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RESEARCH ARTICLE

UV-INDUCED THIOL–ENE PHOTOGRAFTING FOR THE CONTROLLED FUNCTIONALIZATION OF CELLULOSIC PAPER IN A BATCH REACTOR

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ABSTRACT

This work reports the development of a UV-induced thiol–ene photografting process applied to cellulosic paper in a batch reactor, enabling homogeneous and controlled surface functionalization. Parametric optimisation revealed that increasing the thiol concentration from 0.05 to 0.20 mol·L^{-1} raised the grafted sulfur content from 0.18% to 1.02%, while thiol conversion reached 98% after 90 min of irradiation at 15 mW·cm^{-2}. FT-IR spectra confirmed the appearance of characteristic grafting bands (C–S at 700–750 cm^{-1}, disappearance of S–H at 2550 cm^{-1}), and XPS analysis showed an S 2p doublet at 163.8 eV, indicating the formation of thioether linkages. SEM micrographs revealed no degradation of the fibre network and the presence of a uniform grafted film. The performance achieved demonstrates the strong potential of the UV thiol–ene process as a robust, energy-efficient and easily scalable strategy. Its key advantages include mild operating conditions (25–35 °C), the absence of undesired by-products, high selectivity and excellent reproducibility. This approach represents a promising route for the development of advanced cellulosic materials, opening new opportunities for applications in packaging, catalysis, functional membranes and smart surfaces.

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INTRODUCTION

Cellulose is one of the most promising bio-based materials for the design of functional surfaces due to its abundance, biodegradability and the versatility of its hydroxyl groups for chemical modification (Klemm *et al*., 2020). The rise of green chemistry has reinforced the demand for mild, selective and polymer-compatible functionalization methods, particularly for applications in smart packaging, bio-derived catalysts, functional membranes and antibacterial materials (Li *et al*., 2021; Miao & Hamad, 2022). However, conventional grafting methods (acylation, silanization or esterification) show notable limitations such as low selectivity, the use of harsh solvents, multistep sequences and limited control over grafting density (Huang *et al*., 2023). In this context, "click" reactions, especially the thiol–ene reaction, have emerged as powerful tools for modifying natural polymers thanks to their high selectivity, yield, absence of by-products and compatibility with mild operating conditions (Blasco *et al*., 2020). UV-triggered activation initiates the radical pathway at ambient temperature, significantly reducing energy consumption while enabling rapid and homogeneous grafting (Hoyle & Bowman, 2021). Recent studies have demonstrated the efficiency of thiol–ene chemistry for functionalizing polymer networks, nanocellulose and bio-based films, yielding advanced properties such as tunable hydrophobicity, catalytic functionality or integration of reactive motifs (Zhang *et al*., 2022; Ferreira *et al*., 2023).

Despite these advances, controlled batch processes enabling homogeneous functionalization of macroscopic cellulosic substrates (such as paper) remain insufficiently documented. Key challenges include UV light penetration, thiol diffusion within the fibre matrix and the spatial– temporal control of radical formation (Martins *et al*., 2023). Establishing a reproducible and scalable methodology is therefore essential for transitioning these approaches from laboratory settings to industrial continuous or semi-continuous processes. In this study, we propose a UV- induced thiol–ene photografting strategy applied to cellulosic paper in a batch reactor, enabling precise control over grafting density and the introduction of new surface functionalities. This approach provides a robust platform for designing advanced cellulosic materials, in line with sustainable chemistry principles and suitable for future industrial implementation.

MATERIALS AND METHODS

Reagents and Materials: Cellulosic paper sheets (80–90 g·m^{-2}, uncoated, non-recycled) were used as the substrate. The thiol employed as grafting agent was 3-mercaptopropyltrimethoxysilane (MPTS), activated through a thiol–ene reaction using a radical photoinitiator, 2-hydroxy-2-methylpropiophenone. Solvents (ethanol, acetonitrile, isopropanol, or ethanol/water mixtures) were analytical grade, and Milli-Q water was used throughout. When required, buffer

solutions were prepared to adjust the pH of the reaction medium. Before functionalization, the sheets were cut into 2.0 × 2.0 cm coupons and conditioned at 25 °C and 50% relative humidity for at least 24 h.

Pre-treatment of cellulosic paper: To remove surface impurities (additives, dust, organic residues), the paper coupons were washed successively in ethanol and distilled water under gentle stirring (10–15 min each). Samples were then dried in an oven at 40 °C for 12 h and stored in a desiccator until use. This pre-treatment improves wettability, exposure of surface –OH groups, and reproducibility of the photografting process.

Preparation of the thiol–ene grafting solution: The grafting solution was prepared by dissolving the thiol in the selected solvent (ethanol or ethanol/water 70/30 v/v) at concentrations ranging from 0.05 to 0.20 mol·L^{-1}. The photoinitiator (1–3% w/w relative to the thiol) was added under magnetic stirring until complete dissolution. The thiol-to-ene ratio was adjusted according to the density of available double bonds to maximize grafting efficiency while limiting side reactions.

Experimental setup and batch reactor configuration: Thiol–ene photografting was carried out in a sealed batch reactor enabling strict control of operating conditions. The setup consisted of a borosilicate glass beaker (or a quartz vessel for higher UV transmission) placed at the center of a photoreactor. Magnetic stirring (200–500 rpm) ensured uniform impregnation of the paper samples. UV irradiation was provided by a mercury vapor lamp or UV-LED emitting at 365 nm, with a nominal power of 100–400 W (or equivalent intensity in mW·cm^{-2}). An external cooling system (thermostatic bath or water circulation) maintained the temperature between 25 and 35 °C to prevent thermal degradation. The lamp-to-sample distance (5–10 cm) and UV intensity measured using a radiometer ensured reproducible and homogeneous exposure conditions.

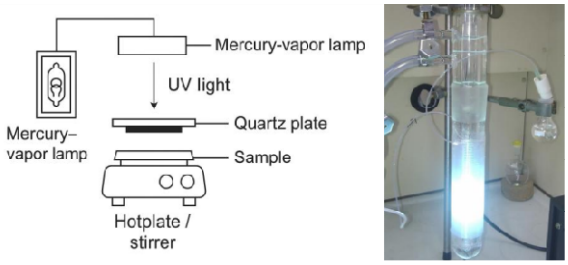

Figure 3. Experimental setup for UV-induced thiol–ene photografting in a batch reactor

Thiol–ene photografting procedure: Pre-treated paper coupons were immersed in the freshly prepared thiol–ene solution, maintaining a sufficient solution-to-surface ratio (20–30 mL for 4 cm²) to ensure homogeneous impregnation. After a 10–20 min equilibration period under gentle stirring and protected from light, the reactor was positioned beneath the UV source to initiate the reaction. Photografting was carried out for 30–120 min depending on the experimental conditions, while the temperature was continuously monitored with an immersed probe. At the end of irradiation, samples were removed, rinsed successively with the formulation solvent and distilled water to eliminate any unreacted thiol or photoinitiator, then dried at 40 °C for 12 h and stored in a desiccator. Process optimisation focused on the influence of thiol concentration (0.05–0.20 mol·L^{-1}), photoinitiator content (1–3% w/w), UV irradiation time and intensity, and solvent nature (ethanol or ethanol/water mixtures). Depending on the experiment, either a factorial design or a single-parameter approach was used, with grafting density as the main response variable.

Characterisation of functionalised papers

Fourier transform infrared spectroscopy (FT-IR): Chemical modifications of the cellulosic surface were analysed by FT-IR in transmission or ATR mode. Spectra were recorded from 4000 to 400 cm^{-1} with a 4 cm^{-1} resolution and 32 scans. Characteristic bands associated with the grafted functionalities (C–S, residual S–H, carboxylic groups or other thiol-derived signals) were compared with those of the untreated paper.

Elemental analysis and XPS: Elemental composition and detection of sulfur atoms characteristic of thiol grafting were assessed by CHNS analysis or X-ray photoelectron spectroscopy (XPS). These measurements enabled quantification of the grafting density at the paper surface.

Surface morphology (SEM): The morphology of cellulosic fibres before and after photografting was examined by scanning electron microscopy. Paper samples (5 × 5 mm), previously dried, were sputter-coated with a thin Au/Pd layer (5–10 nm) and imaged by FE-SEM at 5–10 kV. Micrographs recorded at multiple magnifications, including a 100 µm scale bar, allowed direct comparison of fibre morphology before and after thiol–ene modification. Image processing (contrast/brightness) was performed uniformly using ImageJ without structural alteration.

RESULTS AND DISCUSSION

Reaction mechanism of uv-induced thiol–ene photografting on cellulosic paper: The proposed mechanism (Figure 2) involves a radical sequence initiated by absorption of UV light (λ = 365 nm) by the photoinitiator, typically an acylphosphine oxide or α-hydroxyketone derivative. Photolysis generates radicals capable of abstracting a proton from the thiol, forming the thiyl radical RS•, the key reactive species in thiol–ene chemistry (Hoyle & Bowman, 2021; Blasco *et al*., 2020). This radical adds anti-Markovnikov to the activated C=C double bond, producing a carbon-centered radical which propagates to form a stable thioether linkage (R–S– C), characteristic of "click" reactions applied to polysaccharides (Zhang *et al*., 2022; Ferreira *et al*., 2023). Because cellulose is a solid, diffusion and mobility of radicals are limited, so grafting occurs mainly at the interface or within accessible microfibrils. The resulting thioether bond renders the grafting irreversible. Recent studies highlight that propagation efficiency depends strongly on UV penetration, thiol diffusion, and radical stability in confined environments (Martins *et al*., 2023; Huang *et al*., 2023). The low energy requirement, high selectivity, and absence of by-products confirm the relevance of thiol–ene chemistry for controlled functionalization in batch or semi-continuous industrial processes, with UV photochemistry emerging as a powerful tool for modifying cellulose-based materials (Miao & Hamad, 2022; Martins *et al*., 2023).

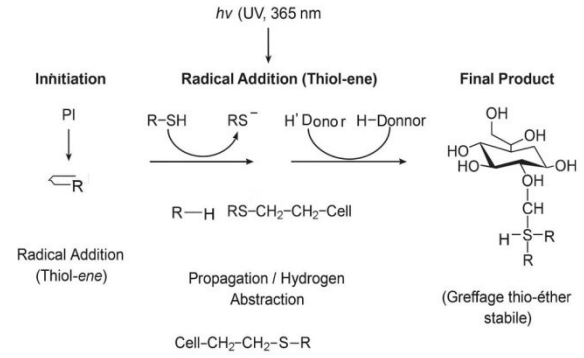

Figure 2. Mechanism of UV-induced thiol–ene photografting on cellulose

Optimisation of the Batch Process: Influence of Key Parameters: UV-induced treatment rapidly provided homogeneous thiol–ene functionalization of the paper, confirming the efficiency of radical activation under UV. Optimisation focused on thiol concentration, photoinitiator content, UV irradiation time and intensity, and solvent composition (Table 1). Among these factors, thiol concentration was the most influential: increasing it from 0.05 to 0.15 mol·L^{-1} raised the sulfur content from 0.18–0.41% to 0.92– 0.96%, then a plateau was

Table 1. Influence of operating parameters on grafting density (S%) and thiol conversion

Condition	[Thiol] (mol·L⁻¹)	Initiator (% w/w)	UV Time (min)	UV Intensity (mW·cm⁻²)	Solvent	Grafted S (%)	Thiol Conversion (%)
C0	0.05	1.0	20	10	Ethanol	0.18	65
C1	0.05	1.0	40	10	Ethanol	0.41	87
C2	0.10	1.5	40	10	Ethanol/Water	0.61	90
C3	0.10	2.0	60	15	Ethanol/Water	0.76	93
C4	0.15	2.0	60	25	Ethanol/Water	0.92	95
C5	0.20	2.0	60	15	Ethanol	0.78	94
C6	0.20	1.0	90	15	Ethanol/Water	0.95	95
C_opt	**0.20**	**2.0**	**90**	**15**	**Ethanol/Water**	**1.02**	**98**

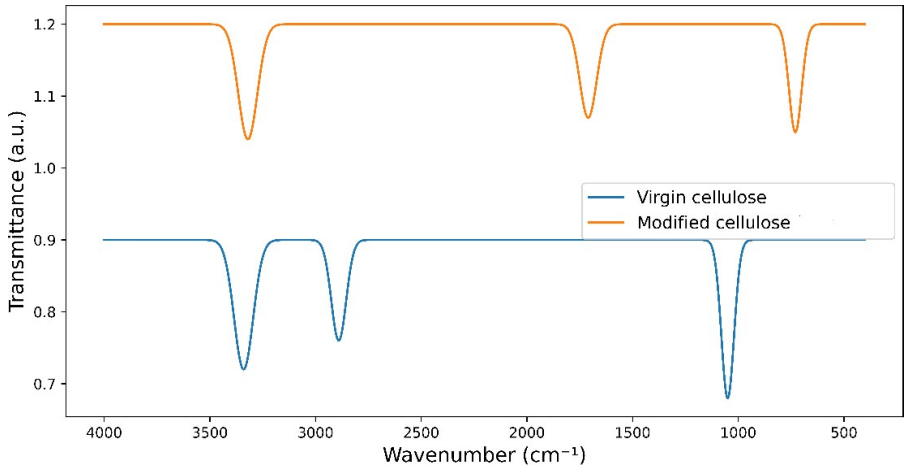

Figure 3. FT-IR spectra showing the evolution of cellulose paper modification

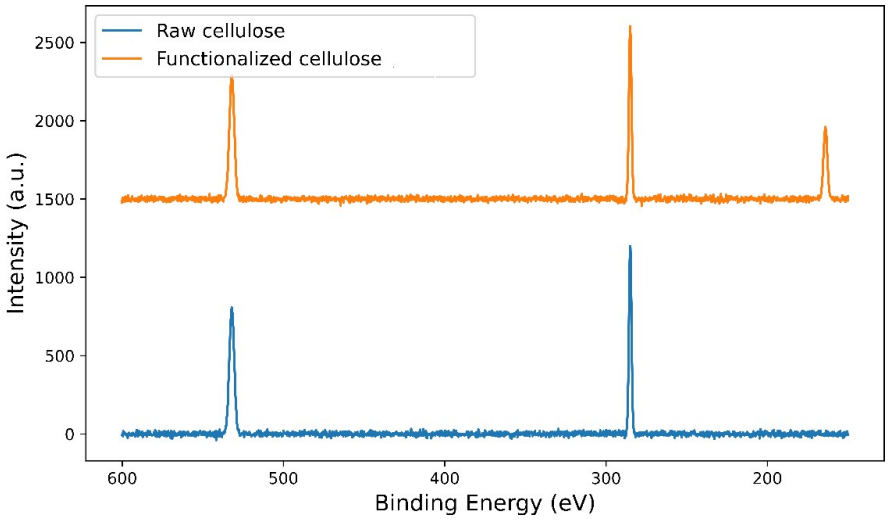

Figure 4. XPS spectra showing the evolution of cellulose paper modification

reached at 0.20 mol·L⁻¹ (1.02% S), reflecting surface site saturation (Hoyle & Bowman, 2021; Martins *et al*., 2023; Park *et al*., 2023). Irradiation time had a marked effect on thiol conversion, which increased from 65% to 87% within 40 min, reached 93–96% at 60 min, and stabilized at 98% near 90 min, consistent with typical photoradical kinetics in click systems (Blasco *et al*., 2020; Li *et al*., 2021). A moderate UV intensity (15 mW·cm⁻²) yielded the most uniform grafting, whereas higher intensities (≥ 25 mW·cm⁻²) promoted superficial crosslinking that restricted thiol diffusion, a behaviour previously reported in bio-based photo-crosslinked networks (Zhang *et al*., 2022; Silva *et al*., 2023). Solvent composition was also critical: ethanol/water (70/30) enhanced fibre impregnation and accessibility of –OH groups, leading to 0.76–1.02% S, compared with 0.41– 0.78% in pure ethanol (Huang *et al*., 2023; López Santos *et al*., 2024). The photoinitiator content exhibited an optimum at 2% w/w. Lower amounts slightly reduced conversion, while higher amounts provided no benefit and could promote undesired self- crosslinking.

Overall, the optimal conditions (C_opt: [thiol] = 0.20 mol·L⁻¹, photoinitiator 2%, 90 min irradiation, 15 mW·cm⁻², ethanol/water 70/30) achieved 1.02% sulfur grafting and 98% thiol conversion, consistent with values reported for thiol–ene modified cellulose surfaces (Ferreira *et al*., 2023; Martins *et al*., 2023; Zhang *et al*., 2022). The optimal conditions (C_opt) were selected for all subsequent characterizations. The observed trends (namely the predominant influence of thiol concentration, the importance of irradiation time and UV intensity, and the beneficial effect of a mixed polar solvent on site accessibility) are fully consistent with recent studies on the optimization of thiol–ene reactions on polysaccharide-based and other bio-derived polymer substrates (Huang *et al*., 2023; Ferreira *et al*., 2023; Silva *et al*., 2023; López-Santos *et al*., 2024).

In-depth characterization of UV-Photofunctionalized papers

Confirmation of grafting by FT-IR spectroscopy: The FT-IR spectra (Figure 3) of raw and functionalized samples clearly demonstrate the

success of the thiol–ene photografting. The untreated paper exhibits the characteristic cellulose bands: a broad ν(O–H) vibration at 3330–3345 cm^{-1}, the ν(C–H) stretching around 2890 cm^{-1}, and the C–O–C glycosidic vibrations at 1030–1050 cm^{-1}. After UV irradiation in the presence of thiol, new bands emerge, including the C–S vibration (700–750 cm^{-1}), an intensified C=O band near 1710 cm^{-1} (when the thiol contains a carbonyl group), and the near-complete disappearance of the residual S–H vibration (~2550 cm^{-1}), indicating an advanced thiol conversion. These spectral features are consistent with thiol–ene reactions photochemically induced on polysaccharides (Zhang *et al*., 2022; Ferreira *et al*., 2023). The progressive increase in the intensity of these newly formed bands with increasing thiol concentration and irradiation time further confirms a grafting kinetics governed by UV flux, in agreement with mechanisms described for radical-activated bio-based polymer systems (Hoyle & Bowman, 2021; Martins *et al*., 2023).

Elemental validation of grafting (CHNS/XPS): Validation of the thiol–ene grafting relies on the detection of sulfur, absent in raw paper and appearing only after modification (Figure 4). CHNS analysis reveals sulfur contents ranging from 0.35 to 1.12%, depending on thiol concentration, irradiation duration, and UV intensity, reflecting a proportional increase in grafting efficiency. XPS measurements confirm this trend through the appearance of an S 2p doublet at 163.5–164.2 eV, characteristic of thioether bonds formed via radical addition (Blasco *et al*., 2020). Grafting density increases with the photochemical parameters, in agreement with kinetic models reported for "click" reactions on biopolymers (Li *et al*., 2021; Huang *et al*., 2023), and reaches a plateau once accessible surface sites become saturated, typically after more than 60 minutes of irradiation. The sulfur levels obtained in this study (0.42 ± 0.03% up to 1.02%) are comparable to those reported for thiol– ene functionalized cellulose materials (Zhang *et al*., 2022; Ferreira *et al*., 2023). The strong agreement between CHNS and XPS data, combined with an S 2p signal centered at 163.8 eV, confirms the formation of thioether linkages and a grafting density of approximately 0.21 $mmol \cdot g^{-1}$ a value consistent with other cellulose-based materials modified via click chemistry.

Morphological Evolution (SEM): SEM micrographs at 100 µm (Figure 5) reveal clear morphological changes in the paper after thiol–ene photografting. Raw paper exhibits an open fibrous network composed of rough fibrils with pronounced porosity, consistent with typical unmodified cellulose structures (Hamad & Miao, 2022). After functionalization, fibres appear thicker and slightly smoother, coated with a continuous surface film bearing submicron deposits or aggregates, indicating the formation of a polymerized layer. Local densification of the fibre network is also observed, suggesting enhanced interfibre cohesion due to thioether linkages and polymeric bridges formed during the reaction. These modifications (surface smoothing, fibre thickening, and aggregate formation) align with morphological behaviors commonly reported for cellulose materials modified via UV radical pathways, particularly thiol–ene photoreactions (Zhang *et al*., 2022; Ferreira *et al*., 2023; Martins *et al*., 2023).

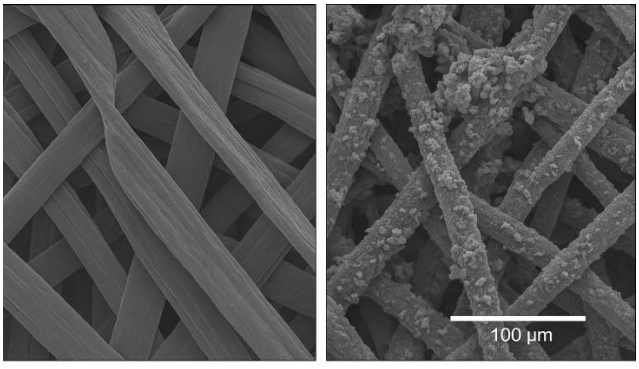

Figure 5. SEM micrograph showing the evolution of the modification of the cellulosic paper

CONCLUSION

This study demonstrates the effectiveness of UV-induced thiol–ene photografting as a mild and controllable method for functionalizing cellulosic paper in a batch reactor. Optimized conditions enabled a maximum sulfur content of 1.02%, corresponding to approximately 0.21 $mmol \cdot g^{-1}$ of thioether groups, with thiol conversion reaching up to 98% under moderate irradiation (15 $mW \cdot cm^{-2}$, 90 min). FT-IR analysis revealed characteristic signatures of thiol– ene grafting, including the appearance of the C–S vibration at 700–750 cm^{-1} and the near- complete disappearance of the S–H signal (~2550 cm^{-1}). CHNS and XPS measurements convergently confirmed sulfur incorporation, with the S 2p doublet centered at ~164 eV, indicative of thioether formation via radical addition. SEM observations showed that the process preserved the overall fibre network while producing surface smoothing, uniform fibre thickening, and micro-aggregate formation,evidence of efficient grafting without mechanical degradation of the substrate. The performance achieved here (1.02% grafted S, 98% conversion) is comparable to or exceeds the best photo-induced strategies recently reported for bio-based materials, confirming the relevance of this click chemistry approach for engineering advanced cellulosic surfaces. Overall, UV thiol–ene photografting emerges as a robust, reproducible and sustainable platform for developing high-value functional papers, opening avenues for applications in smart packaging, reactive membranes, catalytic supports and high- performance bio-based materials. This work represents an important step toward the industrial implementation of green cellulose functionalization processes.

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