Gold Nanorods Grant an ON-OFF Control over the Kinetics of the Z-E

Isomerization of Azobenzene-Based Photoswitch via Thermoplasmonic Effect

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Abstract

Proper formulation of systems containing plasmonic and photochromic units, such as gold nanoparticles and azobenzene derivatives, yields materials and interfaces with synergic functionalities. Moreover, gold nanoparticles are known to accelerate the Z-E isomerization of azobenzene molecules in the dark. However, very little is known about the light-driven, plasmonassisted Z-E isomerization of azobenzene compounds. Additionally, most of the azobenzene-gold hybrids are prepared with nanoparticles of small, isotropic shapes and azobenzene ligands covalently linked to the surface of nanostructures. Herein, a formulation of a novel system combining azobenzene derivative, gold nanorods, and cellulose nanofibers is proposed. The system's structural integrity relies on electrostatic interactions among components instead of covalent linkage. Cellulose, a robust scaffold, maintains the material's functionality in water and enables monitoring of the material's plasmonic-photochromic properties upon irradiation and at elevated temperatures without gold nanorods' aggregation. Experimental evidence supported by statistical analysis suggests that the optical properties of plasmonic nanometal enable indirect control over the Z-E isomerization of the photochromic component with near-infrared irradiation by triggering the thermoplasmonic effect. The proposed hybrid material's dual plasmonicphotochromic functionality, versatility, and ease of processing render a convenient starting point for further advanced azobenzene-related research and 3D printing of macroscopic light-responsive structures.

Introduction

The isomerization of azobenzene and its derivatives (Azo) has remained topical since the 1930s.^[1] The number of potential advanced applications of azobenzene photoswitches^[2] is still growing,^[3] ranging from molecular electronics,^[4] through light-controlled catalysis,^[5] and photoactuators,^[6] to chemical biology^[7,8] and beyond.^[9] Such a dynamic advancement demands constant development of individual Azo photoswitches and systems utilizing them. Pivotal examples of current challenges are synthesis of new Azo molecules, proper harnessing of the collective activity of molecular photoswitches,^[10–12] and control over Azo properties by other adjacent chemical species.^[13–15]

For many years, gold has been used as one of the best substrates to deposit azobenzenes onto due to its high affinity towards amine- and thiol-terminated molecules.^[16,17] Research attention was focused on Azo self-assembled monolayers (SAMs) - initially on planar, macroscopic gold surfaces^[18–22] and subsequently on positively curved surfaces, such as gold nanoparticles (AuNPs).^[23-29] Current research is mainly devoted to hybrids formed via covalent linkage between the photochromic unit and nanoplasmonic core (Azo-AuNPs), and substantial emphasis is put on the investigation of the Light-Induced Self-Assembly (LISA) phenomenon.^[15,24,26-28] However, preparing chemically linked Azo-AuNPs hybrids is usually limited to small, spherical nanostructures^[23,24,30] that exhibit limited light-harvesting capability and spectrally overlap with the profile of the photochrome. This greatly limited exploration of possible plasmon-assisted Azo isomerization, leaving this aspect virtually unexplored. Additionally, the properties of Azo-AuNPs hybrids are mainly investigated in organic solvents,^[31,32] yet water-functional plasmonicphotochromic systems could be beneficial for biological and medical applications.^[33] Furthermore, the uncontrolled Brownian motion of Azo-AuNPs hybrids and their light-induced aggregation, although advantageous for, e.g. preparation of self-erasing media, constitute important limitations in the fields relying on stable plasmonic properties. These limitations can be overcome by exploring novel composite formulations and applying new chemical components that are able to stabilize the initial constituents. Hence, systems utilizing poly(vinyl alcohol),^[34] polydopamine,^[35,36] carbon nanotubes,^[37] or even DNA^[38] serving as a matrix or scaffold for both AuNPs and Azo have emerged in recent years. We perceive that the introduction of a third, inert component can render new plasmonic-photochromic systems incorporating entirely new classes of Azo molecules and bigger nanoplasmonic cores of anisotropic geometries. As a result, this approach can give rise to new, previously unattainable experimental scenarios and possibilities.

New Azo-AuNPs formulations certainly contribute to the ongoing research on the modulation of Azo isomerization. Expansion of the Azo excitation wavelengths into the red or near-infrared (NIR) range^[13,14,39] or modification of the Z-isomers lifetimes^[40,41] are valuable for neuronal activity control^[42] and photopharmacology.^[43] These goals can be achieved not only by synthetic modification of the chemical structures of Azo molecules^[44–49] but also by alternative strategies (often called indirect modifications) relying on electron transfer^[13,50–53] or intra- and intermolecular energy transfer.^[54–67] Alternative approaches are especially useful and appealing for advanced, multi-component, Azo-based systems. The alternative pathways modify and broaden the properties of the already existing Azo molecules beyond their intrinsic limitations and simultaneously maintain their profitable features, such as robustness.^[13,65]

For a long time, AuNPs have been scarcely mentioned in the context of indirect modification of azobenzene photoswitching and, if so, only as multiphoton sensititzers.^[68] Recently, however, AuNPs have been recognized^[51,53] as factors modulating Azo Z-E isomerization in the dark (socalled thermal relaxation), presumably via electron transfer (eT), as proposed for the first time by Hallett-Tapley et al.,^[69] and further supported in the ensuing research.^[70-72] However, these reports focused solely on the catalytic influence of spherical AuNPs on Azo isomerization in the dark. Shape-limitation of plasmonic cores is understandable due to the possible aggregation of bigger and anisotropic nanostructures in the presence of Azo, especially in organic solvents. Nonetheless, by using small, isotropic nanoparticles exhibiting limited light-harvesting properties, studies were restricted to the exclusive investigation of Azo's dark (thermal) Z-E isomerization. Both intraband transitions and Localized Surface Plasmon Resonance (LSPR) bands of spherical AuNPs are in tooclose proximity to the absorption maxima of the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions of Azo compounds. As a result, plasmon contributions cannot be properly isolated, and the investigation of the light-driven isomerization of such binary systems is complicated. Hence, the knowledge about plasmon-assisted isomerization of Azo is very scarce. Yet, plasmonic nanostructures are a source of powerful lightinduced catalytic tools^[73,74] such as heat,^[75] electric field enhancement,^[76] and hot (i.e. highly energetic) carriers.^[77] It can be hypothesized that these phenomena could be potentially used to indirectly control Azo isomerization, both *E-Z* and *Z-E* reactions, affecting their mechanisms and kinetics.

Here, we introduce a novel, water-functional and light-addressable macroscopic plasmonicphotochromic material (Figure 1). The proposed novel formulation exhibits plasmon-assisted Z-E isomerization of Azo. The control over the kinetics of the photochromic reaction is granted via the thermoplasmonic effect triggered in gold nanorods (AuNRs). Our work is at the intersection of materials science, photochemistry, and thermoplasmonics and constitutes a five-fold contribution. First, we propose a formulation based on cellulose nanofibers (CNFs) as a versatile scaffold for the facile non-covalent binding of AuNRs and chosen Azo molecule (AzoGly). The resulting hybrid material exhibited stable plasmonic and photochromic properties and structural integrity in water under elevated temperatures and UV-Vis-NIR irradiation. Second, we provide new insight into the acceleration of the Z-E Azo isomerization in the dark by using, for the first time, gold nanorods in the process. Our results contribute to the discussion regarding the eT mechanism of the reaction.^{[69–} ^{72]} Third, we show the indirect modulation of AzoGly photoswitching by performing plasmonassisted Z-E isomerization (Figure 1). We subjected our composite in its Z-rich photostationary state (PSS_Z) to red light and NIR irradiation (650-1100 nm, continuous waves, no overlapping with the AzoGly spectral profile), thus triggering solely thermoplasmonic effect. The resulting temperature rise affected the Z-isomer's stability and modulated the Z-E isomerization kinetics. Fourth, we propose means to quantify the extent of the thermoplasmonic effect by monitoring kinetic changes in the Z-E isomerization of Azo. Hence, we present prospects for Azo molecules as molecular thermometers. Finally, through advanced statistical modelling of the kinetic data, we confirm the major contribution of the thermoplasmonic effect upon irradiation and the instantaneous, ON-OFF control it grants over Azo Z-E isomerization. Hence, we also suggest the application of the Autoregressive Integrated Moving Average (ARIMA)^[78] statistical model in the analysis of photochemical phenomena.



Figure 1. Cellulose nanofibers provide support for the plasmonic (gold nanorod, AuNR) and photochromic (azobenzene derivative, Azo) units in a functional hybrid material, preventing aggregation of components. In the dark, AuNRs catalyze Azo Z-E isomerization via electron transfer. Under light conditions not accessed by photochrome (NIR spectral range), AuNRs convert absorbed energy into heat, resulting in a faster Azo Z-E isomerization and granting an instantaneous ON-OFF control over the photochromic reaction in the hybrid material, as revealed upon statistical modelling of kinetic data.

Results and discussion

To investigate plasmon-assisted isomerization of azobenzene derivative, we designed a new formulation containing photochromic (azobenzene modified with glycine – AzoGly, see Scheme S1 and Figure S3) and plasmonic (gold nanorods, AuNRs, labelled as Au-1 and Au-2, depending on the size of the plasmonic core, see Figure S4 and Figure S5) components. We used TEMPO (2,2,6,6-tetramethylpiperidinyl-1-oxyl) oxidized cellulose nanofibers (CNFs) as a scaffold to preserve the intrinsic properties of both functional units and ensure their compatibility and co-

functionality in water. In the first step, we prepared **pre-composite material** by relying on electrostatic attraction between AuNRs and CNFs.^[79–85] Nanoparticles, stabilized by a positively charged bilayer of surfactant (cetyltrimethylammonium bromide, CTAB, containing $-N(CH_3)_3^+$ head group, **Figure 2a** – stage I), were uniformly immobilized on a cellulose scaffold rich in carboxyl groups, $-COO^-$ (Figure 2a – stage II). The adsorption of CTAB (as micelles or AuNRs bilayer) on cellulose lowered the hydrophilicity of the fibers^[79,86,87] and resulted in the sedimentation of the Au-decorated CNFs. We obtained the pre-composite as a phase-separated system (Figure 2b, top) convenient for further processing via centrifugation.

Since AzoGly is water-insoluble (see **Figure S6** and solubility discussion in Section 1.3. of the SI), separated pre-composite was transferred to ethanol (EtOH), a native solvent of AzoGly, to incorporate photochromic molecules in the final formulation (Figure 2a – stage III and Figure 2b). Upon transfer, **Au-CNFs** formed a clear dispersion in organic solvent (Figure 2b, bottom). The critical micelle concentration of CTAB in EtOH is over 250 times higher compared to water. Hence, the disintegration of CTAB structures on Au and CNFs surfaces occurred. Typically, the destruction of the surfactant shell upon nanoparticles' transfer to EtOH causes their immediate aggregation. However, here, cellulose scaffold replaced, to some extent, CTAB bilayer in its protective role and ensured the stability of AuNRs, preserving the material's structural integrity (Figure 2b) and optical properties (Figure 2c). Once Au nanocrystals' surface is free from the insulating CTAB shell, nanoparticles become more accessible to physical and chemical processes. Thus, our approach enables precise optical addressing of the plasmon-related phenomena in the resulting material. The proposed method of AuNRs stabilization in EtOH does not depend on the size or shape of AuNPs and is easy to replicate.



Figure 2. Preparation of Au-CNFs pre-composite. **a)** Schematic representation of the underlying interactions between components. **b)** TEM images of Au-1-CNFs in water and ethanol present the material's structural integrity and its ability to form self-standing films upon drying. Insets: digital images of the samples showing differences in the physical appearance of the pre-composite before and after transfer to ethanol (EtOH). **c)** UV-Vis-NIR extinction spectra of the Au-CNFs pre-composite in water and EtOH. Colour codes between panels b) and c) are matching.

The as-prepared **Au-CNFs** pre-composite served as a platform for further impregnation with the photochromic dye of choice. We used a model photochrome, AzoGly (Figure S3), in the form of salt to promote interactions between its protonated end group, $-NH_3^+$, and $-COO^-$ groups of CNFs (**Figure 3a** – stage IV). Due to the solvent transfer, well-dispersed Au-decorated CNFs were accessible for dye sorption during an overnight incubation step (Figure 3a). CNFs are rich in $-COO^-$ groups and, hence, trifluoroacetate counterion (TFA⁻) of azobenzene salt does not remain in the composite. We rationally assume that TFA⁻ is entirely removed during the purification step. The resulting plasmonic-photochromic material (Figure 3b) was transferred to water, and the presence of the photochromic unit in the final formulation was confirmed using IR spectroscopy (Figure 3c).

Upon designing the protocol, we had two main hypotheses regarding formulation of the final hybrid material. We relied on the comparative IR spectra analysis to test them (Figure 3b-c, **Figure S7**, and **Table S1**).

The first hypothesis assumes a crucial role of intermolecular interactions (electrostatic attraction and hydrogen bonds formation, Figure 3b) between AzoGly and CNFs. The observed 6-10 cm⁻¹ coherent spectral shifts of crucial IR bands corroborate this hypothesis. A peak appearing at 2924 cm⁻¹ for AzoGly (-N - H stretching of $-NH_3^+$ end group, grey highlight) is shifted to 2918 cm⁻¹ in AzoGly-Au-2-CNFs. Simultaneously, a similar change occurs in the position of the symmetrical vibration band of $-COO^-$ group of CNFs (vivid green highlight). The original peak appearing at 1429 cm⁻¹ in Au-2-CNFs shifts to 1419 cm⁻¹ in the final material.

The second hypothesis concerns the role of CTAB as a molecular glue. CTAB mediates **Au-CNFs** interactions starting from the pre-composite formation. The C - H symmetric stretching band of $-CH_2$ – group (blush highlight) is indicative of CTAB presence when comparing CNFs (no CTAB, no peak) and pre-composite (CTAB present, peak at 2858 cm⁻¹). In the final formulation $-CH_2$ – group is present due to both CTAB and AzoGly and hence, another band needed to be selected for surfactant identification. We analyzed the evolution of $-CH_3$ band of ammonium salt appearing in the final material at 1456 cm⁻¹ (vivid red highlight) and the appearance of $-C - N^+$ stretching band at 906 cm⁻¹ (very weak shoulder of the β -glycosidic band) instead. Their presence (particularly clear for the 1456 cm⁻¹ band – see **Figure S8**) indicates that the **AzoGly-Au-2-CNFs** composite contains residual CTAB molecules. Albeit a thorough washing process (see **Materials and methods** section in the SI) excludes free surfactant molecules in bulk solution, it is reasonable to assume that CTAB molecules remain intercalated in the **CTAB-CNFs** system. The surfactant remains either (1) solely on the surface of CNFs or (2) as a residual bilayer with lower integrity, mediating **Au-CNFs** interactions (Figure 3b). Thus, CTAB serves as molecular glue in the plasmonic-photochromic formulation and further supports the interactions between Au nanocrystals and cellulose nanofibers.

Finally, identification of other peaks in the AzoGly-Au-2-CNFs sample (Table S1) confirmed the material's structural integrity. The following bands support the presence of all crucial components: C - C cellulose ring stretching at 1161 cm⁻¹, C - O - C cellulose pyranose ring stretching centred at 1059 cm⁻¹, and C - O - C cellulose β -glycosidic linkages at 905 cm⁻¹ (all marked with pale yellow colour), as well as AzoGly bands occurring as a part of the broad 1653 cm⁻¹ peak, namely -C = O amide signal (marked with vivid green), C = C (in plane, bright yellow), and N = N (pale purple). These results are pivotal and emphasize the strength and importance of intermolecular electrostatic interactions in the design of advanced materials (Figure 3b).

Over the years, several examples of cellulose impregnation with dyes (including photochromes) have been presented. Liu *et al.* adsorbed negatively charged stilbene derivative on cellulose using a divalent cation, Ca^{2+,[88]} Iamazaki and Atvars facilitated the sorption of Tinopal CBS on cellulose fibers using surfactants.^[89,90] Araki showed that sorption of cationic dyes on cellulose is so efficient it can be used as a quantitative analytical method for assessing the number of cellulose surface groups.^[91] Our strategy for preparing a functional plasmonic-photochromic composite via the use of CNFs was developed independently, yet it corresponds very well with the literature examples. In our case, Au nanocrystals do not mediate **AzoGly-CNFs** interactions, as we proved in control experiments with bare cellulose nanofibers (**Figure S9**). Bare CNFs, upon impregnation with AzoGly, yielded composites exhibiting distinct photochromic bands, indicating high efficiency of dye adsorption on the fibers (Figure S9). In principle, the higher the concentration of AzoGly upon impregnation, the better the photochromic properties of the resulting composite. The increase of ~3.8 times in dye concentration gave ~26 times higher intensity of the $\pi \rightarrow \pi^*$ band (based on the corrected values in Figure S9b, comparison between concentrations of AzoGly.

In our protocol, most of the Au surface is cleared from the CTAB bilayer and thus becomes accessible for potential Au-S interactions. To further investigate whether our approach can be adapted to mimic the most popular designs of Azo-Au hybrid structures and materials,^[24,92,93] we

substituted AzoGly with thiolated THF-soluble AzoSH (Figure S10a) and EtOH-soluble AzoSS (Figure S10b). Such or similar molecules have already been used to form SAMs on the surface of planar^[94] or nano^[23] Au. Nevertheless, the applied Azo change did not grant the desired synergy of components and compromised material properties (Figure S11a and Figure 3d). Due to the heavy aggregation of the resulting composites (see Section 3.3. of SI), the as-prepared materials did not exhibit plasmonic or photochromic properties. Hydrophobic AzoSH and AzoSS prevent hybrids from dispersing in water, which causes aggregation, whereas more polar, protonated AzoGly forms with Au-CNFs entirely water-functional plasmonic-photochromic material. Hence, our protocol constitutes an important contribution to the already existing knowledge.

Transfer of water-insoluble photochrome to the aqueous environment results in its aggregation, as presented by Sun and co-workers, who used nanocrystalline cellulose as a platform for hydrophobic spirooxazine derivative.^[95] Our material does not contain any clumps of Azo, as confirmed by TEM (Figure 3e). Our protocol enables uniform impregnation of nanofibers and assures homogenous nature of the hybrid material. CNFs ensure system's stability, and the as-prepared AzoGly-Au-2-**CNFs** composite maintains its dual plasmonic-photochromic functionality. The presence of both functional units is distinctly visible on the UV-Vis-NIR absorption spectra (Figure 3f). The intensities of the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ photochromic bands in a solvent in which AzoGly is not soluble clearly confirm the success of the proposed material design in transferring Azo properties to the new environment. We attribute small differences in their positions and profiles compared with pristine AzoGly (Figure S3) to the solvent change^[96,97] and interactions with CNFs.^[95] Plasmonic bands of Au-2 (transverse, t-LSPR and longitudinal, l-LSPR) are distinct, well separated, and not distorted. Slight spectral shifts (3 nm blueshift for t-LSPR and 18 nm redshift for 1-LSPR, Figure S12) are observed. We attribute this to the change in the effective refractive index due to the CTAB exchange at the surface, especially at the AuNRs' tips.^[98] In our case, CTAB is replaced by CNFs. In principle, we distinguish three different spectral regions of the sample as marked on top of Figure 3f. First (1) covers the $\pi \rightarrow \pi^*$ and part of the $n \rightarrow \pi^*$ band of AzoGly. This spectral region can

be used to directly trigger photoisomerization of the photochromic component. Second (2) corresponds with partially overlapping Azo $n \rightarrow \pi^*$ band and t-LSPR band of Au-2. AzoGly undergoes *Z*-*E* isomerization when irradiated in close proximity to the $n \rightarrow \pi^*$ band, e.g. 500-600 nm (**Figure S13**). This precludes us from further use of region (2) in the plasmon-assisted experiments. Otherwise, it would be impossible to assess which phenomenon (direct Azo isomerization or plasmon-related effects) is responsible for the potential photocontrol of the occurring reaction. Hence, the third region (3), covering the position of the 1-LPSR band of Au-2, is the most suitable to trigger plasmon-derived effects and gain potential indirect control over Azo isomerization. The 1-LSPR band of AuNRs typically appears in region (3), is more suitable for light harvesting,^[99] and its position can be precisely tuned during synthesis. It is also spectrally well-separated from Azo bands as presented for AzoGly-Au-2-CNFs. In summary, our approach enables efficient preparation of stable, hybrid materials with well-defined optical characteristics and maintained plasmonic and photochromic features. Beneficial spectral separation of the optical properties of Azo and AuNRs can be used to potentially perform plasmon-assisted isomerization of the photochrome.



Figure 3. AzoGly-Au-2-CNFs – hybrid plasmonic-photochromic fibers. **a)** Impregnation process and schematic depiction of the AzoGly-CNFs interactions within the material's structure. **b)** Proposed chemical structure with a visual indication of the underlying interactions. Colour codes match highlights on the IR spectra to facilitate the analysis. **c)** IR spectra reveal the role of the underlying electrostatic interactions and hydrogen bonds in providing material's structural integrity. **d)** Typical sulphur-containing ligands exhibit worse affinity to Au-CNFs framework compared to AzoGly. The resulting materials aggregate, and their photochromic and plasmonic properties are compromised. **e)** TEM image of the AzoGly-Au-2-CNFs sample, indicating a homogenous distribution of components. **f)** UV-Vis-NIR spectrum of the hybrid sample, showing three spectral regions for potential use for (1) direct photoisomerization of the Azo component, (2) simultaneous triggering of the photoisomerization and plasmon-related effects (not used in this paper), (3) exclusive triggering of the plasmon-derived effects and gaining potential indirect photocontrol over Azo isomerization.

The main functionalities of any Azo-containing material are its photoswitchability, photo-, and thermostability (**Figure 4**). Hence, to describe the photochromic behaviour, we subjected AzoGly-Au-2-CNFs hybrid sample to the alternate induction of the *E*-*Z* and *Z*-*E* isomerization of the photochromic component (Figure 4a, left). The drop of the $\pi \rightarrow \pi^*$ band upon UV (365 nm) irradiation and its rise upon irradiation at 436 nm (**Figure S14**) indicate the occurrence of *E*-*Z* and *Z*-*E* isomerizations, respectively (Figure 4a, right). The observed changes are coherent with photoswitching of pristine AzoGly (Figure S3) and AzoGly-CNFs control sample (**Figure S15c,d**). We also observed a slight, reversible shift of 2 nm in the position of the Au-2 1-LSPR band without any significant distortions or damping (Figure 4a). This is a key difference between our material and other literature Azo-plasmonic hybrids, where *E*-*Z* isomerization causes nanoparticles aggregation. As a result, hybrids exhibit weakened or even none of the initial plasmonic properties. In the case of our design, due to the macroscopic size of CNFs, the collective molecular motion of

AzoGly with respect to the plane of the N = N band is not causative enough to result in aggregation or global changes in the material's 3D structure. Hence, the optical properties of plasmonic cores are preserved and can be potentially used to induce plasmon-assisted phenomena.

We clearly see the catalytic effect of Au nanoparticles by comparing rate constants of the isomerization reactions occurring in hybrid material with (Au-2) and without Au (no Au). Analysis of the extinction changes at the maximum of the $\pi \rightarrow \pi^*$ band plotted as a function of time reveals that both reactions obey first-order kinetics (Figure S15), just as free Azo molecules in solution. *E-Z* and *Z-E* AzoGly isomerization reactions are enhanced by 52.2% and 48.6%, respectively in the presence of gold (Figure 4b and Figure S15). These changes reflect the catalytic influence of AuNRs on directly photoinduced Azo isomerization. We suppose that the catalytic boost occurs via the electron transfer (eT) mechanism, as it has been proposed for Azo photoswitching in the dark in the presence of Au nanospheres.^[69] We hypothesize that eT is triggered by UV irradiation addressing interband transitions of AuNRs, which gives rise to the generation of highly energetic carriers. Transfer of those carriers to Azo molecules is reflected in the observed coherent changes of the l-LSPR position upon simultaneously occurring photoisomerization.^[100–102]

Both types of hybrid materials (with and without Au) exhibit stable photoswitchability upon interval UV (3 min) and Vis (3 min) irradiation (Figure 4c). Both isomerizations can be induced and repeated in the materials over many cycles. The intensity of the $\pi \rightarrow \pi^*$ band in both photostationary states remains stable over the course of the experiment. This proves that the degradation of photochromic component or material does not occur.

Azobenzenes, being T-type photochromes, exhibit temperature-dependent *Z*-*E* isomerization in the dark. We measured thermal back-isomerizations of AzoGly component at several temperatures to assess kinetic and thermodynamic differences between the stability of the *Z*-isomer in materials with and without Au. Samples were first irradiated with UV (to reach PSS_{*Z*}), and then, their return at a specific temperature in the dark to the *E*-rich PSS (Figure 4d) was monitored by measuring changes in the extinction of the $\pi \rightarrow \pi^*$ AzoGly band as a function of time. Collected data confirm

the first-order kinetics of the process (**Figure S16**). Our results indicate an increased reaction rate with increasing temperature regardless of the presence of Au (Figure 4e). We determined the set of kinetic and thermodynamic parameters of the ongoing reaction (**Table S2** and **Figure S17**) by employing Arrhenius (**Equation S2**) and Eyring (**Equation S3**) equations. We observed that the activation energy of the Au-containing sample, (69.9 ± 4.2) kJ mol⁻¹, is about 30 kJ mol⁻¹ lower than for the control sample without gold, (99.8 ± 12.5) kJ mol⁻¹ (Table S2). A lower activation barrier for the thermal *Z-E* isomerization of Azo in the presence of gold proves the catalytic role of AuNRs in the dark. This catalytic boost is also visualized on the thermal relaxation profiles. Sample with **Au-2** plasmonic core reaches a plateau at the same temperature faster than composite without Au. However, the catalytic influence of nanoparticles decreases with increasing temperature (Figure 4e).

Previous works postulated that AuNPs catalyze Azo *Z-E* isomerization in the dark via electron transfer.^[69,70,72] As presented by Mulvaney and coworkers, ^[102] electron transfer from AuNRs can be confirmed by redshift of the 1-LSPR band. Indeed, we observed such spectral change (ca. 1.8 nm) upon Azo isomerization in the dark (**Figure S18**). Hence, our results indicate the eT mechanism, although there are three general differences between our and former contributions. Firstly, by immobilizing Azo and AuNPs on CNFs, we limited their Brownian motions in contrast to free components in solution. Secondly, AuNPs are present upon UV irradiation before PSS_Z is reached, similar to the chemically bound Azo-AuNPs hybrids, which are not explored in terms of the catalytic influence of Au. Finally, we utilize anisotropic Au nanostructures instead of spherical ones. Thus, our contribution addresses some of the less discussed aspects of Au-Azo hybrid systems and potentially broadens their understanding.

Another important factor in the context of Azo isomerization mechanism in the proposed hybrid material is the significant acceleration of the isomerization after Azo binding to CNFs. By transferring AzoGly functionality to water, we created a scenario and environment in which *Z*-isomer half-life at 298 K in the dark drops from 24.6 hours for free AzoGly dissolved in EtOH

(Figure S17) to 16.13 min for water-based AzoGly-CNFs sample. Although such a dramatic change in Z-isomer stability upon solvent change is not unusual for Azo photochromes, we propose it also originates from the Azo entrapment in the material's structure. A simple experiment in which different amounts of CNFs (Figure 4f, 100% [CNFs] represents 'no Au' control sample used in the previous experiments) are impregnated with AzoGly solution of the same concentration shed some light on this aspect. Since Azo exhibits first-order kinetics of thermal isomerization, the rate constant is neither dependent on molecule's concentration in the hybrid material nor on material content in the sample. As presented in Figure 4f, thermal isomerization at 25°C in the dark becomes faster with the increasing CNFs content. The 3-fold increase of CNFs content (300%[CNFs]) results in the +107.7% kinetic boost, while the 5-fold decrease (20%[CNFs]) results in the -28.5% kinetic slowdown (reference value of the first-order rate constant for 100% [CNFs]: $k_{Z-E} = (5.826 \pm 100\%)$ $(0.027) \cdot 10^{-4} \text{ s}^{-1}$). CNFs do not exhibit any electron-donating character,^[79] and hence, their catalytic influence on the AzoGly isomerization is ruled out. Since AzoGly is tethered to CNFs via a glycinelike side group, its movement and steric freedom are limited. At the same time, CNFs form an entangled network, contributing to the steric hindrance and confinement experienced by Azo molecules. Logically, the more CNFs we use, the denser the network created by the fibers. Thus, by changing CNFs content, we also supposedly change the environmental constraint imposed on AzoGly, which results in the differences in the kinetics of thermal back-isomerization. This is coherent with azobenzenes' tendency to exhibit decreased switchability without a high degree of conformational freedom.^[103] However, we assume that the nature of confinement imposed on AzoGly in this system is not too rigid, as the photoswitchability of the photochromic component remains distinct and stable (Figure 4c). Moreover, it is possible that interactions between hydroxyl groups of CNFs and N=N bond also contribute to the dramatic decrease of the $\tau_{1/2}$, similar to Azo isomerization in the presence of background ligands.^[15]

Presented thermal relaxations of AzoGly-Au-2-CNFs constitute valid points for further development of hybrid materials with desired stabilities of photochromic components. We

identified key points of the material's design that influence its final photochromic functionality. We also determined for the first time a complete set of thermodynamic parameters describing thermal back-isomerization of Azo in the presence of gold and presented that application of standard Azo-related research procedures can be utilized in complex hybrid systems.



Figure 4. Photochromism, photostability, and thermal relaxations of hybrid samples. **a)** Azo-component maintains photochromic functionality in the hybrid material and undergoes E-Z and Z-E isomerization upon UV and Vis light irradiation, respectively. Plasmonic properties of the material are preserved the whole time. **b)** Presence of AuNRs grants a kinetic boost of E-Z (+52.2%) and Z-E (+48.6%) isomerizations comparing to control sample without Au. **c)** Hybrid materials exhibit distinct and stable photoswitching upon interval UV (3 min) and Vis (3 min) light irradiation throughout many cycles. $\pi \rightarrow \pi^*$ band intensities are indicated by purple points at PSS_Z and blue points at PSS_E. **d)** Hybrid samples exhibit thermal Z-E isomerization in the dark, just as

pristine azobenzenes. e) Thermal back-relaxation in the dark is faster in the presence of gold. Kinetic boost decreases with increasing temperature. f) CNFs influence the isomerization of AzoGly by creating specific environmental conditions. The CNFs' network imposes steric constraints and confinement, hence changing the stability of the photochrome. With increasing CNFs content, Azo thermal back-isomerization occurs faster.

Finally, we present plasmon-assisted isomerization of Azo and show the possibility of an instantaneous indirect photocontrol of this reaction in an ON-OFF manner. We designed proof of concept experiments to use two crucial advantages of our hybrid material. Firstly, our material contains anisotropic nanostructures, and AuNRs exhibit better light-harvesting properties than Au nanospheres. For this reason we switched to Au-1 NRs, which exhibit higher anisotropy (AR = 3.30) and better light-to-heat conversion. Secondly, thanks to the beneficial separation of Azo and AuNRs' spectral features, we utilized third spectral window (Figure 3f) and irradiated only AuNRs. These advantages guarantee that changes in the Azo Z-E isomerization kinetics are derived strictly from plasmon-related effects and are the result of indirect control over Azo isomerization. To support our claims, we used a custom setup with real-time UV-Vis-NIR spectra acquisition and sample irradiation cell integrated with LED Solar Simulator and heating stage (Figure 5a, top). This minimizes sample heating and ensures constant thermal conditions of the process (25°C). We selected 650-1100 nm spectral range (Figure S14) corresponding to the position of the 1-LSPR band of Au-1 plasmonic core (Figure 5a, bottom). We carried out two types of experiments to investigate the influence of AuNRs upon red-NIR irradiation on (1) AzoGly in a form of free molecules in EtOH or (2) CNFs-bound photochrome in the hybrid materials in water.

To benefit from plasmon-derived phenomena we also increased the loading of CNFs with AuNRs to 19.6 wt%. We observed that this results in a lower experiment resolution (**Figure S19**) due to significant overlap of the $\pi \rightarrow \pi^*$ band of a photochrome with the extinction of **Au-1-CNFs** framework. Moreover, increased loading contributes to faster composite sedimentation and

randomizes its macroscopic behaviour. These aspects make consecutive spectroscopic experiments less comparable and require proper data treatment and new experimental design. We substantially reduced the influence of sedimentation by correcting spectra to keep material's isosbestic point (296 nm) and, where necessary, increased the number of repetitions. Moreover, we also designed an OFF-ON experimental approach for hybrid Azo-Au systems (vide infra).

First, we investigated plasmon-assisted *Z*-*E* isomerization of free Azo molecules as a prelude to understanding this process in the hybrid material. By examining the reaction in the native Azo solvent (EtOH) we increased the temporal resolution of the measurement. In this experimental scenario, bare CNFs or **Au-1-CNFs** pre-composite were added directly to the *Z*-form of AzoGly, i.e. after UV irradiation. Temporal separation of Au addition from the UV exposure excludes possible participation of intraband excitations. Chosen irradiation conditions (650-1100 nm, 64.9 mW cm⁻²) and bare CNFs have a negligible effect on pristine Azo isomerization kinetics (**Figure S20** and Figure 5b). Observed differences in $k_{Z,E}$ values (dark vs. light conditions as well as pristine Azo vs. bare CNFs addition) are characterized by typical relative errors^[104] (see Section 5.1. of the SI). This proves the inert nature of CNFs scaffold. A significant catalytic boost is clearly seen once **Au-1-CNFs** pre-composite is added to the PSS_Z of AzoGly (Figure 5b). The rate constant value in the dark, $k_{Z,E,Au}^{dark} = (7.09 \pm 0.04) \cdot 10^4 \text{ s}^{-1}$, is one order of magnitude higher comparing to samples without Au. Furthermore, in the presence of Au and upon irradiation with red-NIR, two orders of magnitude increase is observed, $k_{Z,E,Au}^{light} = (3.15 \pm 0.03) \cdot 10^{-3} \text{ s}^{-1}$.



Figure 5. Plasmon-assisted isomerization of AzoGly (**top**) as a free molecule in EtOH and in the presence of Au-1-CNFs pre-composite or (**bottom**) in the hybrid AzoGly-Au-1-CNFs material in water (19.6 wt% of Au with respect to the mass of cellulose in both scenarios). **a**) Measurements were performed using custom setup with real-time data acquisition. Spectral range of irradiation (650-1100 nm) matched the position of 1-LSPR band of AuNRs and did not trigger isomerization of AzoGly. **b**) Bare CNFs scaffold is inert and does not influence isomerization of AzoGly. The catalytic effect of AuNRs manifests upon the addition of pre-composite in the dark due to the electron transfer. Upon irradiation thermoplasmonic effect boosts thermal back-isomerization of AzoGly by two orders of magnitude. **c**) Rate constants describing AzoGly Z-E isomerization in the presence of Au can be recalculated into virtual temperatures of the process, and hence, the extent of the thermoplasmonic effect can be estimated. **d**) Data collection for hybrid materials in water

requires a special experimental design (OFF-ON interval experiment) and the use of statistical modelling for data analysis. Autoregressive Integrated Moving Average (ARIMA)-based approach was used. Dependent variable Y₁ is forecast based on the previous observations (Y₁₋₁), random error term (c₁₋₁), and stability of the time series (Y'₁). Illustration depicts ARIMA (1,1,1) and Ramp effect estimation as a method to evaluate influence of switching light on (the intervention). Influence of light is manifested in the slope change of the data subseries (paired dark and light intervals). e) Presence of AuNRs (bottom) grants photocontrol over Azo isomerization in an ON-OFF manner, which manifests as characteristic breaking of the linear trend of the data at times of the intervention. Irradiation does not affect the reaction when AuNRs are not present in the sample. f) Quantitative measure of statistical significance tests for each modelled pair between Au-containing sample and control sample without Au. Results indicate that only in the presence of Au change in the slope of the data upon irradiation is statistically significant. Hence, plasmon-assisted isomerization of AzoGly in the hybrid material via triggering thermoplasmonic effect is entirely manifested.

We propose looking at this data through the lens of a photochrome and translating the determined rate constants into 'virtual temperatures' of the process, meaning temperatures in which equivalent Azo *Z-E* isomerization in the dark and without Au would occur at the same rate. Virtual temperatures can be assessed by comparing AzoGly isomerization rate constants in the presence of AuNRs ($k_{Z-E,Au}^{dark}$ and $k_{Z-E,Au}^{light}$, Figure 5b) with Arrhenius plot for a free photochrome (Figure 5c; $lnk = a \cdot \frac{1}{T} + b$, where a = -9224.0 [K], b = 19.2 [-], according to Figure S17). Hence, in the dark, the sole catalytic effect of electron transfer manifests as a virtual temperature of 76°C (Figure 5c). Upon irradiation, when the thermoplasmonic effect is triggered, the process remains pseudo-first order, and the rate constant, $k_{Z-E,Au}^{light}$, translates into a virtual temperature of 97°C (Figure 5c). We propose that these values constitute a quantitative measure of the catalytic effect of AuNRs. The

difference between the virtual temperature upon irradiation and the base virtual temperature in the dark reflects the extent of the thermoplasmonic effect. Thus, we assume the collective heating of AuNRs to raise the temperature of the sample by 21°C.^[105] Certainly, more efficient electron transfer upon irradiation (due to interband excitations) cannot be entirely ruled out, however, we assume the contribution of photothermal effect to be more substantial. To confirm photothermal effect upon red-NIR irradiation, we measured the kinetics of Azo *Z-E* isomerization in the hybrid material under varied power density of incident light. The exponential fit of the data, in accordance with Arrhenius law (**Figure S21**), indicates towards the dominant role of the thermoplasmonic effect.^[106] With these results, we propose a new perspective for azobenzenes as molecular thermometers to detect and quantify thermoplasmonic effect and assess temperature changes at the nanoscale. We foresee that this preliminary idea can further flourish, gaining from an immense library of various Azo derivatives, which grants the possibility of choosing molecules differing in solubility, grafting potential, and thermal stability. Hence, different types of materials and structures can be prepared, and proper resolution and sensitivity of the measurement can be asserted for specific system and application.

The second experimental scenario concerns plasmon-assisted isomerization of a photochromic component in the AzoGly-Au-1-CNFs hybrid material. For this purpose we designed an OFF-ON experiment by subjecting composite to the consecutive intervals of dark and light conditions during individual measurement. This minimized the possibility of systematic errors, accounted for random deviations stemming form high Au-loading, and facilitated the depiction of material's susceptibility towards light. Conditions were identical through the whole experiment and the only difference was either presence or lack of irradiation and triggered plasmon-related effects. Thus, we propose an experimental design based on real-time analytics aided by advanced statistical modelling.

After reaching PSS_Z in the hybrid material, AzoGly back-isomerization was monitored under the same-length dark (OFF) and light (ON, red-NIR irradiation, 650-1100 nm, 145.8 mW cm⁻²) intervals. The collected spectra were accordingly processed (see Materials and methods in the SI) to

conform with the assumptions of the applied statistical modelling approach - interrupted time series^[107] (Section 5.2. of the SI, Figure 5d). We consider observations before and after an intervention, which is the introduction of light. Intervention occurs a few times during each experiment (irradiation source was switched on and off multiple times). Dark and subsequent light intervals are paired up (in this exact order) and each pair is considered separately for a given sample. Our central hypothesis is that in the presence of Au, due to the plasmon-assisted Azo isomerization triggered upon irradiation, there are statistically significant differences within subsets (pairs) upon intervention (Figure 5d). Once thermoplasmonic effect is triggered and the collective heating of AuNRs causes temperature rise in the vicinity of the nanostrucutres, AzoGly as a T-type photochrome should undergo Z-E isomerization faster. Hence, the slope of the linearized data should increase in absolute value during light period (Figure 5d), which can be qualitatively assessed through naked eve inspection (Figure 5e). However, a non-trivial composition of our materials requires appropriate statistical tools to extract quantitative data. Auto-correlation of the observations violates the assumptions of classical linear models and to account for the temporal structure of the data we analyzed it with an Autoregressive Integrated Moving Average (ARIMA)based approach.^[78] ARIMA models represent a single variable of interest Y_t as a function of its previous values (e.g. Y_{t-1}), random error (ϵ_t), and previous values of the random error (e.g. ϵ_{t-1}), seasonal effect, differencing, and optional covariates (Figure 5d,e and Section 5.2. of the SI). We investigated four samples in total (Table S3) – with AuNRs (1 and 2) and control samples

without Au (**3** and **4**) – and maintained the same conditions for each light interval (650-1100 nm, 145.8 mW cm⁻²) changing only its duration – either 5.0 min (for **1** and **3**) or 2.5 min (for **2** and **4**). For each sample at least four OFF-ON pairs were modelled, corresponding to the time frame of the biggest extinction change. By comparing sample **1** (Au) and **3** (no Au) presented in the Figure 5e (bottom and top, respectively), we recognize that intervention causes slope change only for sample containing AuNRs. This manifests as a characteristic breaking of the linear trend of the data at the times corresponding to the intervention (so-called Ramp effect) and is in contrast to the overall

smooth linear trend for the control sample without gold (Figure 5e, see also **Figure S22** for samples **2** and **4**). Based on the ARIMA modelling (for selected *p*, *d*, and *q* parameters, **Table S4**), we estimated values of the Ramp effect upon intervention (**Table S5**). Negative values imply that the extinction at the maximum of the $\pi \rightarrow \pi^*$ band is changing faster under irradiation. This means that AzoGly isomerization rate increases during light intervals comparing to dark conditions. Visual assessment and point estimates of the Ramp effect are, however, not sufficient for making statistical statements about the significance of the observed slope differences. After taking into account the uncertainty of estimation and correcting for multiple comparisons, we calculated p-values for tests of significance of the Ramp effect (Table S6). At 5% significance level, we treat effects with p-values smaller than 0.05 as significantly different from 0. Testing results (Figure 5f) confirm that the statistical significance of the Ramp effect (slope change upon irradiation) is observed only for sample containing gold. There is no statistical significance of the Ramp effect values for sample without gold. Conclusions are identical for samples **2** and **4** (Figure S2). Testing results prove that introduction of AuNRs enables indirect control over AzoGly isomerization kinetics in the hybrid material in an ON-OFF manner.

Interestingly, our statistical modelling also indicates which plasmon-related effect plays significant role in the presented indirect photocontrol of Azo isomerization. Since there are multiple light and dark periods, the intervention can be defined in two ways, as switching light on or switching it off. Thus, we defined new pairs, ON-OFF, starting from the first light period and pairing it up with the second dark interval. We modelled Ramp effect for new pairs to determine how switching the light off affects the reaction and, hence, the slope of the data. Results presented in **Table S7-S9** and in **Figure S23** and **Figure S24** indicate that switching the light off also results in the data slope change only in the presence of Au. However, the influence of switching light off as an intervention seems to be more subtle once the irradiation intervals are shorter. For sample **2**, with shorter light periods, p-values are larger than the assumed p=0.05 level. Yet, since Ramp effect detects an immediate change upon intervention, we assume that for switching light off, slope change is not as

instantaneous as it is for switching light on. Due to the short lifetime of hot carriers (order of few tens of fs for Au), kinetic changes derived purely from eT and enhanced by interband excitations upon irradiation would be immediate for both types of intervention. For the thermoplasmonic effect, however, after its triggering, heat dissipation needs to occur, especially for such a complex material dispersed in water. Such a process is characterized by a much longer timeframe, and, as a result, slope change is less pronounced for shorter intervals. Thus, we can assume the dominant contribution of the thermoplasmonic effect during plasmon-assisted Azo isomerization. Therefore, we present plasmon-assisted Azo *Z-E* isomerization and, for the first time, the possibility of its indirect kinetic photocontrol in an ON-OFF manner via thermoplasmonic effect.

Conclusions

We demonstrated a method to efficiently incorporate plasmonic and photochromic units within one processable and robust material. By employing intermolecular interactions and utilizing cellulose nanofibers (CNFs) as a functional scaffold, we preserved the photoswitchability of the chosen Azo derivative (AzoGly) and maintained stable plasmonic properties of AuNRs. At the same time, we kept beneficial spectral separation of the optical features of components and presented catalytic influence of AuNRs on Azo isomerization in the dark, upon UV and blue light irradiation. Our study addressed several challenges set in the field of plasmonic-photochromic hybrids by previous research groups. Namely, we showed, for the first time, an entirely water-functional system that does not rely on covalent linkage between components, employs large, anisotropic nanoparticles, and operates without aggregation. We also provided one of the first experimental proofs for the literature hypothesis of the electron transfer-based catalytic influence of AuNPs on Azo *Z-E* isomerization in the dark. Moreover, by applying Au nanostructures with great light-harvesting properties, we proposed light-driven, plasmon-assisted *Z-E* isomerization of Azo. As revealed by statistical modelling, the thermoplasmonic effect, triggered upon red-NIR irradiation in the presence of Au, grants an ON-OFF control over two modes of the plasmon-derived catalytic boost of Azo

Z-E isomerization kinetics in the hybrid material. Our study shows perspectives for the ARIMAbased statistical modelling approach in the analysis of real-time spectroscopy data for experimental scenarios considering spectral changes occurring upon external intervention. We also propose the use of Azo derivatives as molecular thermometers to quantify extent of the thermoplasmonic effect. This work opens up perspectives for further development of multifunctional hybrid materials relying on plasmonic nanostructures and photochromes and methods enabling temperature assessment at the nanoscale. Our material design constitutes a convenient starting point for further advanced azobenzene-related research and 3D printing of macroscopic light-responsive structures with dual functionalities.

Contributions

N.T.S. – initial and final project conceptualization (all aspects, including in particular: material formulation, plasmon-assisted process, and azobenzenes as nanothermometers), in all aspects, namely, material formulation, components identification, photoswitching experiments, thermal relaxations, plasmon-assisted process: methodology development and application, investigation – performing all experiments and all data collection, formal analysis of all acquired data, all data curation, project administration, visualization (all figures and tables), writing – original and final draft, writing – review and editing; **M.S.** – software – designing R language app for the analysis of real-time acquired UV-Vis spectroscopy data ('plasmon-assisted' part), formal analysis – ARIMA modelling and statistical analysis, writing – statistical section, supporting visualization (statistical part), reviewing – final draft; **M.D.** – investigation – synthesis and identification of AzoGly, formal analysis – supporting conceptualization ('electron transfer' and 'plasmon-assisted' parts), methodology development (ON-OFF experiments), supporting analysis of the data related to the plasmon-assisted part of the project, resources – provision of instrumentation necessary for the plasmon-assisted part

of the project, reviewing – original and final draft, supervision; **K.M.** – initial project conceptualization, supporting analysis of the hybrid materials' thermal relaxations, resources – provision of instrumentation necessary for the spectroscopic measurements, supervision, reviewing – final draft.

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Data availability statement

The data supporting the findings of this study are available from the corresponding authors upon reasonable request.

Conflict of interest

Authors declare no conflict of interest.

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Gold nanoparticles and azobenzene derivatives can be incorporated within one, processable, waterfunctional material by using cellulose nanofibers as a functional scaffold. Presence of gold nanorods enables light-driven, plasmon-assisted Z-E isomerization of a photochrome. Statistical modelling indicates that thermoplasmonic effect, triggered upon red-NIR irradiation, grants an ON-OFF control over the isomerization kinetics in the hybrid material.

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