Photochromic TiO₂/PEGDA organogels

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Abstract

Photochromic materials can be used for modulation of the visible and infrared light transmittance for providing privacy or energy saving by blocking the heat. Titanium dioxide (TiO₂) nanoparticles has been well reported as a promising photochromic material. However, a high photochromic response from TiO₂ can be observed only when the nanoparticles are dispersed in a strong photogenerated hole scavenger at a liquid state, but polymer composites are less responsive due to lack of hole scavenging capability. However, it is intricate to apply suspensions in real window devices because of possible leaking. Here, we describe the preparation of TiO₂ quantum dot (QD)-based gels from polyethylene glycol diacrylate (PEGDA), *N,N*-Dimethylformamide (DMF), and ethanol (EtOH). Photochromic gels with TiO₂ contents (1–5 volume%) show performance comparable to their colloidal counterparts with capable of photodarkening within 30 min with a transmittance change ranging from 35.8 to 84.5% at 550 nm. These gels were capable of fully recovering the initial transmittance when not exposed to ultraviolet (UV) light within 3–8 h. The photochromic gel systems with ethanol shows reasonable stability by decreasing in transmittance recovery only by less than 10% in 10 cycles. A potential application for the developed photochromic gels can be photochromic windows.

Graphical abstract

Keywords TiO₂/PEGDA · Hybrid gel · Photochromism · Photodoping

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1 Introduction

In recent years, there has been an increased strive towards a decrease in energy consumption. One of the highest consumers of power are heating, ventilation and cooling (HVAC), that on average consumes around 75 kWh/m² [1].

One way how to combat this issue is to modulate the transmittance of windows using so-called smart window systems. The use of smart windows can save up to 70% of the energy used for heating and cooling in buildings [2]. Different smart window systems has been proposed such as suspended particle devices [3], micro-blinds [4], polymer-dispersed liquid crystals [5], electrochromic [6], thermochromic devices [7], and photochromic materials [8]. Photochromic materials change their optical transmittance in response to light irradiation. Inorganic photochromic materials (mainly transition metal oxides, TMOs) are among the most widely studied photochromic materials due to their good chemical resistance and high thermal stability [9]. Photochromic TMO provide the possibility to modulate the incoming light in a wide spectral range, from near UV to mid-IR [10].

The photochromic effect in the TMO materials has been observed in the presence of hole scavengers due to process of photodoping. During the irradiation by light with the energy higher than the bandgap of the TMO, electrons and holes are excited. The holes are removed by hole scavengers while electrons are accumulating in the conduction band causing partial reduction of the TMOs [11], as well as plasmonic resonance absorption in TMO particles with sizes less than 50 nm, that gets more pronounced as the size decreases [12]. The electron accumulation can also be used for the means of light-driven charge storage and solar energy accumulation [13].

Anatase TiO_2 is most attractive photochromic material among other TMOs material due to non-toxicity, elemental abundancy and strong photoresponse [10]. The photochromic response of anatase TiO_2 can be modified either by changing the hole scavenger [14] or doping [15]. Strong photochromic response from TiO_2 has been demonstrated mainly for colloids so far. However, colloidal photochromic systems have their limits. They cannot be applied in real smart windows due to leaking and solvent evaporation. In addition, the switching back from colored to transparent state is an issue—the introduction of an oxidant is needed [10]. For that reason, solid polymer composite films are tested as the photochromic materials. However, TiO_2 polymer composites show limited photochromic response because of weak hole scavenging properties of the polymer matrix [16].

The photochromic films based on solid TiO_2 films has been also reported. In most cases, the TiO_2 film is either loaded with silver nanoparticles [17] or combined with other oxide material in heterostructure to provide charge separation and modulation of optical properties in the photochromic system [18, 19]. The main issue with incorporating TMO-based photochromic materials in photo-optical devices is the need to prepare thick crack-free films to ensure sufficiently high light absorption [20]. Thickness above several

microns is needed to provide large light absorption density, while crack-free structure is needed to avoid scattering.

Herein, we propose photochromic polymer gels. It is not first time when the photochromic oxide materials are incorporated in polymeric matrix. However, so far solid polymer composite systems have been proposed. Different photochromic systems based on TiO_2 and polymers, such as, urethane resin [16], polymethyl methacrylate (PMMA) [21] and polyvinyl alcohol (PVA) [22] has been demonstrated. However, these are slow and provides small total change in transmittance due to a slow hole scavenging rate. We report the polyethylene glycol diacrylate (PEGDA) gels containing up to 5 volume % (vol%) (19.45 weight %) of photochromic TiO_2 QDs prepared via photopolymerization. Gels can be made thick, thus ensuring large optical absorption density in response to UV light. Small QD size (< 5 nm) ensures high optical clarity without loss of transmittance from scattering. Gels are also perfect for exchanging the reactants for rapid photochromic response and recovery.

2 Experimental

2.1 TiO_2 QD synthesis and characterization

For the full TiO_2 QD synthesis procedure, reader is advised to see our previous publication [15]. Briefly, titanium tetra *n*-butoxide was added to a solution of acetylacetone in *n*-butanol. After this, the solution was brought up to reflux and a solution of 4-dodecylbenzene acetic acid in deionized water was added dropwise and kept at reflux for 12 h. Following this, the particles were separated, washed twice with methanol, and dispersed in DMF to obtain a colloid that was used for gel preparation. The particle crystalline composition and morphology was studied using x-ray diffraction (XRD, *Panalytical X'pert Pro*), Raman spectroscopy (*Renishaw inVia*) using a 532 nm laser and TEM (*FEI Tecnai*). The X-ray photoelectron spectra (XPS) were acquired using a *Scienta SES100* hemispherical analyzer and a non-monochromatized Mg K α radiation source (a *Thermo VG Scientific XR-4* dual anode X-ray gun), with a resulting overall resolution of approximately 0.7 eV. The binding energy scale of the slightly charging sample was corrected by fixing the C 1s peak of adventitious carbon to 284.8 eV. The XPS sample was prepared by pressing a ground sample powder into indium foil.

2.2 TiO_2 /PEGDA organogel preparation and crosslinking

Gels were prepared with a TiO_2 QD content of 1, 2, 3, 4 and 5 vol% and with different amounts of EtOH (0, 10, 20 and 30 vol%). As the polymer, PEGDA (average molar mass 250 g/

mol) was added to the mixture. Lastly, the remaining volume was filled with DMF. The amount of PEGDA used for the samples was kept at 20 vol% of the sample. To crosslink the PEGDA molecules, photopolymerization was employed by UV irradiation (365 nm). For the photopolymerization, samples with different compositions were filled in microtubes and irradiated with UV light for different time.

2.3 TiO₂/PEGDA organogel characterization

To study the photochromic properties of the composite gels, the sample mixture was irradiated with ultraviolet A (UVA, 365 nm) light in custom test cells. The UVA light source was a triple LED array with an irradiance of 47 mW/cm². A test cell consisted of two glass slides with a 700 μ m polydimethylsiloxane (PDMS, Sylgard 184) spacer in between. The cells were then irradiated, and the transmittance change in response to light was measured using a UV/Vis spectrometer (*Genesys 10S*, *Thermo Scientific*). The photochromic performance was expressed in terms of the relative transmittance change time derivative. This showed the relative change during each subsequent minute and was used to compare the photochromic kinetics of the different gel samples with different compositions. For studying the photopolymerization, the Raman measurements were performed. For Raman measurements, samples were injected into a sample cell consisting of glass/PDMS/quartz. The cell was then irradiated for 30 min with UV light and the spectra were recorded before and after UV irradiation using a *Renishaw InVia* Raman spectrometer using a 532 nm laser.

3 Results and discussions

3.1 Properties of TiO₂ QDs

The synthesized TiO₂ QDs used in this study were crystalline with size 3.5–4.5 nm (TEM image Fig. 1A). According to both XRD (Fig. 1B) and Raman spectroscopy (Fig. 1C), the particles consist purely of anatase with no secondary phases. The XRD corresponds to JCPDS 21 1272. The Raman bands observed a slight shift to higher wavenumbers as compared to literature, due to deformation in the scattering paths of Ti–Ti (corresponds to bands at 148 cm^{−1} and 198 cm^{−1} as compared to 144 cm^{−1} and 197 cm^{−1}) and Ti–O (corresponds 398 cm^{−1}, 515 cm^{−1} and 638 cm^{−1} as compared to 399, 513 and 639 cm^{−1}) [23]. This is caused by the phonon confinement characteristic of ultrafine nanoparticles [24]. Figure 1D and E shows XPS of Ti 2p and O 1s, indicating no presence of either Ti³⁺ or oxygen vacancies, before photodoping.

3.2 The formation of photochromic gels

The photochromic gels were obtained by mixing TiO₂ QDs (1–5 vol%) with PEGDA (20 vol%), DMF (13–79 vol%) and EtOH (0–30 vol%) at various ratios (composition of all the samples can be seen in in SI Table 1). PEGDA is acting as a gel matrix, DMF as the stabilizer of the network with the particles, and ethanol as a hole scavenger. The PEGDA matrix was crosslinked by UV irradiation, while TiO₂ was photodoped (see Fig. 2A). PEGDA crosslinking has been previously carried out in both DMF [25] as well as EtOH

Fig. 1 A TEM micrograph; B XRD; C Raman spectra; D Ti 2p XPS and E O 1s XPS of the used nanoparticles

Fig. 2 **A** Photograph of a TiO₂/PEGDA gel composition (3 vol% TiO₂ and 20 vol% EtOH) before and after UV irradiation; **B** ternary diagram displaying the compositional range where the transparent and opaque gels are obtained (white region indicates no gel formation). Green circle indicates the region of compositions studied further; **C** Raman spectra of a TiO₂/PEGDA gel (2 vol% TiO₂ and 20 vol% EtOH) before and after UV treatment (photochromism and crosslinking)

[26]. There has also been a report on crosslinking PEGDA in the presence of TiO₂ without any solvent present [27]. After the UV radiation, the PEGDA gel was obtained. The addition of 2 vol% of TiO₂ QDs sped up the gelation from 15 min to just 5 min. The maximum amount of TiO₂ that we were able to incorporate into the system without encountering noticeable agglomeration was up to 4 vol%. At 5 and higher vol%, the mixtures are becoming hazy (as seen in Figure S1.A). The light-scattering properties of mixtures containing 5 vol% or more of TiO₂ QDs is the indicator for particle agglomeration. Furthermore, a minimum of at least 10 vol% of PEGDA is necessary to observe gelation (Figure S1.B). The photochromic gel material must be transparent to be used in smart window devices. These results were compiled in a ternary diagram (Fig. 2B). This indicates a region of gel compositions where a transparent photochromic gel is achievable.

The gel formation can be attributed to crosslinking of PEGDA. Crosslinking was confirmed using Raman spectroscopy. The Raman spectra (Fig. 2C) was recorded before and after UV irradiation for a sample with a TiO₂ content of 2 vol% and an EtOH content of 20 vol% and normalized to the peak at 866 cm⁻¹ as this is attributed to CN stretching and only possible in DMF in the studied system [28]. The crosslinking of PEGDA can be proven by following the absorption peak at 1638 cm⁻¹ as this peak is attributed to C=C bond stretching [29]. In the mixture we studied, the C=C bonds are present only for PEGDA molecules before crosslinking [30]. As crosslinking occurs, the amount of these bonds decreases, leading to a decreased signal. In our case, a conversion factor of 52% can be observed (see Figure S2).

3.3 Photochromic response

All the samples, that contained TiO_2 QD, showed photochromism in response to UV light irradiation (list of compositions shown in SI Table 1) due to photodoping and recovery when not irradiated with UV (Fig. 3A). When TiO_2 is irradiated with UV light, electrons (e_{CB}^-) are excited to the conduction band of the anatase, leaving behind holes (h_{vb}^+) in the valence band (Eq. 1). When hole scavengers are present (OHCH_2R), the holes can be filled by electrons from the scavenger (Eq. 2). This leads

accumulation of photogenerated electrons into the conduction band of TiO_2 , thus modulating the optical properties. Delocalized electrons in TiO_2 conduction band are responsible to infrared light absorption [31]. Some photogenerated electrons in TiO_2 start to reduce Ti^{4+} to Ti^{3+} (Eq. 3). This reduction also results in oxygen vacancy ($V_{\text{O}}^{\bullet\bullet}$) formation [10]. Both, oxygen vacancies and Ti^{3+} provides absorption levels in TiO_2 band gap (Eq. 4) [32]. The process occurring during the UV irradiation can be described by the following equations:

Fig. 3 A Photographs of photochromic gel sample in PDMS cell before UV irradiation (left), after 30 min UV irradiation (middle) and after 5 h of recovery (right). The sample consisted of 3 vol% TiO_2 /20 vol% EtOH/20 vol% PEGDA/DMF; B spectra of a sample before and after UV irradiation (3 vol% TiO_2 /30 vol% EtOH/20 vol% PEGDA/DMF); C absolute transmittance change as a function of amount of

TiO_2 in the gel at 550 nm (compositions without ethanol added); D absolute transmittance change for different wavelengths for the sample of 3 vol% TiO_2 /30 vol% EtOH/20 vol% PEGDA/DMF; E absolute transmittance change for different amounts of ethanol added for samples with 3 vol% TiO_2 at 550 nm

Evidence of photodoping can be seen in the Raman spectra of the organogel sample before and after UV irradiation. The loss in the intensity of the Raman bands at 517 and 638 cm^{-1} can be attributed to a loss in Ti–O bonds indicating the presence of oxygen vacancies [23, 32]. Oxygen vacancies are forming to compensate the Ti^{3+} which are forming due to electron accumulation and reduction of Ti^{4+} . Similarly, the decrease in the Raman band at 148 cm^{-1} that is attributed to Ti–Ti sublattice vibrations indicates distortions caused by Ti^{3+} formation [32]. As for the other constituents, the DMF bands at 660, 866, 1400 and 1440 cm^{-1} retained their intensity after irradiation, indicating, that, in the presence of ethanol, DMF, does not partake in the scavenging of photogenerated holes from TiO_2 . Peaks at 493, 553, 580, 616 and 939 cm^{-1} were no longer visible after irradiation. The peak at 553 cm^{-1} corresponds to acetylacetonate (acac) out-of-plane ring deformations, while the peaks at 616 cm^{-1} and 939 cm^{-1} correspond to C–CH₂–C bending and C–C stretching, respectively [33]. The band that increase in intensity is at 493 cm^{-1} and is attributed to acac in plane ring deformations [34]. This indicates that acac undergoes chemical reactions with TiO_2 photodoping byproducts via Knoevenagel condensation [35]. The byproducts being aldehydes from the oxidation of ethanol. The fact that the amount of ethanol decreases is indicated by the decrease in the 1100 cm^{-1} band intensity [36].

Hole scavengers are usually organic molecules containing hydroxyl and carbonyl groups, such as ethanol [37]. DMF has also been shown to act as a hole scavenger due to not only carbonyl groups, but also due to the presence of the nitrogen atom from the amide part [38]. PEGDA has only a very negligible hole scavenging capacity, due to the lack of any hydroxyl groups, with the carbonyl groups at the ends of the molecules being the most potent. However, carbonyl groups are very mild hole scavengers at best; thus, the hole scavenging in the present photochromic gels is mainly done by either DMF or ethanol [37]. The introduction of Ti^{3+} and oxygen vacancies leads to absorption in the visible light range, while the accumulated electrons are responsible for NIR light absorption due to surface plasmon resonance [15]. All these result in a decrease in transmittance, leading to

almost total light absorption in the studied wavelength range of 400–1100 nm (Fig. 3B).

First, we studied the effect of TiO_2 amount in gel of PEGDA and DMF without the addition of EtOH (full spectra available in Figure S3) on the absolute transmittance change during UV irradiation and recovery. For these samples, the absolute transmittance change at 550 nm increased from 35.8 to 84.5% at 550 nm (Fig. 3C) with a similar pattern for other wavelengths (For other wavelengths, please see Figure S8.A). This is to be expected as more TiO_2 QDs would have an increase in the total amount of light absorbed and, in turn, the total transmittance change.

When partially replacing DMF with EtOH, the absolute transmittance change after UV irradiation increased with increasing the EtOH content (full spectra of the samples: Figure S4–7). This effect was more pronounced for samples with a lower TiO_2 content (1–2 vol%), than for samples with a higher TiO_2 content (3–5 vol%). The sample with 30% ethanol and TiO_2 content of 2 vol% after UV irradiation shown higher transmittance change of 79.5% than the sample with no ethanol (52.7%) at 550 nm. Samples with a TiO_2 content of 4 vol% exhibited only a 6.4% increase in the absolute transmittance change adding 30% ethanol. This is due to the fact, that even without EtOH, these samples had a high transmittance change of 80%. At such a low transmittance (high absorption), the correlation between transmittance and absorbance is not linear, but exponential, resulting in diminishing returns can be expected and were observed. The transmittance of the samples was influenced also by the thickness. When increasing the thickness to almost double (1.3 mm), a sample, consisting of 3 vol% TiO_2 /20 vol% EtOH/20 vol% PEGDA showed a mostly identical transmittance spectrum within the wavelength range of 550–1000 nm (Figure S 9) with only 1–4 T% difference. However, due to the visible light absorption caused by the acac adsorbed on the TiO_2 QD surface, the transmittance in the 400–550 nm range for 1300 μm thick samples decreased from 85% (measured for 700 μm thick samples) to 71%.

The partial substitution to EtOH also reduced the irradiation time necessary from 120 min to just 30 min for full saturation in the transmittance change. The transmittance change rate was denoted as the first derivative of the relative transmittance change over time (Fig. 4A). The change rate was exponentially related to the amount of TiO_2 , ranging from -0.034 to -0.505 min^{-1} for samples with a TiO_2 content from 1 to 5 vol% at 550 nm (Fig. 4B, for the rest of the wavelengths please see Figure S10). This indicated that for the samples with the highest amount of TiO_2 (5 vol%) transmittance at 550 nm decreased to 0% in 5 min. The rate constant increased also when DMF in the photochromic system was partially substituted with EtOH. The rate constant increased considerably for all compositions with different TiO_2 content. The rate constants for photochromic gels with different

Fig. 4 **A** Relative transmittance change graph at 550 nm for sample with 3 vol% TiO₂/PEGDA 20 vol%/EtOH 30 vol%/DMF; **B** time derivative of the relative transmittance change under UV irradiation as a function of TiO₂ content (vol%) without EtOH; **C** time derivative of the relative transmittance change during UV irradiation at different wavelengths; **D** time derivative of the relative transmittance change under UV irradiation as a function of EtOH content (vol%) for samples with 3 vol% TiO₂;

amount of ethanol are presented in (Fig. 4D). Samples with a TiO₂ of 2 vol% had a change rate of $-5.6 \times 10^{-2} \text{ min}^{-1}$ at 550 nm without EtOH, while the substitution of 30 vol% of DMF with EtOH resulted in a 5-fold increase in the change rate to $-2.8 \times 10^{-1} \text{ min}^{-1}$ at 550 nm, while at 700 nm this resulted in a 4.86-fold increase from -7.2×10^{-2} to $-3.5 \times 10^{-1} \text{ min}^{-1}$. A similar increase in change rate was also observed for other wavelengths. The rate constant increase can be attributed to effective photogenerated hole scavenging properties of ethanol [14]. A further increase in the EtOH content above 30% shows a decrease on the both the absolute transmittance change as well as the change rate (Figure S11). When increasing the EtOH content past 50 vol%, the sample transmittance no longer recovered, due to agglomeration induced scattering. This shows that a minimum DMF:TiO₂ volume ratio of at least 10:1 should be kept, to eliminate agglomeration.

3.4 Recovery

Lastly, we will look at the transmittance recovery. These gels slowly recovered their transmittance, when not exposed to UV and without addition of oxygen. The accumulated electrons are reduced by the oxidation products of ethanol, that were created during UV irradiation in reaction with photogenerated hole. It has been previously shown, that photodoped TiO₂ can be used to reduce aldehydes to alcohols [39–43]. The recovery time depending on composition and wavelength ranged from 195 to 500 min. The recovery rate was 10–100 times slower than the photodarkening

rate, with the highest rate for the sample with 3 vol% of TiO₂ ($1.7 \times 10^{-3} \text{ min}^{-1}$ at 550 nm, Fig. 5C). The change of transmittance rate was dependent on the amount of TiO₂ and EtOH present. Here, it is more worthwhile to look not only at the absolute transmittance change during recovery (Fig. 5A and B as well as Figure S10), but also to the difference between the initial and recovered states (Figure S13). Without EtOH, the samples with a lower TiO₂ content (1 and 2 vol%) recovered fully throughout the studied wavelength range. However, samples with higher TiO₂ content (3 and 4 vol%) showed complete recovery only in the infrared range above 700 nm, while in the visible light range (400–700 nm), the transmittance recovered for 78.1% and 51.2%, respectively. Transmittance for the photochromic gel with 5 vol% of TiO₂ did not recover completely in both visible and infrared wavelength range reaching only 24.6% and 81.5% from initial transmittance, respectively. The reason for an incomplete recovery for photochromic gels containing 5 vol% of TiO₂ is decrease in transmittance from scattering. Since photodoping requires a hole scavenger, either part of the solvent or other suitable molecules are photo-oxidized. This causes the gel to undergo shrinkage and can lead to the degradation of the gel network [45]. This in turn, bring the TiO₂ particles closer to each other and could facilitate agglomeration.

When DMF was partially substituted with EtOH, both the absolute transmittance change and recovery rate were increased for all TiO₂ content samples. For a sample with a lower TiO₂ content (2 vol%), the recovery rate increased 3.3 times at 550 nm from 1.3×10^{-3} to $4.2 \times 10^{-3} \text{ min}^{-1}$ when

Fig. 5 **A** Transmittance recovery as a dependence of TiO_2 content for samples without EtOH; **B** transmittance recovery as a dependence of EtOH content for samples with 3 vol% of TiO_2 ; **C** recovery rate for samples as a dependence of TiO_2 content for samples without EtOH; **D** recovery rate as a dependence of EtOH for samples with a TiO_2 content of 3 vol%; **E** transmittance recovery during subsequent UV irradiation/recovery cycles at 550 nm for a samples with and without EtOH; **F** transmittance recovery during subsequent UV irradiation/recovery cycles at 1000 nm for a samples with and without EtOH

30 vol% of DMF was substituted with EtOH. For samples with higher TiO_2 content (3 and 4 vol%), the introduction of 30% EtOH resulted in not only increasing the recovery rate (3.76-fold and 2.4-fold increase at 500 nm for compositions with 3 and 4 vol% of TiO_2 , respectively), but also the absolute recovery of transmittance after the UV irradiation was more complete than it was for compositions without ethanol (Fig. 5B and D). In the NIR range (1000 nm), the full recovery in transmittance was measured for large compositional range with TiO_2 content from 1 to 4 vol%. Photochromic gels containing 5 vol% of TiO_2 with ethanol addition also exhibiting increased recovery rate and recovery transmittance change, but recovery was not complete with a difference of 41.5% between the initial and recovered states at 550 nm.

Lastly, we look at the stability of the photochromic gels. The stability was tested for 12 response–recovery cycles by repeatedly irradiating samples with a TiO_2 content of 2 vol% (samples without EtOH 120 min, samples with 20 vol% EtOH 30 min) and allowing them to recover. The recovery in visible and infrared ranges is different. In the visible range (Fig. 5E), the transmittance recovery in response to UV gradually decreases cycle over cycle, with the sample with 20 vol% EtOH decreasing from 99% on the 1st to 92% on the 10th and sample without EtOH decreasing from 98% on the 1st to just 69% on the 10th. This resulted in a transmittance recovery decrease of 7% and 29% for samples with and without EtOH, respectively.

In the NIR region (Fig. 5F), the samples showed a much better recovery from cycle to cycle, especially with the 20 vol% EtOH addition with the transmittance recovery

decreasing from an initial 100% on the 1st to 93% on the 10th cycle. The sample without EtOH showed transmittance recovery change of 18% over 10 cycles, from 100% on the 1st to 82% on the 10th. The difference between the visible and NIR ranges stems from the fact, that shorter wavelengths are more susceptible to the scattering caused by agglomeration and scatter on smaller size agglomerates as per Mie theory [44–47]. This can also be explained by the fact, that the Ti^{3+} and oxygen vacancy defects, created under the TiO_2 QD surface are stable and recover slowly because point defects are migrating slower than electrons. In addition, it is worth pointing out that for both vis and NIR spectral ranges (Figure S14), the recovered transmittance for the sample with 20 vol% EtOH after each cycle was fairly constant and only started no noticeably drop after 8 cycles (at 550 nm 91% on the 1st and 88% on the 8th and at 1000 nm 90% on the 1st and 89% after the 8th) as opposed to the sample without ethanol, that had a drop in the recovered transmittance after just 3 cycles (at 550 nm from 91% on the 1st 90% on the 3rd and 70% after the 8th and at 1000 nm 90% on the 1st and 3rd and 79% after the 8th). This shows that the addition of EtOH had a positive impact on the stability of the system. This also is due to the fact, that EtOH, acting as the hole scavenger, allows the rest of the constituents (DMF and crosslinked PEGDA) to remain untouched, thus making the gel more stable. In addition, it photooxidation products can be photo-reduced on photodoped TiO_2 QDs to facilitate better recovery.

4 Conclusions

In conclusion, we have prepared transparent photochromic gels composed from TiO_2 , EtOH and PEGDA, with DMF as a stabilizer. These gels were crosslinked during initial UV irradiation with the TiO_2 QDs acting as a photoinitiator. To keep the gels transparent, after crosslinking, the maximum TiO_2 content is 5 vol%. At higher TiO_2 contents, the gels become opaque, due to nanoparticles' agglomeration. These gels exhibit photochromism when irradiated with UV light and modulate their transmittance in the whole measured spectral range of 400–1100 nm. The performance of the photochromic gels is dependent on the TiO_2 and EtOH content. Higher TiO_2 content leads to a higher absolute transmittance change as well as a higher transmittance change rate but slows down recovery. Furthermore, if TiO_2 content exceeds 3 vol%, then agglomeration can be observed during UV radiation to a decrease in the overall transmittance. The gels with 1–2 vol% of TiO_2 showed full recovery. Substituting DMF with ethanol, we observed the increase in transmittance change rate and absolute transmittance change during UV irradiation, as well as a more complete and faster recovery for larger number of cycles. However, if the ethanol content

is increased over 50 vol%, the samples become opaque due to nanoparticle agglomeration. The agglomeration observed stems from the shrinkage of the gel network. The transmittance change rate for both photodarkening and recovery was faster in the NIR region than the visible region because the absorbance in the NIR region is governed by delocalized electrons, that accumulate during photodoping. These can also be quenched quicker, than the Ti^{3+} and oxygen vacancies responsible for the absorbance in the visible spectrum.

The best composition was prepared with 2 vol% of TiO_2 and an additional 20 vol% of EtOH. This composition could decrease its transmittance by up to 86.5% in 30 min and recovering in 470 min and could recover fully for 9 cycles. The gels showed a much higher transmittance change amplitude and change rate compared to other TiO_2 QD polymer composites of urethane resin [16], PMMA [21], and PVA [22]. These gels can be made thick to ensure complete modulation of transparency.

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Declarations

Conflict of interest The authors do not have any conflict of interest to declare.

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