. While polyaniline-GO composites are employed in sensors and energy storage, they are less adaptable to dual-functional roles due to the complexities of their synthesis and stability [118].

5.4. Biocompatibility and environmental impact

Preliminary studies suggest that the biocompatibility of coumarin-based materials is favorable, making coumarin-GO composites suitable for biomedical applications and reducing potential environmental hazards [119]. While both polythiophene-GO and polyaniline-GO composites may exhibit cytotoxicity and environmental concerns depending on their processing and degradation products, which necessitates careful evaluation before biomedical application [120].

5.5. Application scope

Coumarin-GO composites show potential not only in electronics and environmental sensors but also in medical applications such as fluorescent probes for bioimaging [121]. Their ability to function both as sensors and therapeutic agents makes them highly versatile. In contrast, polythiophene-GO and polyaniline-GO composites generally focused on electronic applications, including OLEDs and solar cells, rather than typically extending into the biomedical realm to the same extent as coumarin-GO composites [122].

Coumarin-GO composites stand out for their unique photostability, enhanced conductivity, functional versatility, and potential biocompatibility. These attributes make them particularly promising for a wider range of applications, especially in fields such as biomedicine and sustainable technologies, compared to traditional polythiophene-GO and polyaniline-GO composites. As research progresses, further investigations into their unique properties and applications will likely yield exciting opportunities in material science and engineering.

6. Conclusion and future prospects

During the past several decades, significant developments have been made in the field of coumarin-GO composites. This review provides a detailed examination of the various synthetic methods employed to produce graphene oxide (GO), GO-polymer, coumarin-based polymer, and coumarin-GO composites, highlighting their pathways, properties, characterizations, and applications. These fascinating materials are in high demand for optoelectronic and energy applications, as well as in the biomedical field.

From our overview of coumarin-GO composites, several important implications emerge. Firstly, the successful photodimerization of coumarin groups with GO imparts unique properties that enhance stability under UV exposure. Their electro-optic characteristics make them suitable for sensors and devices requiring light manipulation. Secondly, the improved electrical and thermal conductivity of these composites, achieved through careful design and loading of GO, suggests their suitability for applications in flexible electronics, solar cells, and energy transfer materials. Lastly, understanding the kinetic and electrical characteristics of coumarin-GO composites could lead to new polymer materials with tailored functionalities, thereby expanding the scope of specific applications. In particular, examinations of their biocompatibility and environmental impact are crucial for paving the way for practical applications in bioimaging and sustainable technologies.

As the field of coumarin-GO composites continues to evolve, future research directions should focus on modifying functional groups, incorporating different graphitic nanofillers, and exploring various polymer compositions. However, several challenges must be addressed to achieve coumarin-based composites with enhanced features:

- Characterization Techniques: Advanced characterization methods, including Extended X-Ray Absorption Fine Structure (EXAFS) spectroscopy, can provide detailed insights into the local structure of materials, including coordination numbers and bonding lengths. This information is vital for validating the composites' suitability for future applications.
- Practical Scalability: Scaling up the production of these composites while maintaining their unique properties and performance is a significant challenge, especially for applications in organic thermoelectric devices and bioelectronics. Techniques such as microwave- and ultrasound-assisted synthesis may prove useful for obtaining the large quantities of material needed for practical applications. However, standardizing production techniques without compromising quality remains a key hurdle.
- Extending Applications: The synthesis of composites through copolymerization or in combination with semiconductors (i.e., photocatalysts) could create promising materials for wastewater remediation and solar energy conversion by tailoring the bandgap and enhancing light absorption. Future studies should investigate the synergy between these materials and their potential in dual-functional roles.

Conclusively, exploring the full potential of coumarin-GO composites is essential for developing next-generation applications in electronics, biomedicine, and sustainable technologies. Overcoming the challenges of scalability and modification will ultimately contribute to advancements in material science and engineering.

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