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# Synthesis of PVA-based macromolecular photoinitiators through esterification with TXOCH<sub>2</sub>COOH and cysteine, and investigation of their photophysical properties: *in situ* fabrication of flexible nanocomposite films

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2-(Carboxymethoxy) thioxanthone (TX-OCH<sub>2</sub>COOH), a thioxanthone derivative, was utilized for the esterification of polyvinyl alcohol (PVA) to synthesize a macromolecular photoinitiator, both in the absence and presence of Cysteine (Cys). The covalent attachment of the thioxanthone (TX) group to PVA through esterification enabled the exploration of the photophysical properties of the resulting macromolecular photoinitiators (TXOCH<sub>2</sub>COO-PVA and TXOCH<sub>2</sub>COO-PVA-Cys) via UV-Vis and fluorescence studies. UV-Vis absorption spectrum of TXOCH<sub>2</sub>COO-PVA confirmed the covalent bonding of TX, marked by a characteristic absorption peak at 397 nm corresponding to the thioxanthone chromophore. Fluorescence lifetimes were recorded as TXOCH<sub>2</sub>COO-PVA was cast into a mold and air dried, resulting in a flexible form of PVA esterified with TXOCH<sub>2</sub>COOH. *In-situ* synthesis of both silver and selenium nanoparticles was carried out using both TXOCH<sub>2</sub>COO-PVA and TXOCH<sub>2</sub>COO-PVA-Cys macromolecular initiators, successfully yielding nanocomposite flexible polymeric films.

## KEYWORDS

photoinitiator, flexible polymeric films, thioxanthenes (TX), polyvinyl alcohol (PVA), esterification reaction, silver nanoparticles (AgNPs)

## Highlights

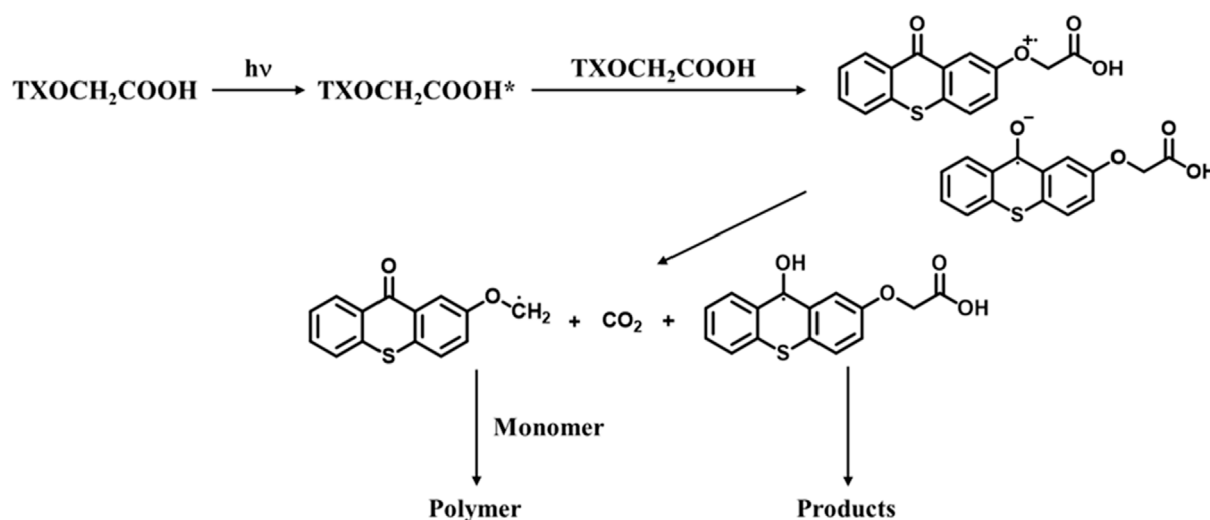
- PVA-based macromolecular photoinitiators were prepared with and without cysteine.
- Photophysical characterizations of macro photoinitiators were performed.
- Nanocomposite thin films consisting of AgNPs and SeNPs were synthesized by *in situ* photochemical method

## 1 Introduction

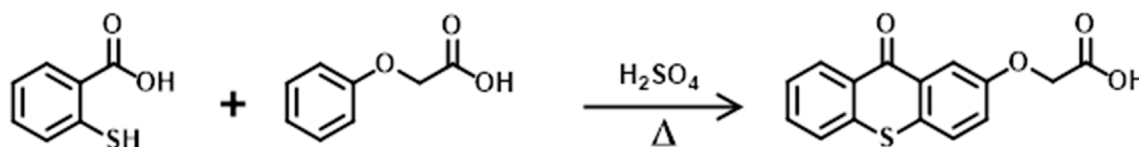
Polyvinyl alcohol (PVA) is an environmentally friendly polymer (Maruoka et al., 2006), and its functionalization can enhance its performance in various applications, including adhesives, coatings (Nassar et al., 2023; Nishiyabu et al., 2020; Madhusudhana et al., 2022) and biomedical materials (Rafique et al., 2016; Chong et al., 2013). This process involves chemical modifications such as esterification (Ko et al., 2020; Salavagione et al., 2009; Schanuel et al., 2015), acrylation (Mühlebach et al., 1997; Crispim et al., 2006) and grafting (Alexandre et al., 2014). By attaching different molecules to PVA, its properties can be enhanced, improving characteristics like flexibility (Dicharry et al., 2006), biodegradability (Acik and Karatavuk, 2020) and thermal stability (Singh et al., 2020; Chiou et al., 2013). Photoinitiators absorb light and generate

reactive species that initiate the photopolymerization reaction (Dietliker et al., 2004; Yagci et al., 2010; Keskin Dogruyol et al., 2023). Radical photoinitiators are classified as Type I and Type II based on their photoinitiation mechanisms (Aydin et al., 2003). Type I photoinitiators, such as benzoin and amino acetophenones, produce radicals through homolytic bond cleavage (Hammoud et al., 2022). On the other hand, Type II photoinitiators require co-initiators such as amines or thiols to initiate the photopolymerization (Balta et al., 2008). One-component type II photoinitiators feature both light-absorbing and hydrogen-donating regions within a single structure (Koyuncu et al., 2021; Metin et al., 2020) (see Scheme 1).

A macromolecular photoinitiator can be synthesized by reacting a polymer with a photoinitiator containing carboxyl groups (Kork et al., 2015). These macromolecular photoinitiators



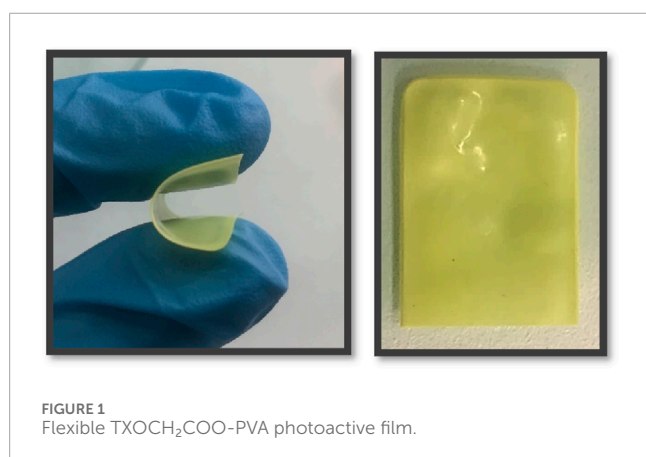
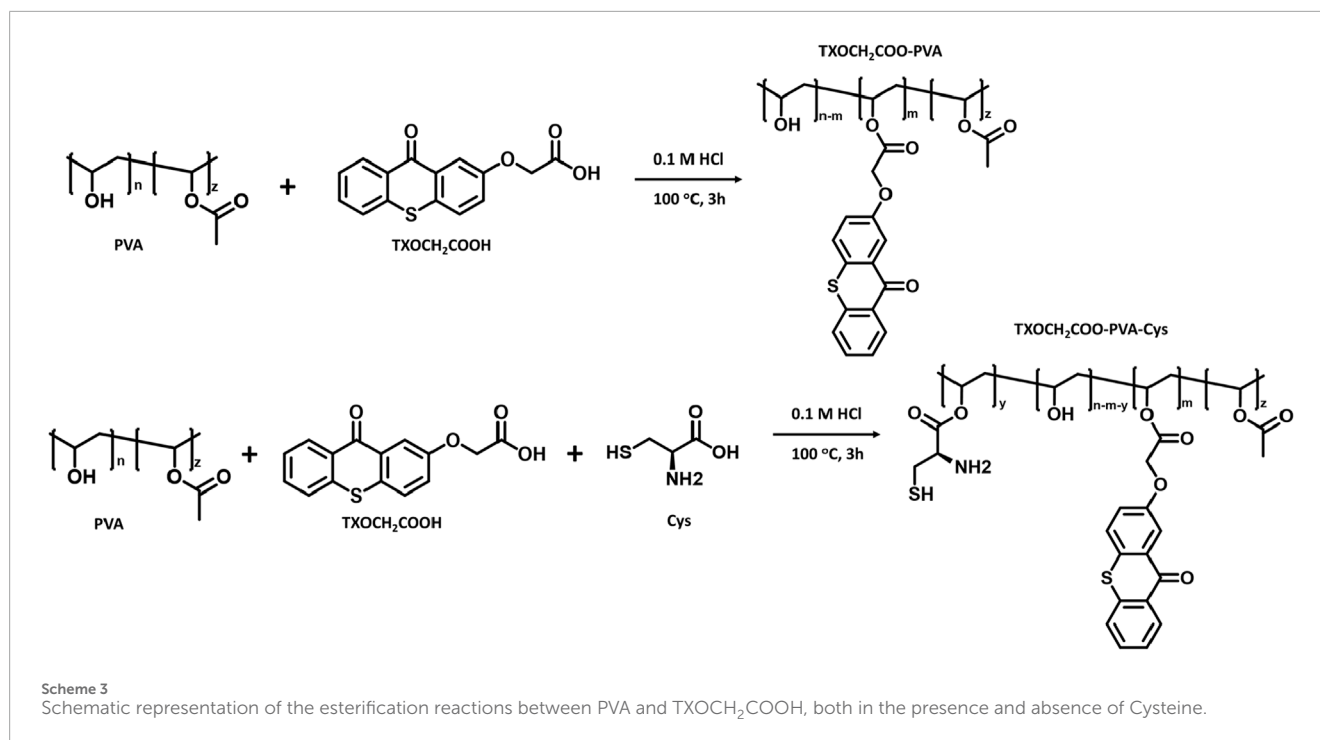
Scheme 1  
Photoinitiation mechanism of TXOCH<sub>2</sub>COOH.



Scheme 2  
Synthesis mechanism of TXOCH<sub>2</sub>COOH.

TABLE 1 The composition of reaction formulations.

Formulation	PVA (wt%)	TXOCH <sub>2</sub> COOH (wt%)	Cys (wt%)	Name
F1	5	0.5	-	TXOCH <sub>2</sub> COO-PVA 0.5%
F2	5	0.5	0.8	TXOCH <sub>2</sub> COO-PVA-Cys 0.5%
F3	5	1	-	TXOCH <sub>2</sub> COO-PVA 1.0%
F4	5	1	0.8	TXOCH <sub>2</sub> COO-PVA-Cys 1.0%



offer many advantages, such as high molar absorption, low migration, and good dissolution in polymerizable formulations due to their unique structures (Deng et al., 2020). Therefore, they are strong candidates for photopolymerization processes. Photopolymerization is an environmentally friendly process (Tehfe et al., 2013) that consumes less energy, minimizes waste (Pierau et al., 2022), and operates at low reaction temperatures. These processes, which have long been integral to chemical applications, are currently being explored in areas such as coatings (He et al., 2023), adhesives, 3D printing (Bagheri and Jin, 2019; Voet et al., 2021), self-healing materials (Guo, 2022), and metal nanocomposites (Riad et al., 2020; Ozelik Kazancioglu et al., 2021). In this study, we present the synthesis of an environmentally friendly PVA-based macromolecular photoinitiator, incorporating TX alone as well as both TX and cysteine derivatives via an esterification reaction. Characterization and photophysical properties are also

presented to highlight the impact of cysteine on the macromolecular chain of PVA. Furthermore, nanocomposites containing Ag and Se nanoparticles were fabricated.

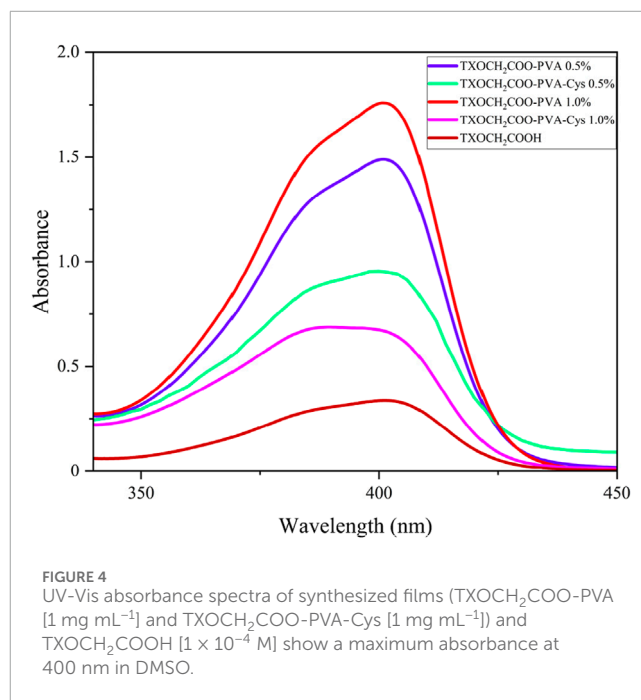
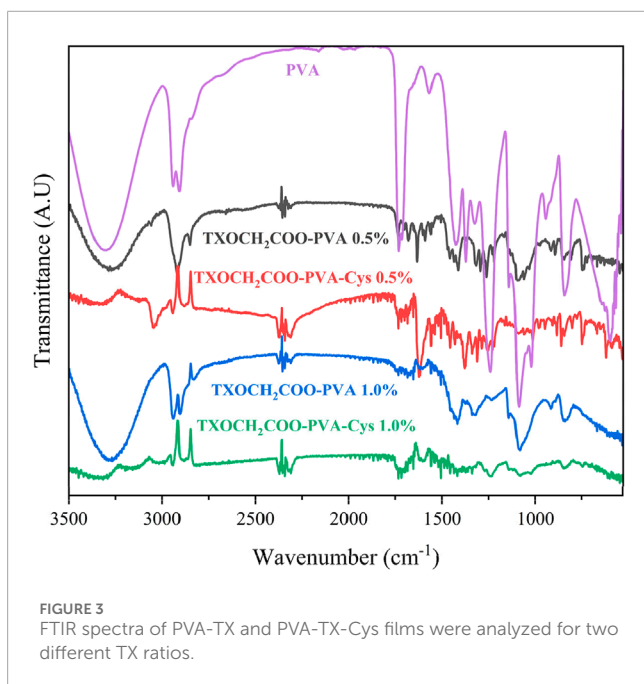
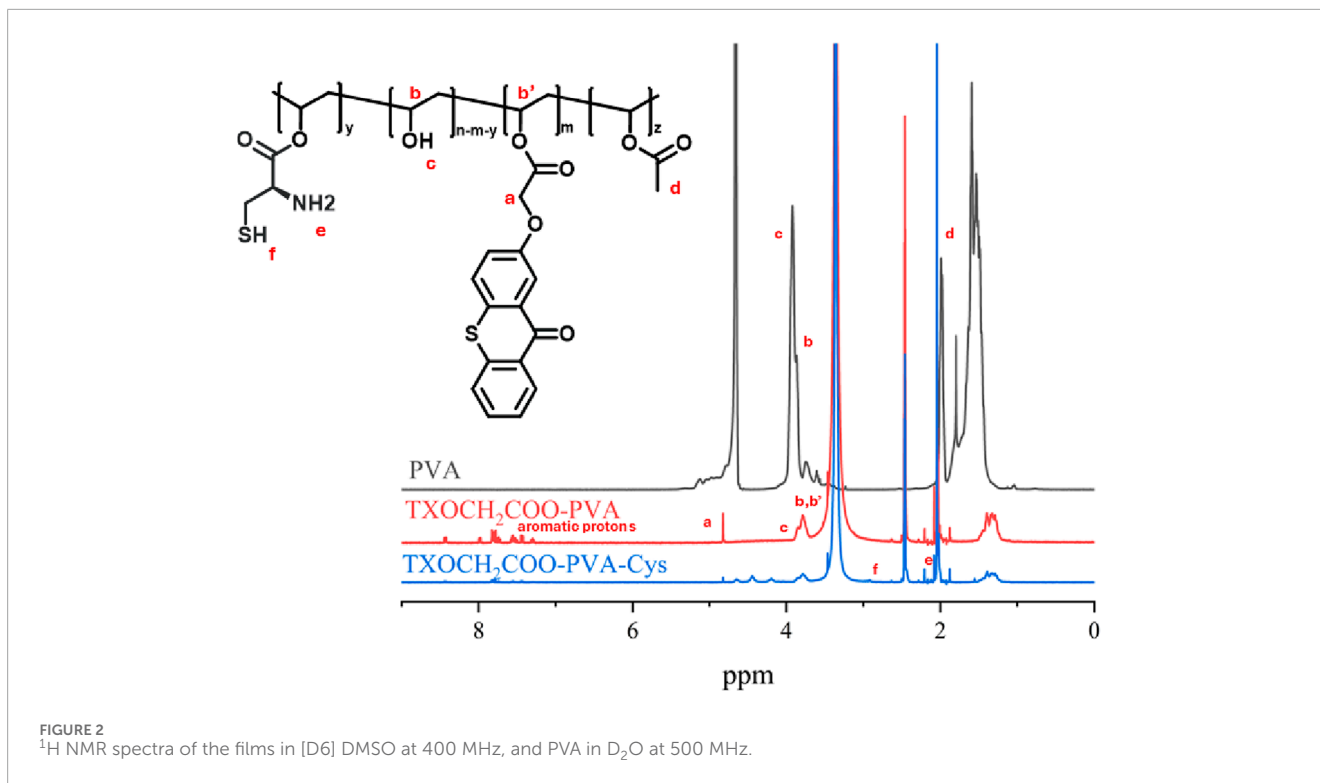
## 2 Experimental section

### 2.1 Materials

Silver nitrate (AgNO<sub>3</sub>, Sigma-Aldrich, 99%), Polyvinyl alcohol (PVA, Alfa Aesar, Mn: 12,500 g/mol, 80% hydrolyzed), Acrylamide (AA, Fluka, ≥98%), L-cysteine (Sigma-Aldrich, C-7755) Thiosalicylic acid (Merck, 97%), Phenoxyacetic acid (Merck, 98%), dimethyl sulfoxide (DMSO, ISOLAB, 99.9%), hydrochloric acid (HCl, Merck, 37%), sulfuric acid (H<sub>2</sub>SO<sub>4</sub>, Merck, 98%), ethanol (Merck, 99%), Hexane (Merck, 99%), and distilled water were used without further purification.

### 2.2 Instrumentation

<sup>1</sup>H NMR spectra were measured with the JEOL ECS 400 MHz NMR spectrometer using DMSO-D<sub>6</sub> as solvents. FT-IR spectra were measured with a Nicolet 6700 FT-IR spectrometer. Hellma Analytics quartz cuvettes were used for spectroscopic measurements. UV-Vis absorption studies were performed with a Varian Cary 50 Conc Spectrophotometer. Fluorescence emission-excitation spectra were analyzed with a Horiba Fluoromax-3P fluorescence spectrophotometer. Fluorescence emission decay measurements were performed at room temperature using a Hamamatsu Quantaurus-Tau C11367 spectrometer. Transmission electron microscopy (TEM) images were recorded using a Hitachi H-7650 TEM electron microscope.



### 2.3 Synthesis of $\text{TXOCH}_2\text{COOH}$

The previously reported method in the literature was used for the synthesis of the photoinitiator (Aydin et al., 2003)  $\text{TXOCH}_2\text{COOH}$  as given in Scheme 2.

### 2.4 Esterification reaction of PVA with $\text{TXOCH}_2\text{COOH}$ in the presence and absence of cysteine

A 10% wt. PVA solution was prepared in 0.1 M hydrochloric acid (HCl). In a separate beaker,  $\text{TXOCH}_2\text{COOH}$  and cysteine were dissolved in 0.1 M HCl at the ratios specified in Table 1, with

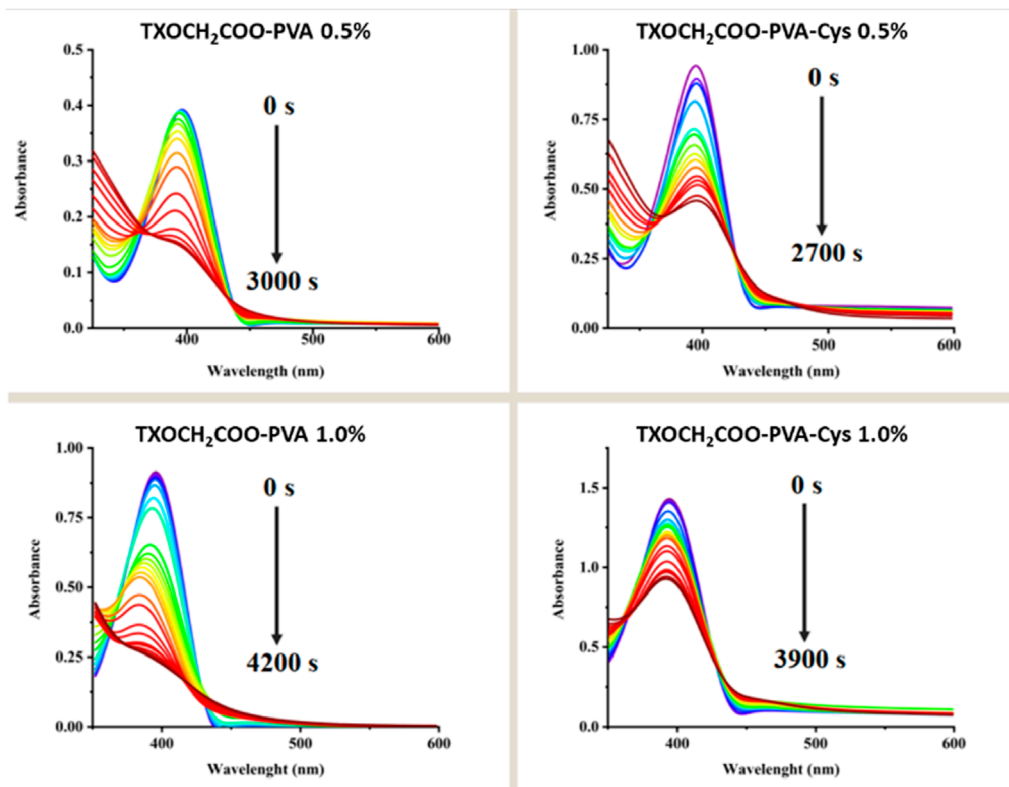


FIGURE 5 Change in UV-Vis spectrum during the photolysis of TXOCH<sub>2</sub>COO-PVA and TXOCH<sub>2</sub>COO-PVA-Cys at different concentrations.

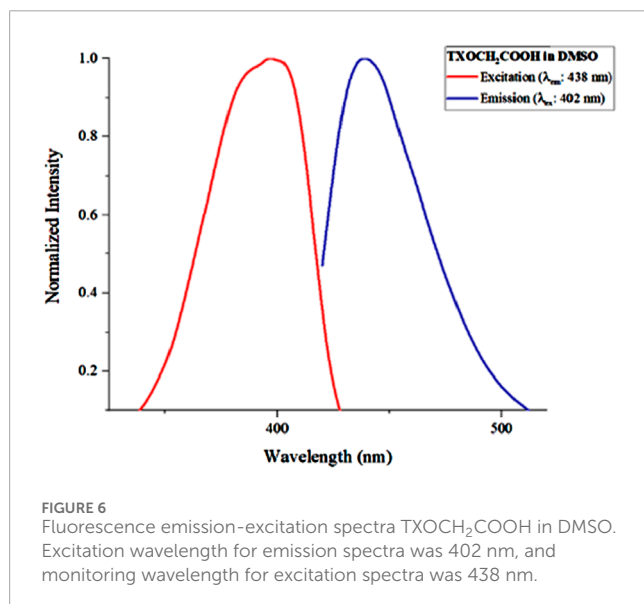


FIGURE 6 Fluorescence emission-excitation spectra TXOCH<sub>2</sub>COOH in DMSO. Excitation wavelength for emission spectra was 402 nm, and monitoring wavelength for excitation spectra was 438 nm.

a volume equal to that of the PVA solution. The two solutions were mixed until a homogeneous mixture was obtained, resulting in a PVA concentration of 5% wt., which was then transferred to a reaction flask. The reaction was carried out under a nitrogen atmosphere for 3 h at 100°C. After the reaction, excess water was

removed using a rotary evaporator. The resulting formulations were poured into a mold, wrapped in foil, and left to dry in a dark cabinet at room temperature.

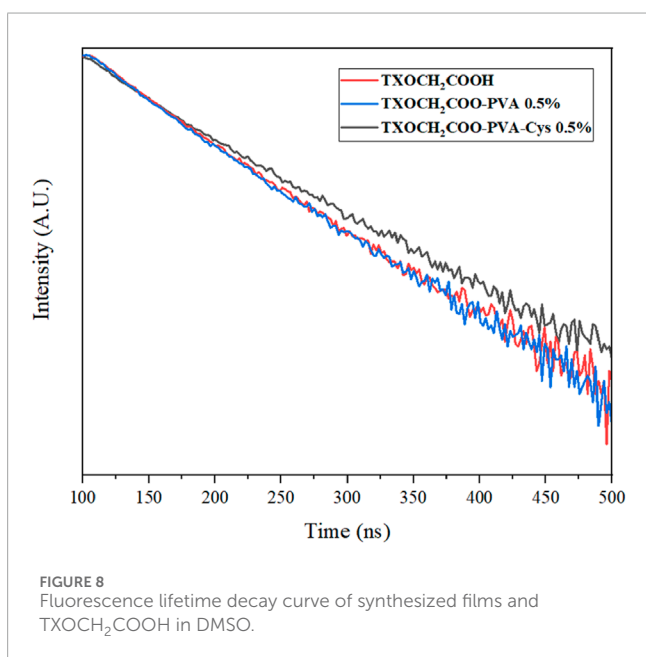
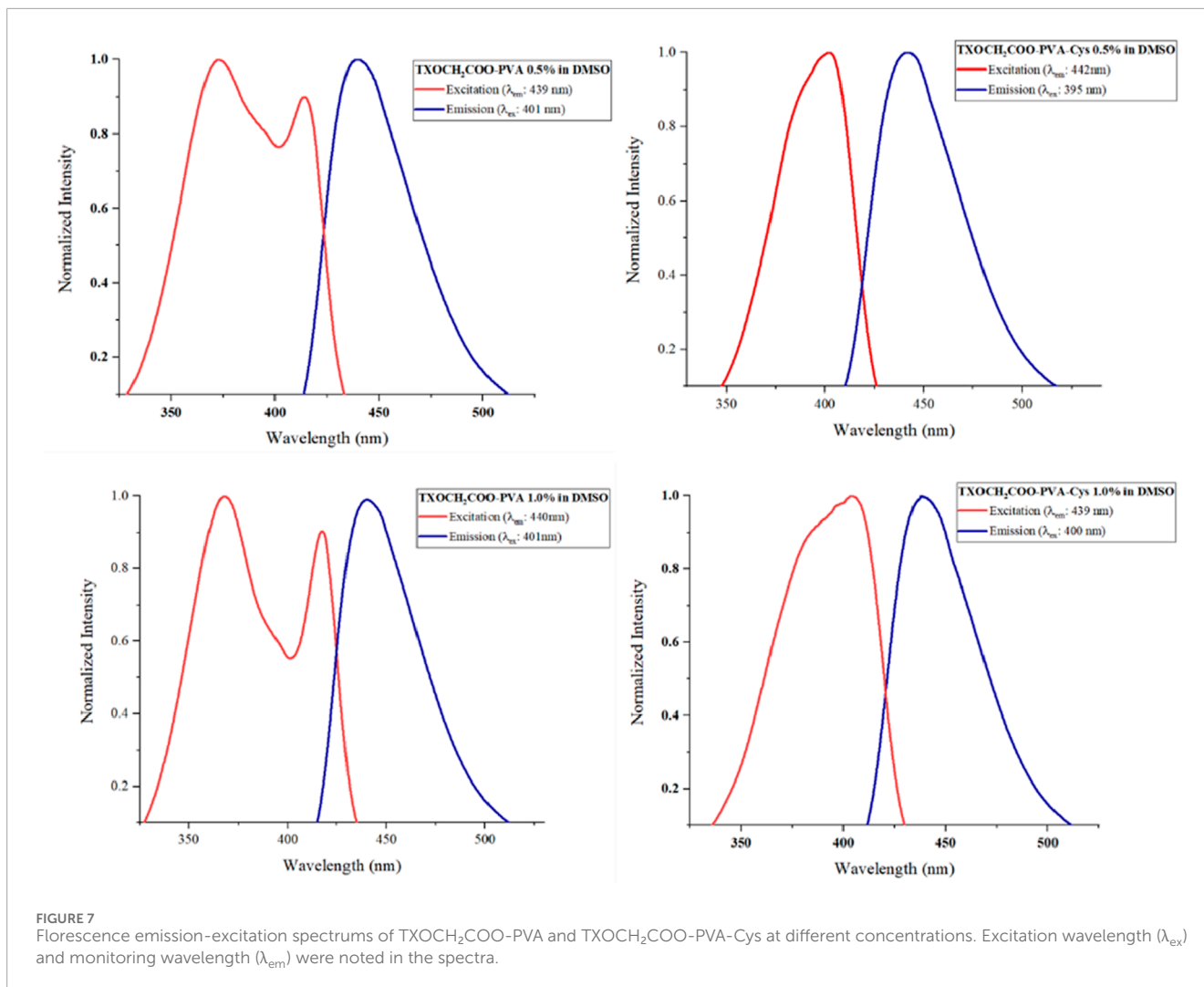
<sup>1</sup>H NMR (400 MHz, DMSO-D<sub>6</sub>, 25°C): δ = 8.47–7.30 (m, aromatic), 4.82 (s, O-CH-O), 2.47 (s, CH<sub>3</sub>-C=O), 1.60–1.28 (m, aliphatic backbone).

## 2.5 *In-situ* photochemical preparation of silver nanoparticles (AgNPs) and selenium nanoparticles (SeNPs)

Each film consisting of TXOCH<sub>2</sub>COO-PVA and TXOCH<sub>2</sub>COO-PVA-Cys was dissolved in pure water, and the corresponding metal salts, such as AgNO<sub>3</sub> and Na<sub>2</sub>SeO<sub>3</sub>·5H<sub>2</sub>O, were added to the formulation at 4% wt. The formulations were irradiated using a medium-pressure mercury lamp for 5–400 s. After irradiation, the formulations were placed in molds and allowed to dry at room temperature. Additionally, a separate formulation containing both metal salts (AgNO<sub>3</sub> and Na<sub>2</sub>SeO<sub>3</sub>·5H<sub>2</sub>O) was also prepared.

## 3 Results and discussion

The esterification reactions are illustrated in Scheme 3. The covalent attachment of the TX group to PVA through



**TABLE 2** Fluorescence lifetimes ( $\tau_1$  and  $\tau_2$ ) of TXOCH<sub>2</sub>COOH, TXOCH<sub>2</sub>COO-PVA, and TXOCH<sub>2</sub>COO-PVA-Cys systems measured at room temperature.

	$\tau_1$	$\tau_2$
TXOCH <sub>2</sub> COOH	3.3065 ns	5.5987 ns
TXOCH <sub>2</sub> COO-PVA	3.3288 ns	5.7485 ns
TXOCH <sub>2</sub> COO-PVA-cys	3.2014 ns	6.4083 ns

an esterification reaction produced a flexible polymeric film, as shown in Figure 1. Interestingly, the covalent linkage of the photoinitiator TXOCH<sub>2</sub>COOH increased the solubility of PVA in water.

The characterization was performed using <sup>1</sup>H-NMR and FT-IR spectroscopy. The <sup>1</sup>H-NMR spectra confirmed the successful esterification reaction between TXOCH<sub>2</sub>COOH and PVA. The spectra of the esterification products, recorded in DMSO-D<sub>6</sub>, displayed characteristic signals for TXOCH<sub>2</sub>COOH and PVA,

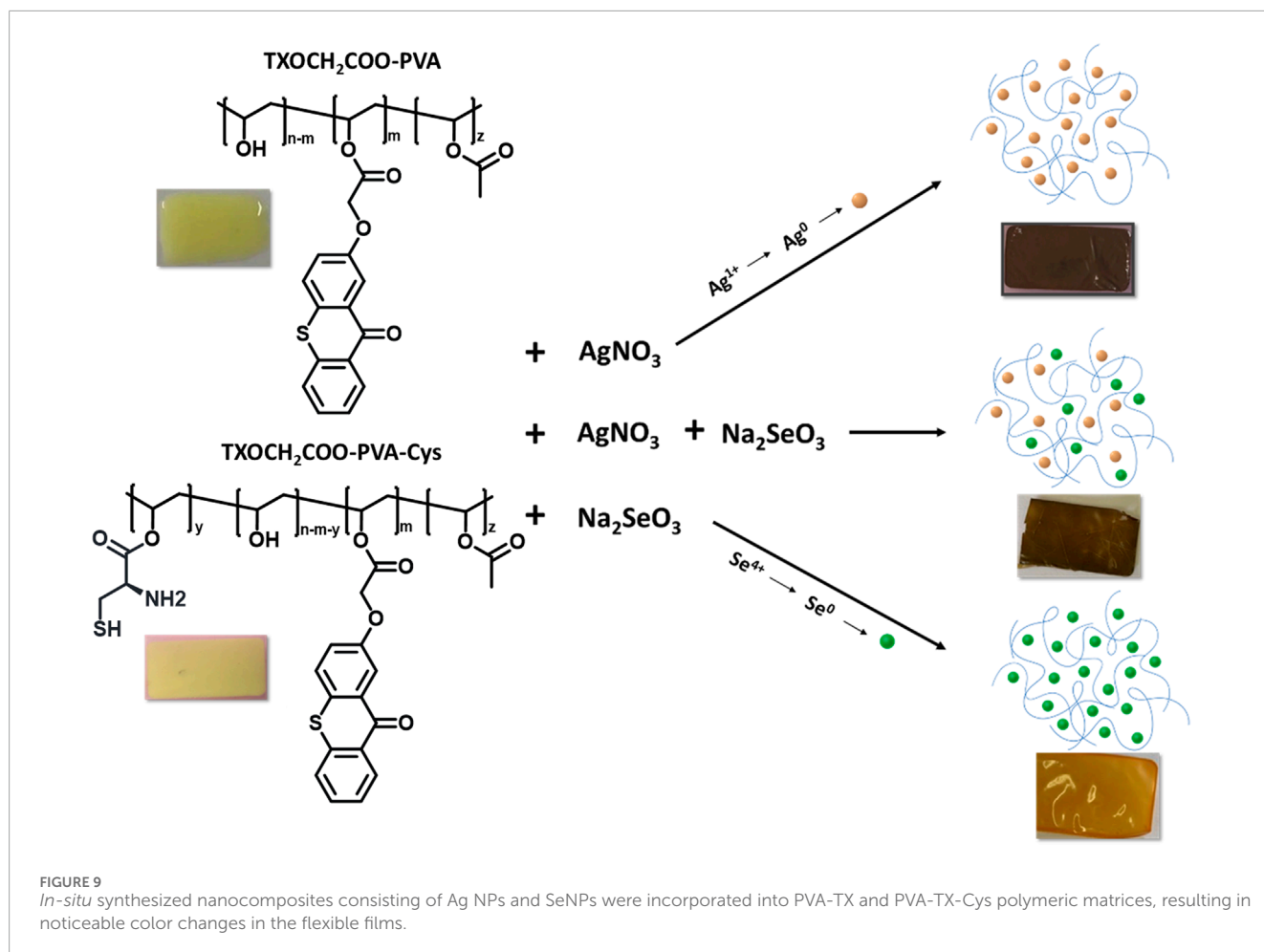


FIGURE 9 *In-situ* synthesized nanocomposites consisting of Ag NPs and SeNPs were incorporated into PVA-TX and PVA-TX-Cys polymeric matrices, resulting in noticeable color changes in the flexible films.

as shown in Figure 2. Aromatic proton signals appeared between 8.47 and 7.30 ppm, with additional signals at 4.82 ppm for the CH<sub>2</sub> group. Aliphatic protons and CH<sub>3</sub> signals from polyvinyl acetate were observed at 2.47 ppm and in the range of 1.60 to 1.28. The H proton of the SH group in cysteine incorporated into PVA was observed at 2.9, and the NH<sub>2</sub> peaks around 2.08 in the NMR spectrum. For the comparison PVA <sup>1</sup>H-NMR spectrum was recorded in deuterium oxide (D<sub>2</sub>O).

The FTIR spectra indicates that all samples obtained from esterification reaction display similar characteristic peaks, as shown in Figure 3. The broad band around 3,400 cm<sup>-1</sup> indicates the presence of hydroxyl (-OH) groups in polyvinyl alcohol (PVA). Peaks around 2,900 cm<sup>-1</sup> correspond to aliphatic C-H stretching vibrations. The strong band near 1700 cm<sup>-1</sup> represents the carbonyl (C=O) stretching vibration resulting from the esterification reaction between thioxanthone (TX) and PVA.

In the spectra of cysteine-containing samples (PVA-TXOCH<sub>2</sub>COO-Cys), a weak band around 2,500 cm<sup>-1</sup> is observed, indicating the presence of the thiol (-SH) group in the cysteine molecule. This observation confirms the successful incorporation of cysteine into the polymer structure.

The films were analyzed for their steady-state and excited-state properties. The steady-state properties of PVA-TX and PVA-TX-Cys were examined using UV-Vis spectroscopy, as shown in Figure 4.

It was observed that the absorption band broadened upon cysteine binding to the PVA-TX.

Photolysis studies of PVA films were carried out to investigate the effect of the covalently bound photoinitiator amount in esterification reactions, using two different initiator concentrations and incorporating the cysteine molecule (see Figure 5).

It was observed that the photolysis of PVA-TX films with higher photoinitiator concentrations required longer time. However, when cysteine molecules were incorporated into the PVA-TX films, the bleaching occurred more rapidly. This finding suggests that reactive thiyl radicals may be generated through hydrogen abstraction from the -SH group of cysteine by TX. These results indicate that both photoinitiator concentration and the covalent attachment of cysteine play a significant role in influencing the photolysis kinetics.

The fluorescence emission spectra of TXOCH<sub>2</sub>COOH, TXOCH<sub>2</sub>COO-PVA and TXOCH<sub>2</sub>COO-PVA-Cys films were recorded after dissolving the films in DMSO and exciting them at 390 nm. The excitation and emission spectra are shown in Figures 6, 7. All emissions from the films closely resembled those of the TX photoinitiator.

Figure 7 displays the fluorescence spectra of TXOCH<sub>2</sub>COOH in DMSO, showing an excitation band at 400 nm and an emission band at 438 nm.

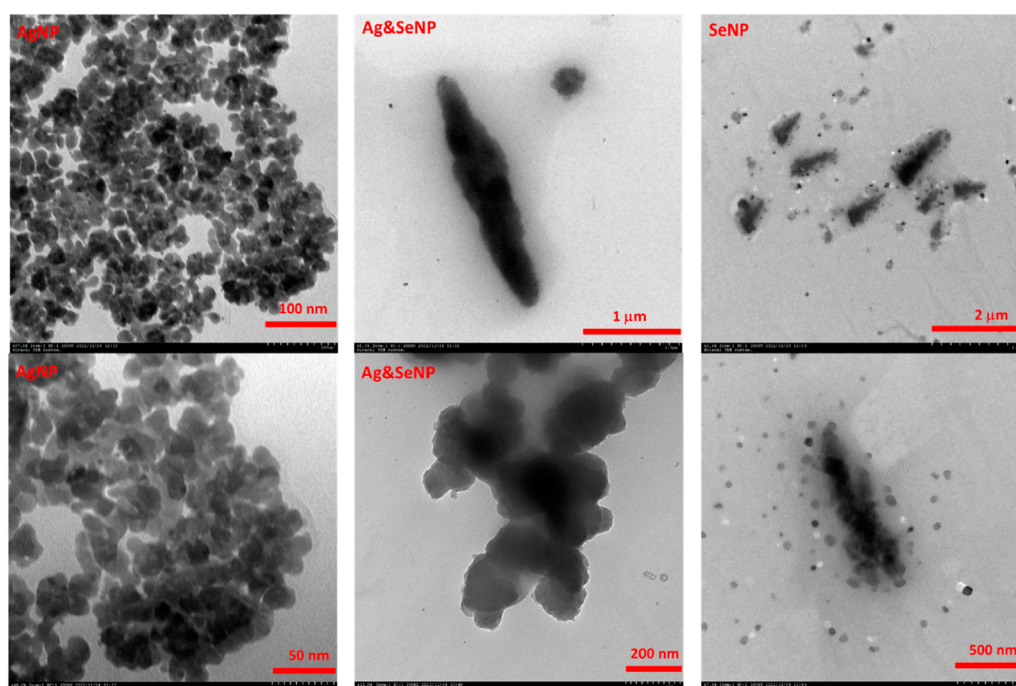


FIGURE 10  
TEM images of Ag and Se nanoparticles.

The presence of cysteine did not notably alter the spectral properties. These results suggest that the fluorescence properties of PVA films are primarily governed by the TX-based photoinitiators, with cysteine molecules having a minimal effect on these properties.

Fluorescence lifetime refers to the duration of a molecule spends transitioning from the excited state to the ground state. The fluorescence lifetimes of TXOCH<sub>2</sub>COOH, TXOCH<sub>2</sub>COO-PVA and TXOCH<sub>2</sub>COO-PVA-Cys were compared and analyzed, as shown in (Figure 8). The polymers and photoinitiators were dissolved in DMSO and placed in a quartz cell with a 1 mm optical path length for lifetime measurements. The excitation wavelength was set to 402 nm, and the monitored wavelength for luminescence was 440 nm.  $\tau_1$ , the shorter lifetime about 3.3 ns observed for nearly all molecules, including the bare compound TXOCH<sub>2</sub>COOH, likely represents the molecule's primary excited state.  $\tau_2$ , the longer duration, may suggest presence of different luminescence conditions of photoinitiators by interacting with surrounding molecules such as DMSO molecule or polymer. Indeed, PVA-TXOCH<sub>2</sub>COOH-Cys exhibited a slightly longer lifetime than other samples. The prolonged excited lifetime of the photoinitiator may enable promotion of intersystem crossing to a triplet state and interactions with nearby molecules (see Table 2).

### 3.1 The *in-situ* photochemical synthesis of silver nanoparticles (AgNPs) and selenium nanoparticles (SeNPs)

Nanocomposite thin films containing either silver nanoparticles (AgNPs), selenium nanoparticles (SeNPs), or both were synthesized using an *in-situ* photochemical method, as illustrated in Figure 9.

TXOCH<sub>2</sub>COO-PVA and TXOCH<sub>2</sub>COO-PVA-Cys were utilized as one-component macromolecular photoinitiators. They were dissolved in water, and ionic salts were added to the formulations before being irradiated by a medium-pressure mercury lamp for 200–300 s. As described in the experimental section, the color change of the cured formulations was observed, offering a visual method to confirm the formation of nanoparticles within the PVA polymer, as shown in Figure 9. The mechanism behind the *in-situ* formed nanocomposites likely involves intramolecular hydrogen abstraction, resulting in the formation of ketyl radicals that act as photoreducing agents for ionic species such as silver and selenium salts. In the case of TXOCH<sub>2</sub>COO-PVA-Cys, the excited state of TX abstracts hydrogen from the thiol group of cysteine, resulting in the formation of thiyl radicals. Both thiyl and ketyl radicals are essential in reducing ionic species, facilitating the nucleation and growth of nanoparticles. Transmission electron microscopy (TEM) was employed to analyze the morphology and size distribution of silver (Ag) and selenium (Se) nanoparticles within PVA-based polymeric films. The polymeric films were dissolved in ethanol, and the nanoparticles were isolated from the polymer matrix through centrifugation. After drying, the separated nanoparticles were placed on a TEM grid for imaging.

TEM images of the synthesized Ag and Se nanoparticles are shown in Figure 10. The images indicate that silver nanoparticles have a spherical morphology, whereas selenium nanoparticles display a needle-like shape. The average size of the Ag nanoparticles is approximately 10–15 nm, while the Se nanoparticles measure around 20–25 nm.



## 4 Conclusion

In this study, polyvinyl alcohol (PVA), an environmentally friendly polymer, was esterified using 2-(Carboxymethoxy) thioxanthone and cysteine as a single-component secondary photoinitiator. The photophysical properties of the PVA-TX and PVA-TX-Cys films were investigated after their preparation, focusing on UV-Vis absorption, fluorescence emission spectra, and fluorescence lifetimes. Furthermore, PVA nanocomposites embedded with silver and selenium nanoparticles were synthesized via the *in-situ* photoreduction of silver and selenium salts in an aqueous medium, followed by their nucleation and growth. The findings indicate that the synthesized polymeric films hold potential as promising materials for optical, electronic, and biomedical applications. Future studies could aim to further optimize their properties and evaluate their performance in specific applications.

## Data availability statement

The original contributions presented in the study are included in the article/Supplementary Material, further inquiries can be directed to the corresponding author.

## Author contributions

MK: Investigation, Methodology, Validation, Visualization, Writing–review and editing, Data curation, Formal Analysis. KN: Investigation, Methodology, Validation, Supervision, Writing–review and editing. NA: Investigation, Methodology, Supervision, Validation, Writing–review and editing, Conceptualization, Visualization, Writing–original draft.

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## Conflict of interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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## Supplementary material

The Supplementary Material for this article can be found online at: <https://www.frontiersin.org/articles/10.3389/fmats.2025.1544162/full#supplementary-material>

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