Nanocomposite hydrogels with TiO_2 nanoparticles as colorimetric sensors for monitoring UV radiation exposure

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Summary

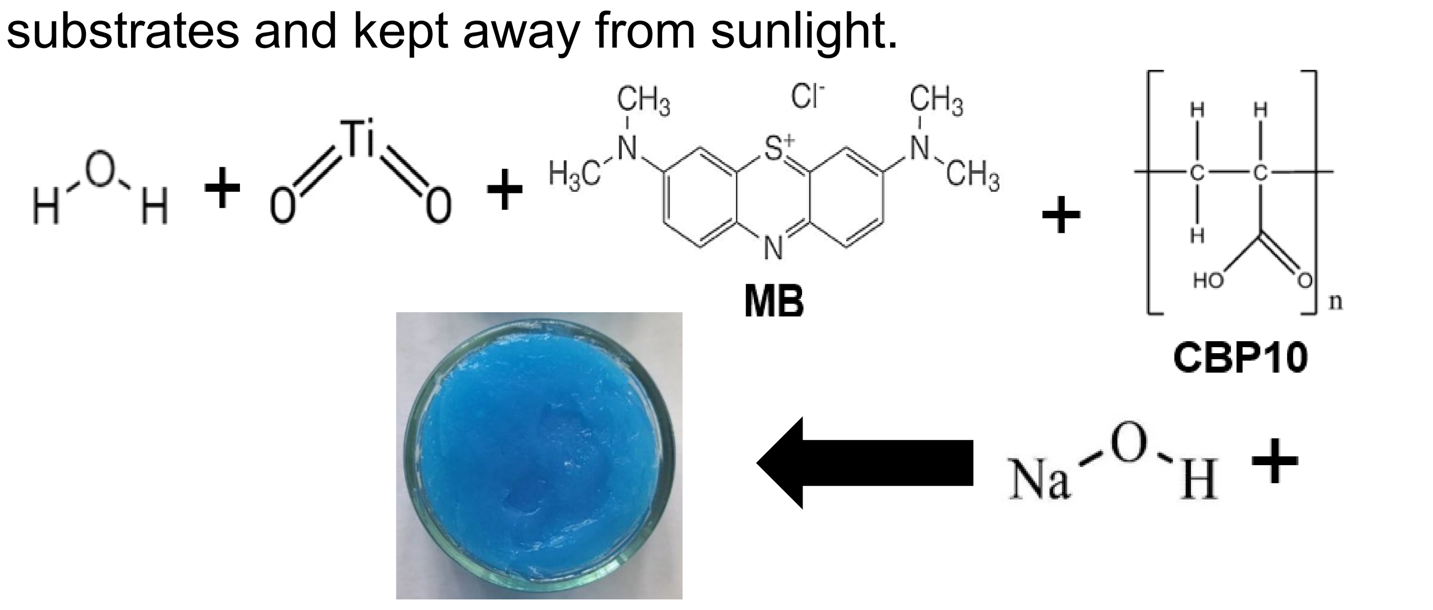
In this study we report the preparation and characterization of nanocomposite hydrogel materials acting as colorimetric sensors upon exposure to UV light. In the last few decades physicians worldwide have stressed the importance of protection from sun exposure. Given the variety of skin types, general exposure limits are not effective when it comes to sun protection. A hydrogel-based sensor to monitor exposure to UV-A radiation and that could possibly be adapted to different types of phototypes would be highly relevant and is presented in this work. The sensor was prepared using a Carbopol gel matrix in which photoactive TiO_2 nanoparticles and methylene blue (MB) dye were integrated. Once irradiated with UV-A light, activation of the TiO_2 nanoparticles occurs leading to reactive oxygen species (ROS) formation and photocatalytic degradation of the MB dye. The dye loses its original colour as the degradation progresses, and therefore the colour intensity change can be used as an indicator of radiation exposure. The nanocomposite hydrogel system was prepared using different concentration of TiO_2 nanoparticles and characterized by optical and physico-chemical techniques. In particular, Raman mapping was used to determine the network structure of the hydrogel and its water distribution, as well as to quantify the decrease of the characteristic Raman band of the MB dye upon exposure to UV-A radiation. Results indicate that at higher concentrations of TiO_2 nanoparticles the loss of colour intensity of the hydrogel sensor becomes more noticeable and saturation is reached at points later in time.

Nanocomposite hydrogels fabrication

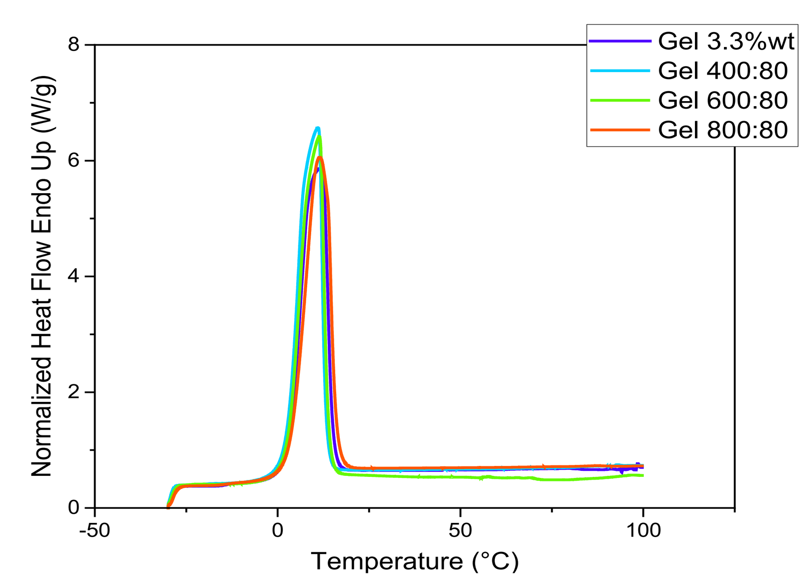
Step 1: A water solution of TiO_2 nanoparticles at various concentrations and methylene blue (80 ppm) was prepared

Step 2: After sonication, CBP10 (3.3 wt%) and NaOH were added and mixed

Step 3: The ready-to-use mixture was deposited on glass substrates and kept away from sunlight.



Thermal analysis and bound water content

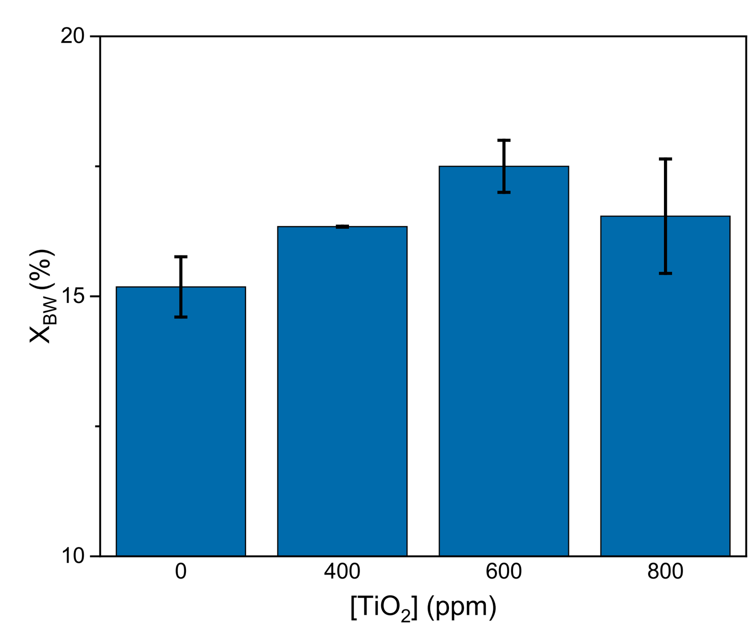


Differential scanning calorimetry (DSC) analysis revealed an endothermic peak at ≅ 10 °C due to the melting of water in the network. Hydrogels appear stable at higher temperatures up to 100 °C.

Bound water fraction (X_{BW}) was calculated as:

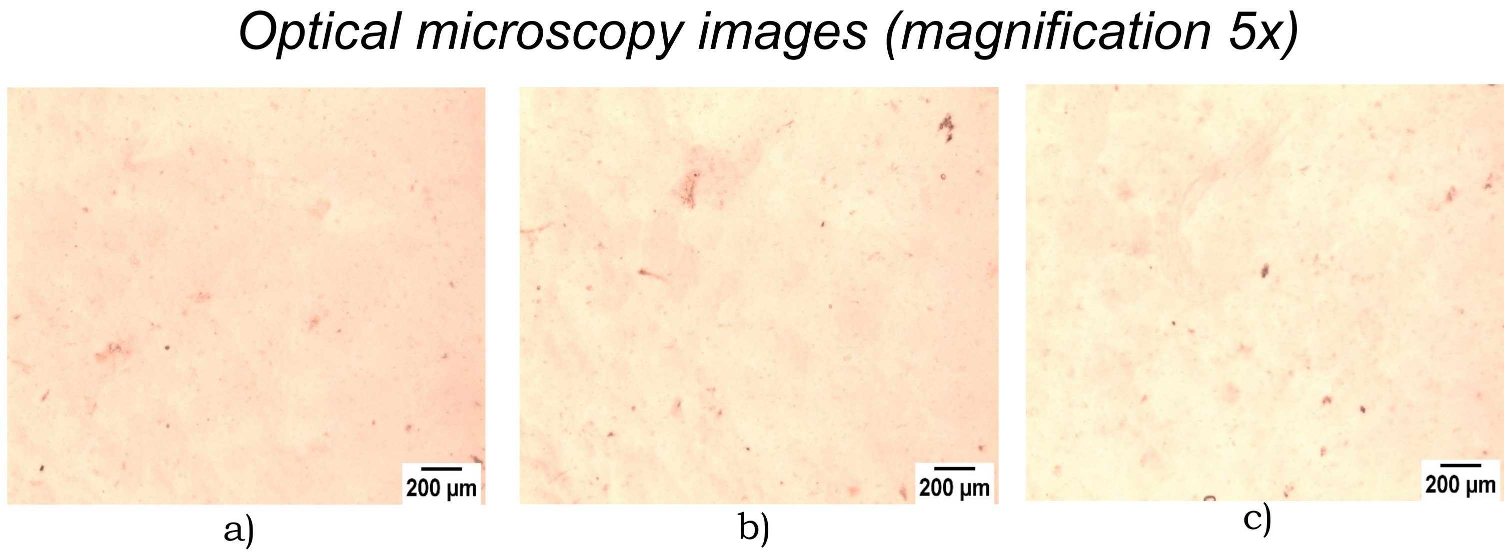
$$X_{BW} = X_{TW} - \frac{Q_{endo}}{Q_f}$$

Results show no significant difference of X_{BW} among hydrogels at different [TiO_2] since TiO_2 does not bind to the polymeric chain the same way as water does.



Morphology investigation

Optical microscopy images (magnification 5x)

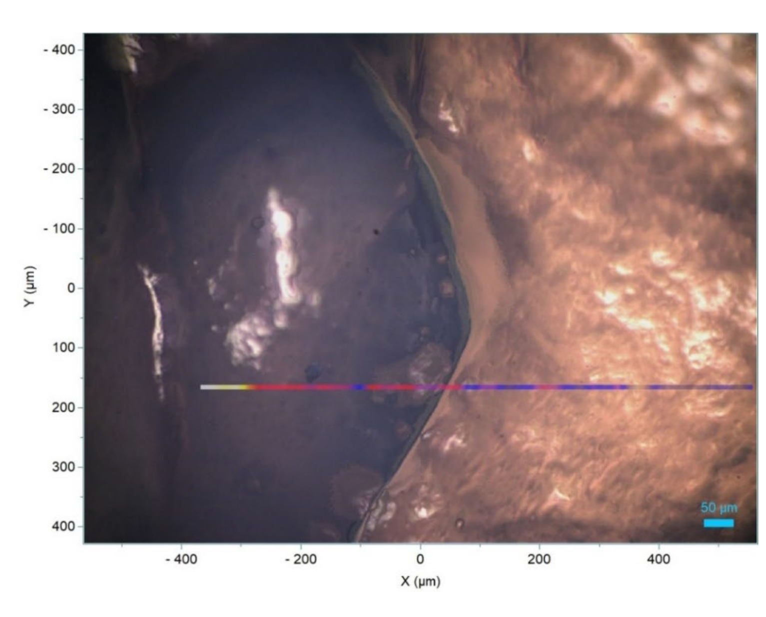


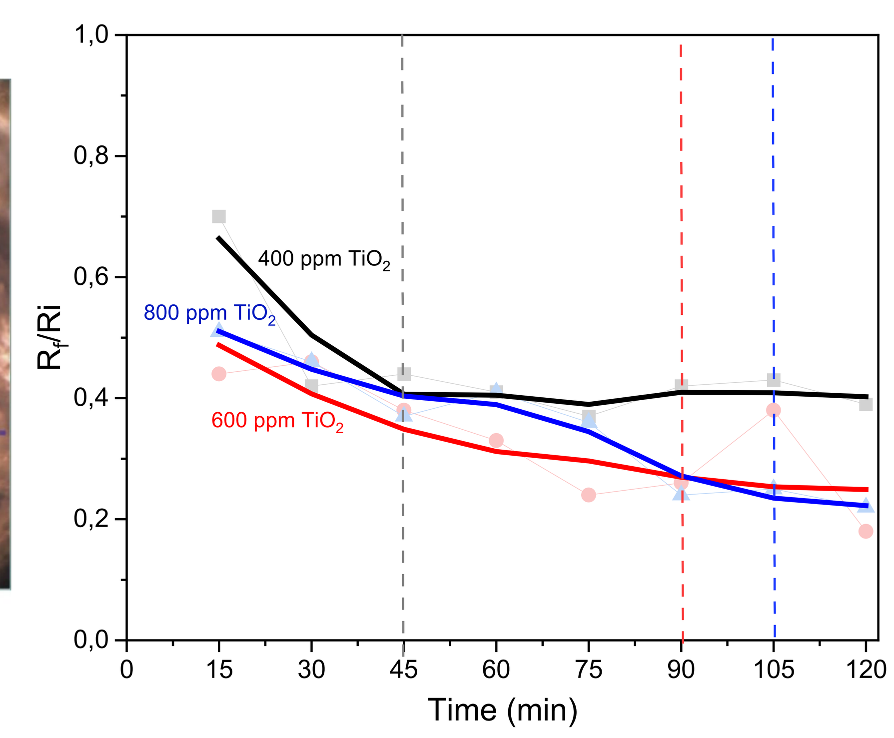
CBP10 hydrogels at (a) 400 ppm, (b) 600 ppm and (c) 800 ppm of TiO2

Aggregates around 10-100 µm. Larger aggregates rarely present in the nanocomposite at 600 and 800 ppm TiO_2 (b, c), reaching up to 300 µm.

Raman spectroscopy of UV-A irradiated gels

Raman spectroscopy along transition lines at the boundary between the non-irradiated (left) and the irradiated portion (right) of the sample.

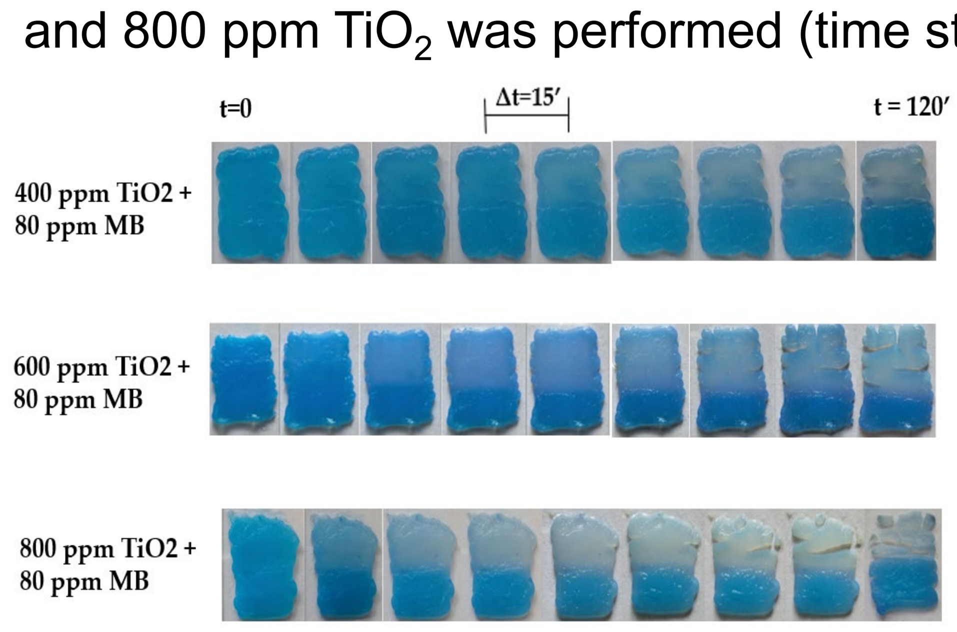


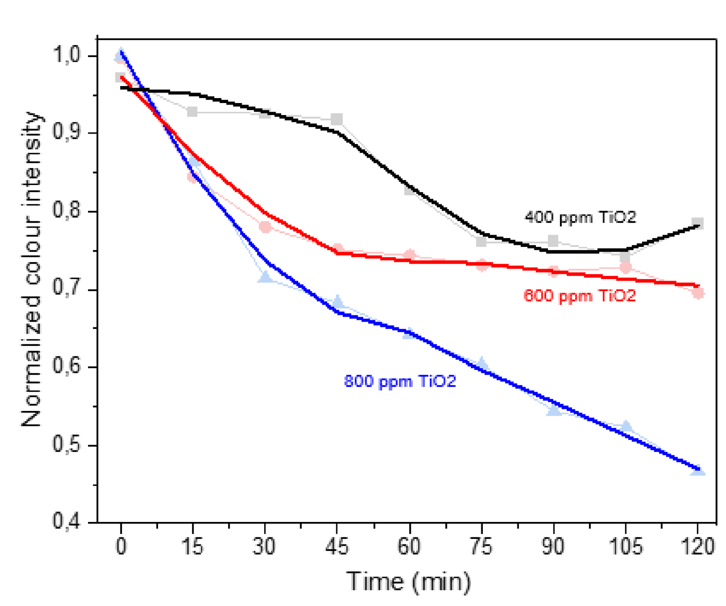


The graph above shows how the ratio between peak areas of MB and water decreases when transitioning from left to right. As expected, the higher the [TiO_2], the greater the decrease. Additionally, the higher the [TiO_2], the longer the exposure needs to be in order for the hydrogels to reach the saturation point.

Colorimetric analysis

Colorimetric analysis of UV-A irradiated hydrogels at 400 ppm, 600 ppm and 800 ppm TiO_2 was performed (time step = 15 minutes).





Results show an increase in dye discoloration at higher [TiO_2], due to the fact that the more TiO_2 the more intense the catalytic degradation of MB.

Conclusions

- Nanocomposite hydrogels with a uniform dispersion of titanium dioxide nanoparticles were successfully prepared. Hydrogel network density is not affected by [TiO_2].
- DSC shows thermal stability up to 100 °C. No significant differences in water content was found.
- Colorimetric analysis and Raman spectroscopy both show stronger catalytic degradation as the content of TiO_2 is increased.

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