

Nanocomposite gels via in-situ photoinitiation and disassembly of TiO₂-Clay composites with polymers applied as UV protective films

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Reagents and Materials

TiO₂ nanoparticles solution were purchased from Dekedaojin (Beijing) Co., Ltd. Clay-NS (Laponite XLG) was purchased from Rockwood Ltd.. All organic reagents in analytical grade, including N, N-dimethylacrylamide (DMAA) and acetic acid (HAc), were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). All materials and reagents were used without further purification.

Characterizations

Elemental analysis: ICP analysis was performed on a Hitachi P4010 plasma spectrometer. The sample was prepared by dissolving 0.01 g dried sample of Micro-TCC into the mixed solution of 20 mL 20% H₂SO₄ and 25 mL concentrated sulfuric acid by heating to 80 °C, then the obtained solution was cooled to room temperature and diluted to 100 mL before measurement.

Mechanical analysis: Compressive measurements were performed on gels with a tensile-compressive tester (FR-108B, Farui Co.). A cylindrical gel sample with diameter of 16 mm and thick of about 6 mm was put on the lower plate and compressed by the upper plate connecting to a load cell (500 N), at a strain rate of 10 mm min⁻¹. Tensile measurements were acquired using a gel sample with a dumbbell shape (20 mm×2 mm×2 mm). The ends of the samples were fixed in the clamps of the tensile-compressive tester and tested at a constant strain rate of 10 mm min⁻¹. The work of extension W_{ex} , which is used to characterize the toughness of the sample, was calculated from the area under the tensile stress-strain curve until fracture.

XRD analysis: The samples are pretreated by freeze-drying and their XRD patterns were obtained on a Bruker Focuss D8 diffractometer with Cu K α radiation. The wide X-ray powder

diffraction is tested from 10-70° with the scanning rate of 0.1 sec step⁻¹ and the increment of 0.02. And the small angle X-ray diffraction is performed from 0.6-2° with the scanning rate of 0.5 degree min⁻¹.

Morphological analysis: The samples for SEM test is pretreated by freeze drying and gold sputtering and observed by a scanning electron microscope (Hitachi S-4800) at a voltage of 1kV. The Micro-TCC samples for TEM test is pretreated by freeze drying and measured by transmission electron microscopy (JEM-2100) at a 200 kV accelerating voltage. For the TEM test of nanocomposite hydrogels, the sample is pretreated through epoxy resin embedding and bio-cutting treatment. It is firstly cut to a cube shape of about 1 × 1 × 1 mm³. The small piece of sample is soaped successively in 50% ethanol (15 min), 70% ethanol (15 min), 90% ethanol (15 min), a mixture of 1:1 90% ethanol and 90% acetone (30 min), a mixture of 1:1 90% acetone and entrapped liquid (12 h), and last in pure entrapped liquid (3 h) at room temperature, to replace the water in hydrogel with entrapped liquid. The treated sample is placed in an oven of 37 °C for 12 h, 45 °C for 12 h and 60 °C for 48 h. Then several pieces with thickness of about 70 nm, are obtained using an ultramicrotome (Leica, German). The pieces of slice are dyed with 3% uranyl acetate. TEM pictures of bio-cutting samples were acquired by JEM-2010 transmission electron microscopy (TEM) at an accelerating voltage of 80 kV.

EPR analysis: EPR measurement of the free radicals was conducted with an EPR Spectrometer (A300, Bruker). In a typical process, DMAA and Micro-TCC suspension (4%) are mixed in the same volume. The mixture was placed in the EPR Spectrometer and irradiated by ultraviolet light for 5 min. As for the signal of OH radical, TiO₂ solution (4%) and DMPO (dimethyl pyridine N-oxide, Electron capture agent) are mixed in the same volume. The mixture was placed in the EPR Spectrometer and irradiated by the ultraviolet light.

NMR for testing monomer conversion: All proton NMR spectra were obtained using a Bruker 400 MHz NMR spectrometer. Dioxane is used as internal standard material to calculate the remaining content of DMAA, as it is stable in the light-induced reaction and shows a single peak at 3.65 ppm. In a typical measurement, DMAA (300 mg, 3.026 mmol), 1,4-dioxane (33.3 mg, 0.378 mmol), Micro-TCC (200 mg) and D₂O (9.4 g) were mixed under vigorous stirring to get a homogenous solution. 0.6 mL of the above solution in the NMR tubes were irradiated by the Xenon lamp (fixed 2.0 mW cm⁻² intensity at 365 nm) for different time.

UV protective test: The transmittance spectra of the TiO₂-based nanocomposite film were measured in a Shimadzu UV-2700 UV-Vis spectrophotometer in the 200-800 nm range. The nanocomposite hydrogel films for the UV-Vis spectra experiments were fabricated by casting precursor solution onto quartz glass panels and being irradiated under UV light for hydrogelation. The thickness of the nanocomposite film is about 200 μm. The UPF values are calculated referring to GB/T 18830-2009: Textiles-Evaluation for solar ultraviolet radiation protective properties. Measurements were performed in a Shimadzu UV-2500 UV-Vis spectrophotometer using an integrating sphere and scanning between 290 and 400 nm with a 5-nm interval at room temperature.

Refractive index test: The samples were placed in a spectrophotometer and the refractive index of the composites was measured by variable angle spectroscopy ellipsometry (VASE, J.A Woollam Co., Inc. W-VASE32TM) on a spin-coated sample on a Si wafer.

Figures

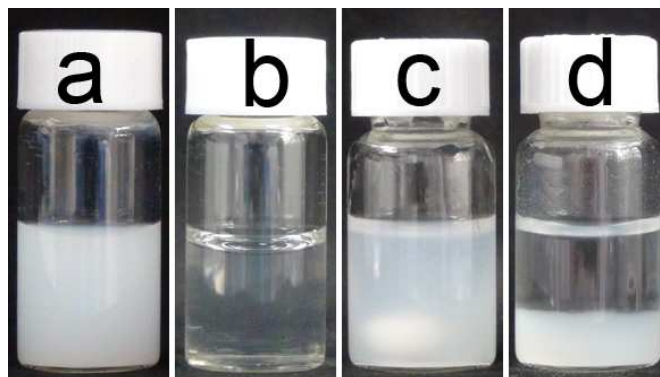


Figure S1. Photographs of precipitation by adding TiO_2 -NP into Clay-NS. (a) TiO_2 nanoparticle dispersion in water (15 wt%). (b) Clay-NS solution (0.5 wt%). (c) Adding TiO_2 NPs dispersion (25 μL) and acetic acid (2.5 μL) into Clay-NS solution (3 mL). (d) the precipitation of Micro-TCC.

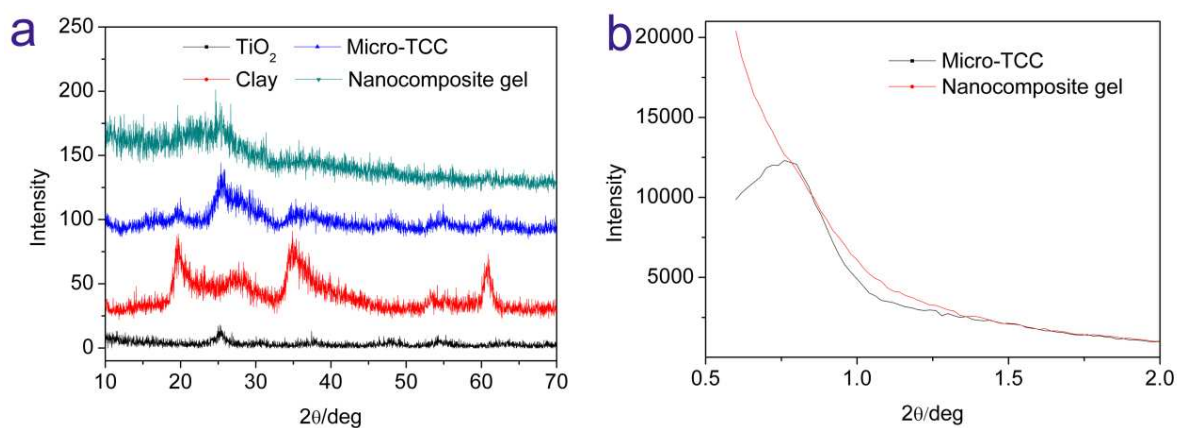


Figure S2. Powder X-ray diffraction patterns for species in preparation of the TiO_2 -based nanocomposite hydrogel (a). SAXD pattern of Micro-TCC and the dried TiO_2 -based nanocomposite hydrogel (b).

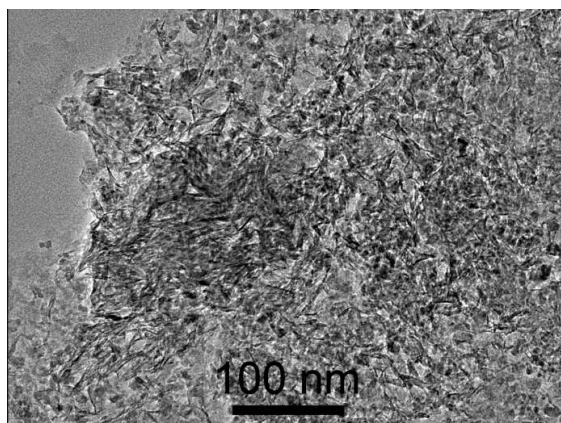


Figure S3. Magnified SEM images of the micrometer-sized TiO_2 -Clay composite (Micro-TCC).

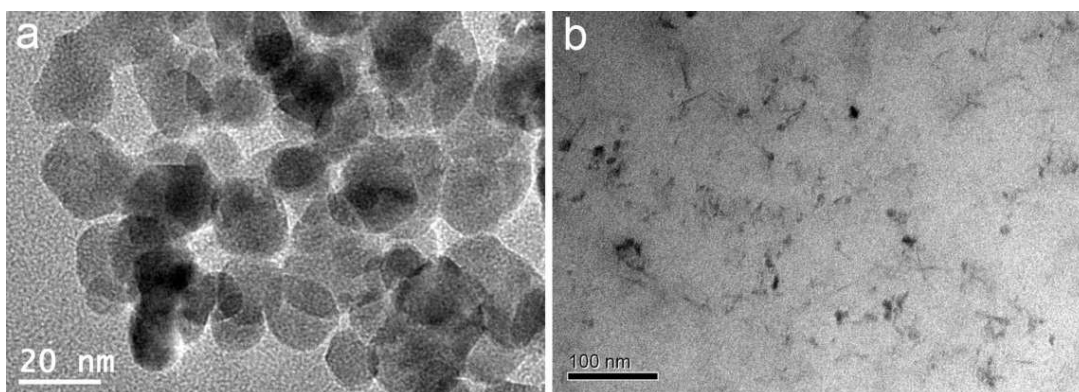


Figure S4. TEM images of TiO_2 -NP and the TiO_2 -based nanocomposite gel.

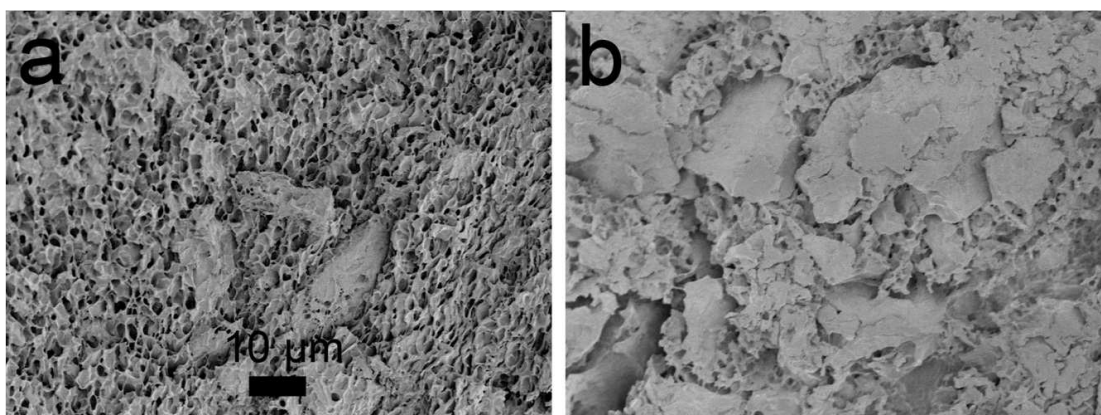


Figure S5. SEM images of the translucent gel (a, with 4% Micro-TCC) and the white gel (b, with 10% Micro-TCC) (The scale bar is the same for (a) and (b)).

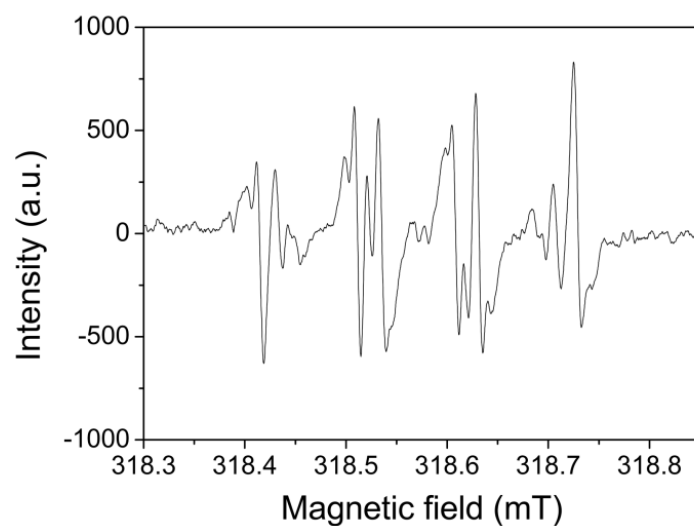


Figure S6. The EPR spectrum of the precursor solution of Micro-TCC and DMAA under UV irradiation.

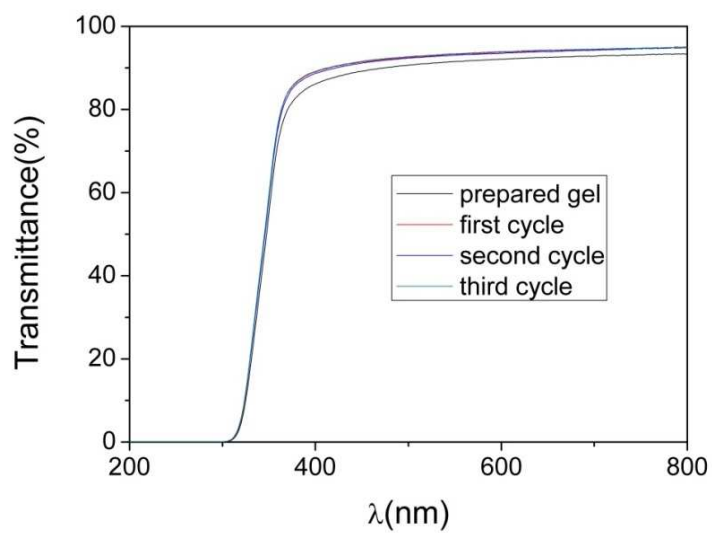


Figure S7. The change of UV adsorption of hydrogel after three swell-drying cycles.

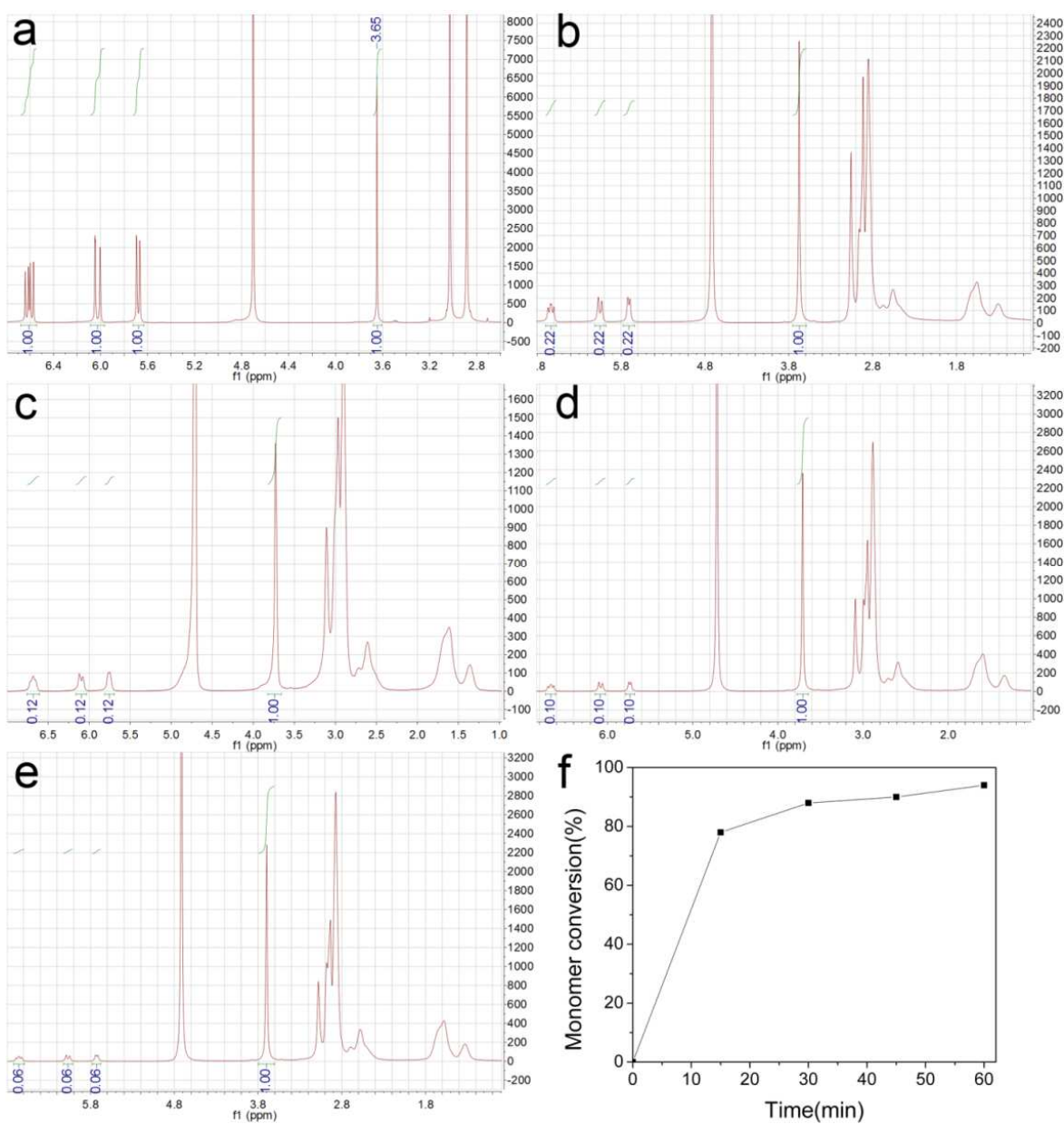


Figure S8. The NMR spectra of the precursor under different reaction time and the conversion of the monomer DMAA. NMR spectra of the precursor containing 2% Micro-TCC and 3% DMAA under different reaction time: 0 min (a); 15 min (b); 30 min (c); 45 min (d); 60 min (e); the conversion of the monomer DMAA (f).

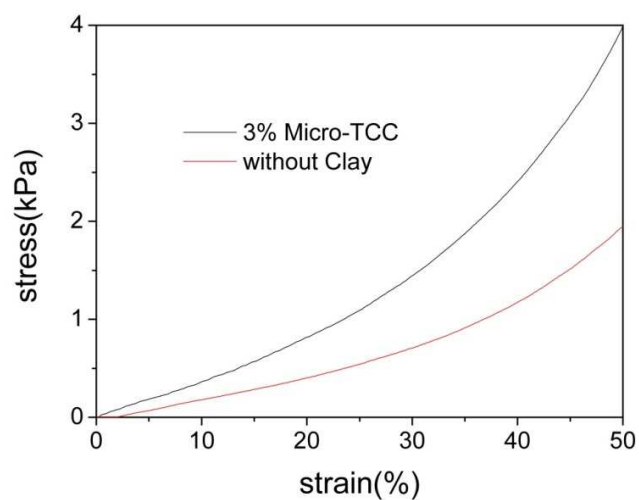


Figure S9. Comparison study of the compressive properties of gels with (3% Micro-TCC and 10% DMAA) and without clay (same content of TiO_2 and 10% DMAA, using N,N'-Methylenebisacrylamide as cross-linker).

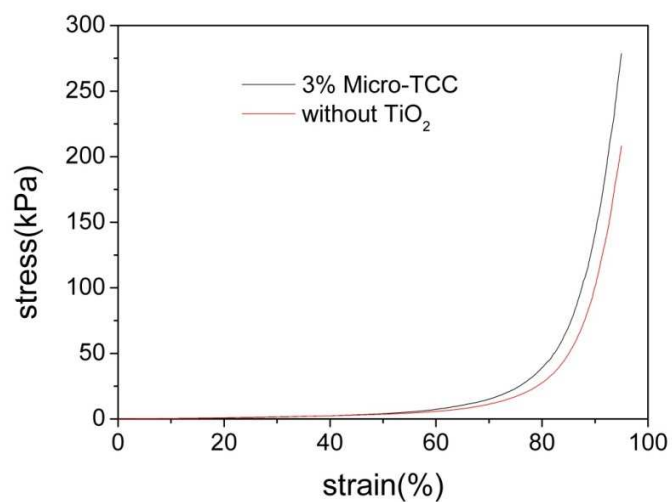


Figure S10. Comparison study of the compressive properties of gels with (3% Micro-TCC and 10% DMAA) and without TiO_2 (same content of clay and 10% DMAA, using 2,2-Diethoxy Acetophenone as photo-initiator).

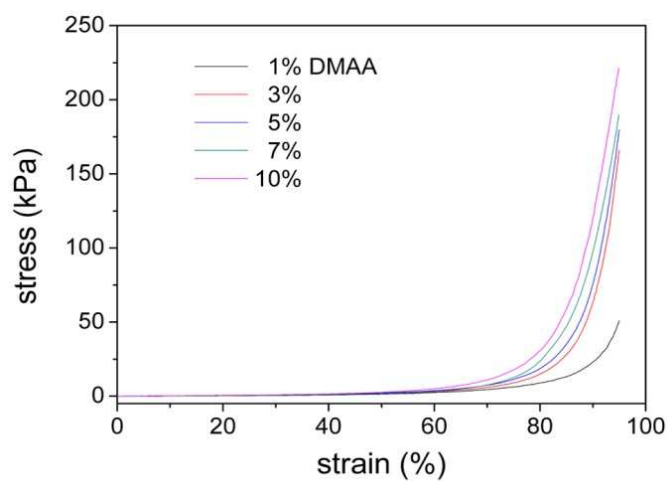


Figure S11. Compressive properties of the TiO_2 -based hydrogels containing 2% Micro-TCC and different DMAA concentrations.

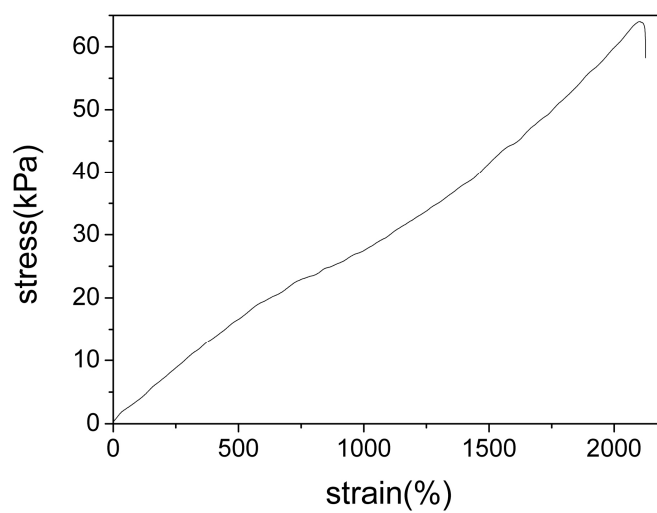


Figure S12. Tensile properties of the selected TiO_2 -based nanocomposite hydrogels containing 2% Micro-TCC and 10% DMAA.

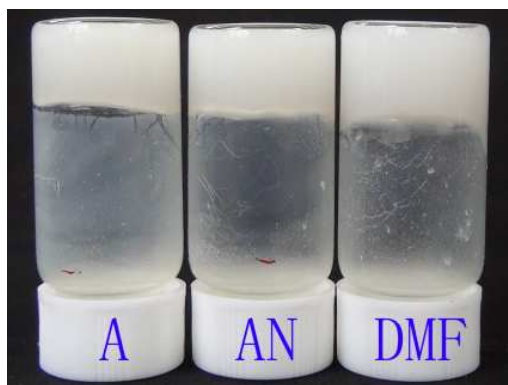


Figure S13. Optical images of the nanocomposite gels with water mixing solvent (1:1 volume ratio) of acetone, acetonitrile, and dimethylamide (A=acetone, AN=acetonitrile, DMF= dimethylformamide).

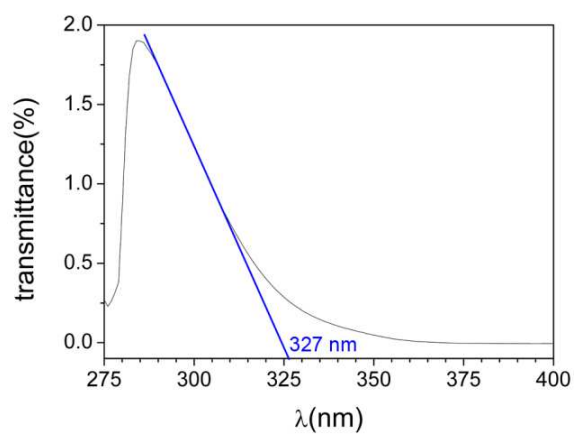


Figure S14. UV absorption edge of the TiO₂-NP.

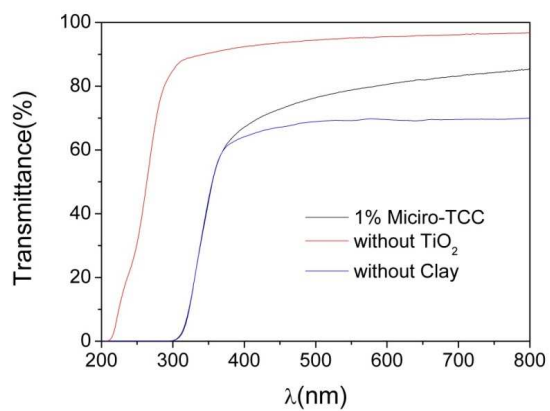


Figure S15. Effect of TiO₂ and clay to the UV absorption curves of the nanocomposite gels.