

Supplementary Information

Semiconductor nanoparticles based hydrogels prepared by self-initiated polymerization under sunlight even visible-light

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1. Materials.

TiO₂, ZnO, Fe₂O₃, ZrO₂ solution were purchased from Dekedaojin (Beijing) Co., Ltd. Clay-NS was purchased from Rockwood Ltd. (Laponite XLG). Their DRS, XRD and TEM characterizations of semiconductor materials are showed as follow.

Synthesis of water-soluble CdTe quantum dots:

The synthesis of CdTe QDs was performed according to the reference^[S1] with some modification. 46 mg tellurium powder and 2 ml Milli-Q water under nitrogen atmosphere. The reaction was kept on for several hours until all tellurium powder was dissolved. 0.092 g (0.5 mmol) of CdCl₂ and 0.092 mg (1 mmol) of thioglycolic acid were dissolved in 100 mL Milli-Q water, followed by adjusting pH to 8.2 by addition of 1 M NaOH solution. The mixture was deaerated by N₂ bubbling for 30 min. Then NaTeH solution (0.062 mmol) was quickly injected into the mixture under vigorous stirring, followed by refluxing the mixture for 2 h under open-air conditions.

Synthesis of SnO₂ nanoparticles:

The synthesis of SnO₂ nanoparticles was performed according to the reference^[S2] with some modification. 10 mL of 0.2 mol/L SnCl₄ solution was added to a beaker. The PH of the solution was adjusted to 1.45 with 10 mol/L NaOH solution. Then the precursor was transfer to a Teflon-lined stainless autoclave with a capacity of 15 mL. The autoclave was sealed and maintained at 140 °C for 4 h and then cooled to room temperature naturally. The precipitation was separated by centrifugation and washed with deionized water and absolute ethanol several times, respectively. Finally, the as-obtained products were dispersed in a proper content of water for further use.

2. Hydrogelation under different conditions.

Hydrogelation under sunlight

The hydrogelation experiment (Supplementary Fig. S2) induced by various semiconductor nanoparticles under sunlight was done in 28 May, 11:30-12:30 noon.

Typically, DMAA (500 mg) is added to a stirred suspension of Clay-NS (500 mg) in water (9 mL). After 10 minutes, the suspension turns to a clear solution, thereafter 0.06 mL of an aqueous suspension of ZnO (10% in water) is added to 1 mL of the above solution with severe shocking. The final transparent and elastic ZnO-NC gel is prepared by the last irradiation with sunshine for 1 h (average 2.0 mW cm^{-2} intensity at 365 nm).

Hydrogelation under Xenon lamp

Xenon lamp with an AM 1.5 G filter (Model 91160, 300W, Newport, USA, Full Spectrum Solar Simulator) is used to simulated sunlight in laboratory. Typically, DMAA (500 mg) is added to a stirred suspension of Clay-NS (500 mg) in water (9 mL). After 10 minutes, the suspension turns to a clear solution, thereafter 0.06 mL of an aqueous suspension of ZnO (10% in water) is added to 1 mL of the above solution with severe shocking. The final transparent and elastic ZnO-NC gel is prepared by the Xenon lamp irradiation for 1 h (average 2.0 mW cm^{-2} intensity at 365 nm).

Hydrogelation under visible light

The Xenon lamp with a filter cutting off the light below 420 nm is used to get the visible light. Typically, DMAA (300 mg) is added to a stirred suspension of Clay-NS (300 mg) in water (9.4 mL). After 10 minutes, the suspension turns to a clear solution. Thereafter 0.2 mL of CdTe solution (0.15% in water) is added to 2 mL of the above solution with severe shocking. The final transparent and elastic CdTe-NC gel is prepared by visible light irradiation for 1 h.

3. Pre-treatments and characterizations.

Pre-treatment of SEM samples

The hydrogel is cut to a cube shape of about $2 \times 2 \times 2 \text{ mm}^3$. The small piece of sample is soaped successively in 50% ethanol (15 min), 70% ethanol (15 min), 90% ethanol (15 min), 100% ethanol (15 min), a mixture of 1:1 ethanol and isoamyl acetate (30 min) and last in pure isoamyl acetate (30 min) to replace the water in hydrogel with isoamyl acetate. The treated sample is dried by Critical point drying (Critical Point Dryer CPD, K850, Quorum) and observed by SEM (Hitachi S-4800) at a voltage of 3kV.

Pre-treatment of TEM samples

The hydrogel is cut to a cube shape of about $1 \times 1 \times 1 \text{ mm}^3$. 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 and observed by TEM (JEM-2010, JEOL) at an accelerating voltage of 120 KV.

GPC measurement

The molecular weight of polymer was got by Gel Permeation Chromatography measurement (Waters 2695, GPC). Typically, DMAA (3%), TiO₂ or ZnO (0.2%) and H₂O (97%) are mixed under vigorous stirring. The mixture is irradiated by Xenon lamp with AM 1.5 G filter for 1 h and then centrifuged at 8000 rpm/min to remove the TiO₂ nanoparticles. The upper clear liquid is diluted, flowed through 4.5 μm membrane and tested by the GPC measurement. The concentration of DMAA or TiO₂ could be adjusted by altering the amount of the reactants.

DLS measurement

The DLS results were obtained on a Zetasizer instrument (Nano-ZS, Malvern). In the products analysis in the reaction process, DMAA (300 mg), Clay-NS (300 mg), TiO₂ solution (0.1 mL of 10% solution) and H₂O (9.4 mL) are mixed under vigorous stirring to get a homogenous solution. Six sample pools for DLS measurement, each containing about 2 mL of the above solution are irradiated by Xenon lamp with AM 1.5 G filter for different time 0 min, 10 min, 15 min, 30 min, 45 min and 60 min.^[S3] The gelation process is showed in Figure 2b.

NMR measurement

All proton NMR spectra were obtained using a Bruker 400 MHz NMR spectrometer. In our conversion calculation experiments, dioxane is used as internal standard material to calculate the remaining content of DMAA, because 1,4-dioxane has no change in the light-induced reaction and its only peak at 3.65 ppm separates from other peaks of DMAA and the products. In a typical measurement, DMAA (300 mg, 3.026 mmol), 1,4-dioxane (33.3 mg, 0.378 mmol), Clay-NS (300 mg), TiO₂ (100 μ L of 10% in D₂O) and D₂O (9.4 g) were mixed under vigorous stirring to get a homogenous solution. Six NMR tubes, each containing 0.6 mL of the above solution were irradiated by the Xenon lamp with AM 1.5 G filter (fixed 2.0 mW cm⁻² intensity at 365 nm) for different time 0 min, 10min, 15 min, 30 min, 45 min and 60 min. In the control experiment without TiO₂, a precursor solution with DMAA (300 mg, 3.026 mmol), dioxane (33.3 mg, 0.378 mmol), Clay-NS (300 mg) and D₂O (9.4 g), was placed at the same condition for 1h.

In the mechanism study experiment, the precursor is consisted of DMAA (300mg), TiO₂ solution (200 μ L of 10%) and water (9.7mL). The polymerization was carried out under Xenon lamp with AM 1.5 G filter (fixed 2.0 mW cm⁻² intensity at 365 nm) for 1h. The suspended particulate matters were separated from the viscous solution. The PDMAA polymer in the solution was obtained by freeze-drying and then dissolved in Tetrahydrofuran-D8 for NMR test. The suspended particles, a mixture of TiO₂ and adsorbed PDMAA, were washed by water for two times and then freeze-dried. Then

Tetrahydrofuran-D8 was used to dissolve the PDMAA from the TiO₂ particles, followed by ultra centrifugation to remove TiO₂, and NMR spectrometer was used to analyze the sample.

EPR (Electron Paramagnetic Resonance) measurement

The EPR results were obtained by an EPR Spectrometer (A300, Bruker). In a typical process, DMAA and TiO₂ solution (10%) are mixed in the same volume. The mixture was placed in the EPR Spectrometer and irradiated by ultraviolet light for different time. The visible light induced free radical measurement is shown as follows. DMAA and CdTe solution (0.15%) are mixed in the same volume. The mixture was placed in the EPR Spectrometer and irradiated by an in-situ visible light ($\geq 420\text{nm}$). As for the signal of OH radical, TiO₂ solution (10%) 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 in-situ ultraviolet light.

SAXS (Small Angle X-ray Scattering) measurement

The SAXS measurements were completed in the Shanghai Synchrotron Radiation Facility (SSRF), Shanghai, China, with a small angle X-ray scattering station (BL16B1) with a long-slit collimation system. Two dimensional diffraction patterns are recorded using an image intensified CCD detector. The experiments are carried out with the radiation of X-ray with the wavelength of $\lambda = 1.24 \text{ \AA}$ at room temperature (25 °C). The intensity profiles are output as the plot of scattering intensity (I) versus scattering vector, $q = (4\pi/\lambda) \sin(\theta/2)$ ($\theta =$ scattering angle).^[S4] The final samples (3% of Clay-NS, 3% of DMAA, 94% of H₂O and 0.1% of TiO₂) with different irradiated time by the Xenon lamp with AM 1.5 G filter from 0 to 60 min, are all filled in an ample pool with a thickness of 2 mm, and placed in the light path.

UV-vis spectra and Photoluminescence (PL) spectra measurement

The UV-vis spectra and Photoluminescence (PL) spectra were obtained on a UV-vis spectrophotometer (Agilent 8453) and a Fluorescence spectrometer (Hitachi F-7000),

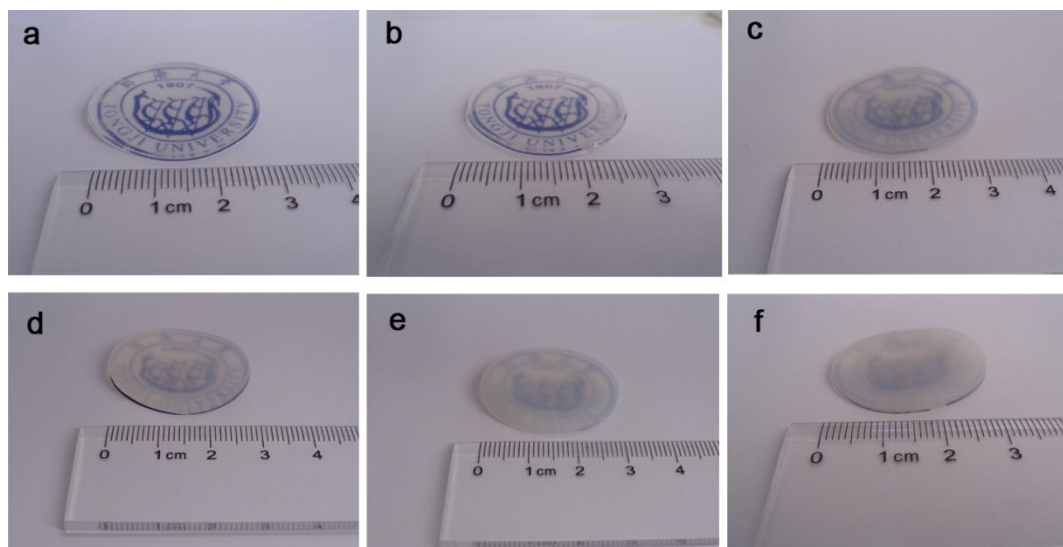
respectively. The excitation and emission slit width were both 10 nm. DMAA (300 mg) is added to a stirred suspension of Clay-NS (300 mg) in water (9.4 mL). After 10 minutes, the suspension turns to a clear solution and then the pH of the solution is adjusted to 8.0 by addition of 0.1 M acetic acid solution. Thereafter 0.2 mL of CdTe solution (0.15% in water) is added to the previous 2 mL solution with vigorous stirring and the mixture was placed in a quartz cell (10 mm) for the UV-vis and PL measurement. Then the quartz cell was put under the visible light for 1 h irradiation. The UV-vis and PL results of the final transparent and elastic CdTe-NC gel in quartz cell were measured the same way.

4. Photocatalytic activity of TiO₂-NC hydrogel

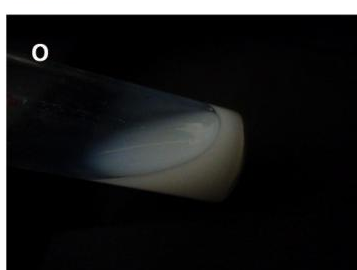
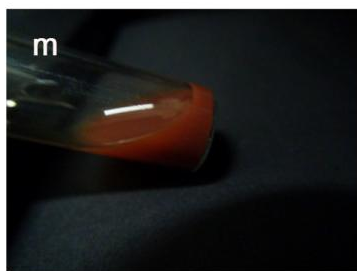
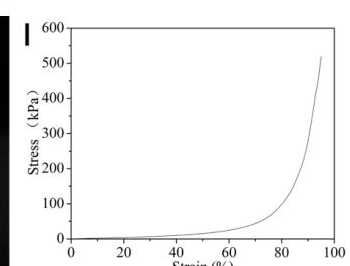
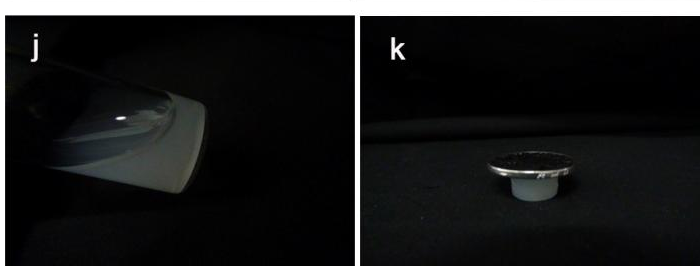
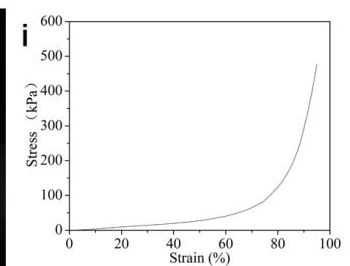
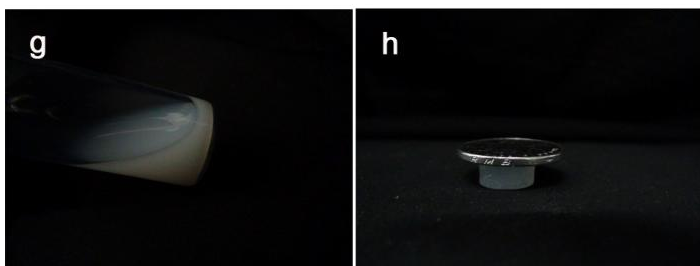
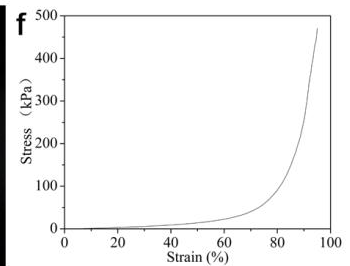
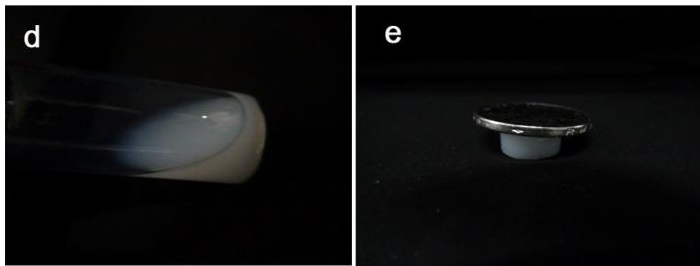
The photocatalytic activity of the TiO₂-NC hydrogel for the decomposition of methylene blue (MB) in aqueous solution is performed in a system designed below. A mixture of 800 mL of 20 mg/L MB aqueous solution and 2 g of TiO₂-NC hydrogel sample (dried mass of 0.192g) are put in a 1L breaker. The above solution is magnetically stirred and the TiO₂-NC hydrogel sample is fixed by yard nets. After a given time, about 2 mL of the mixture is withdrawn. The concentration of MB solution is determined by measuring its absorption in the main absorbance centered at 663 nm.

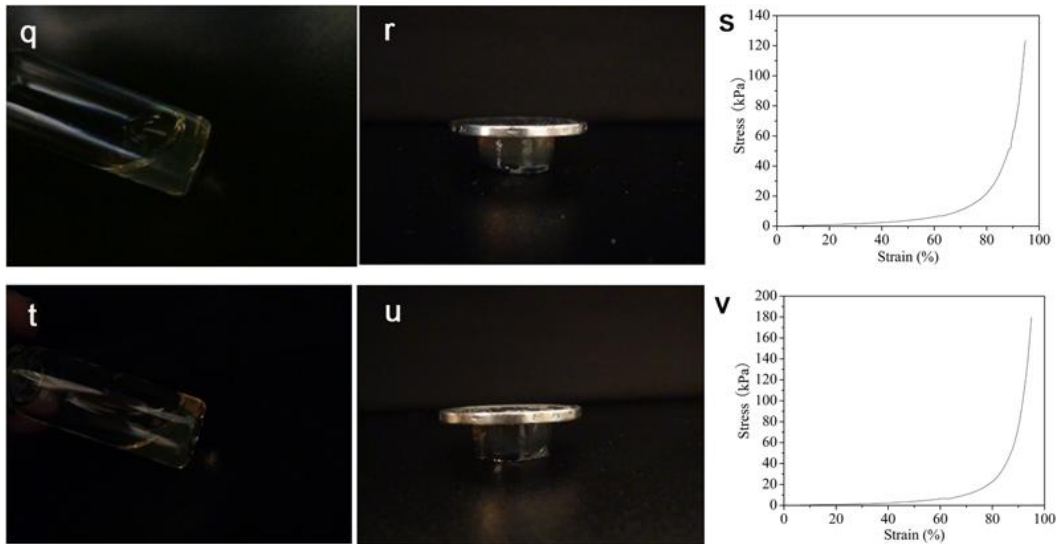
The dark blue gel is put in 5 weight times water and irradiated by a 300 W middle-pressure Hg-lamp (λ_{\max} =365 nm) for 2 h. The reused TiO₂-NC hydrogel can adsorb the methylene blue and be re-treated by the immobilized photocatalyst. The second and third-time absorption amounts are measured as the same method. Acid fuchsin also can be captured and degraded by the TiO₂-NC hydrogel. The control experimental is designed to demonstrate the role of TiO₂ nanoparticles in the hydrogel. Traditional DMAA-clay gel, obtained according to Haraguchi's method^[55], was performed to adsorb and degraded the MB the same as above. Without TiO₂ in the hydrogel, the organic molecular could not be well degraded under the same UV light irradiation.

5. Figures

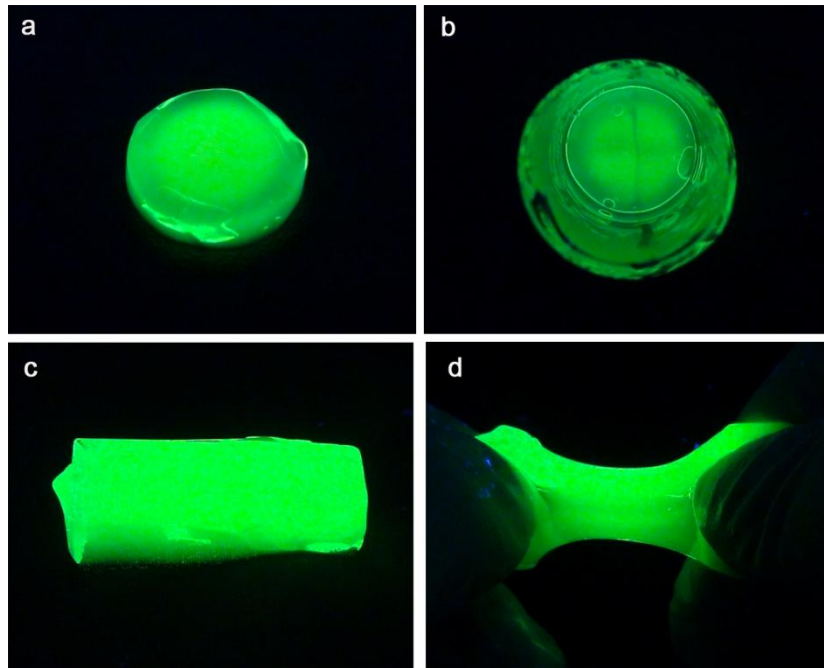


Supplementary Figure S1 | Photographs of ZnO-NC hydrogels. The original precursors include the 5% DMAA, 5% clay and 90% H₂O) with different ZnO contents: 0.2% (a), 0.4% (b), 0.6% (c), 0.8% (d), 1% (e), 2% (f). The thickness is about 2 mm.

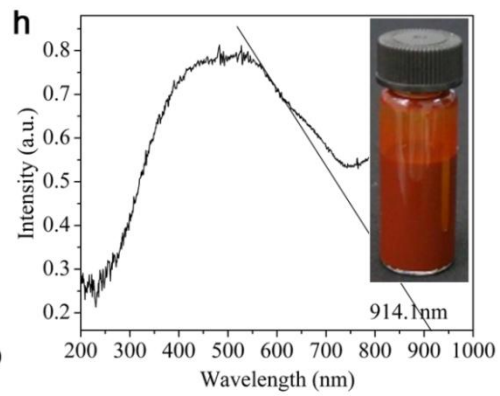
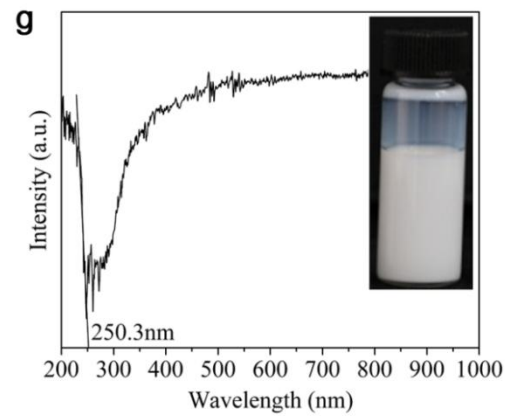
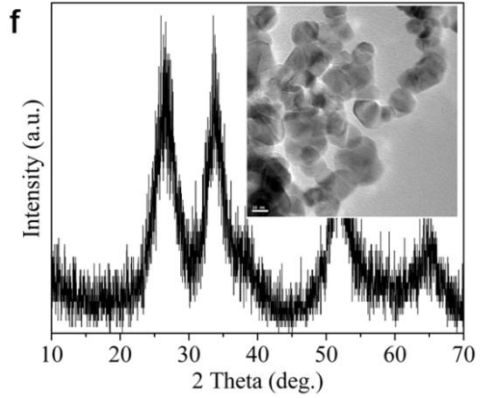
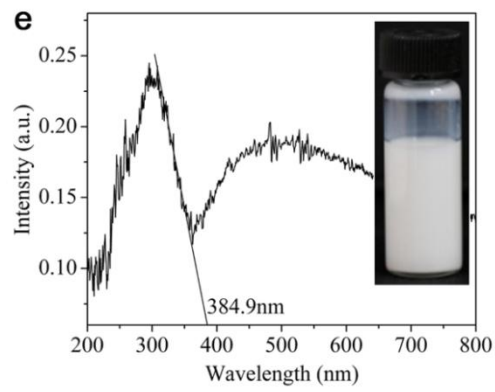
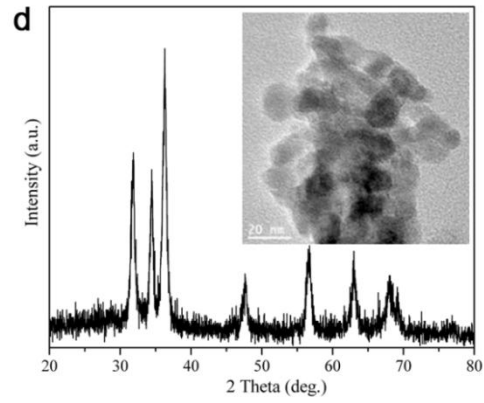
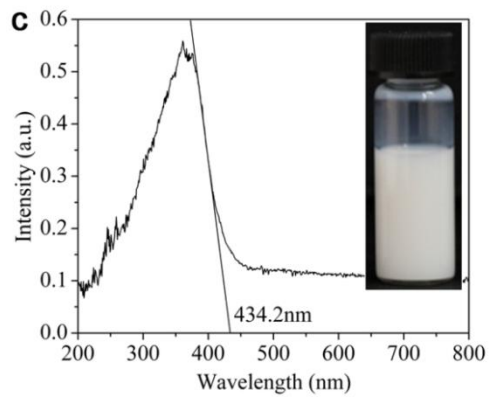
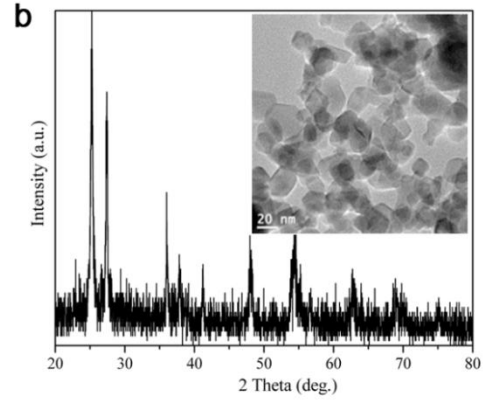
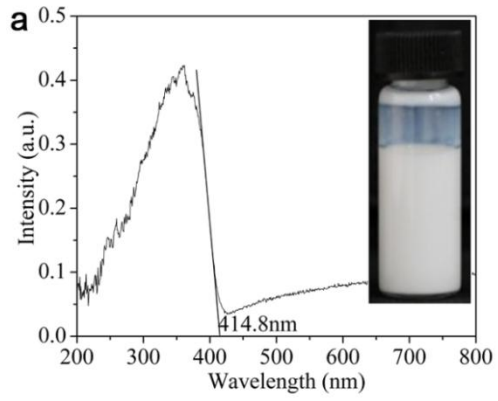


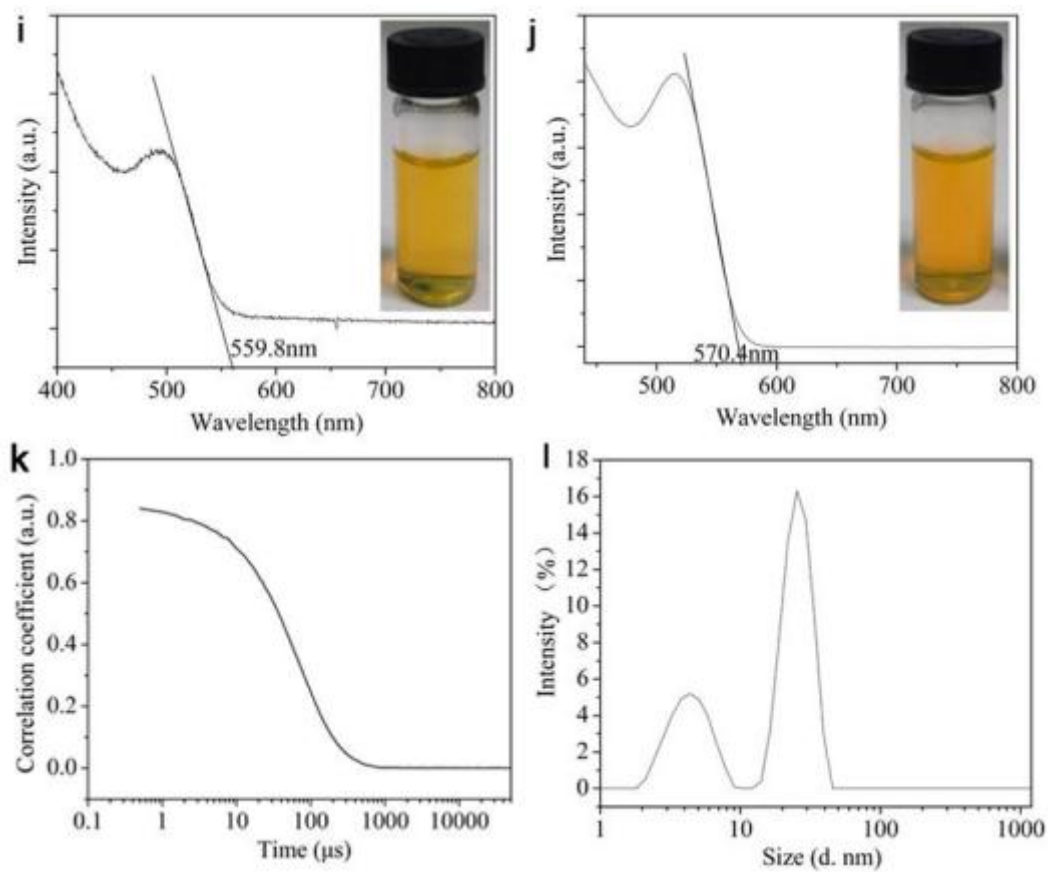


Supplementary Figure S2 | The hydrogel preparation via sunlight irradiations. The functional NC hydrogels induced by sun light ($\approx 2.0 \text{ mW cm}^{-2}$ at 365 nm) for 0 min (a), 30min (b), 60 min (c). The photographs of TiO_2 (d-f), ZnO (g-i), SnO_2 (j-l), Fe_2O_3 (m, n), ZrO_2 (o, p), CdTe (q-s), and CdSe (t-v) -NC hydrogels before or after the gelation and their compressive curves.

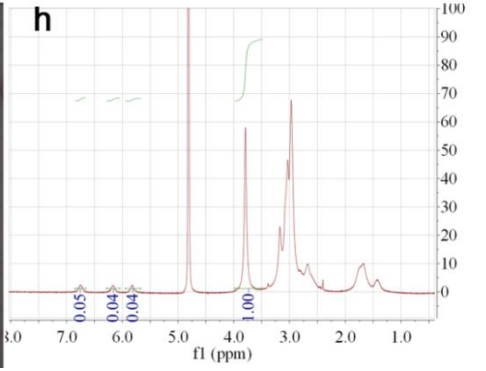
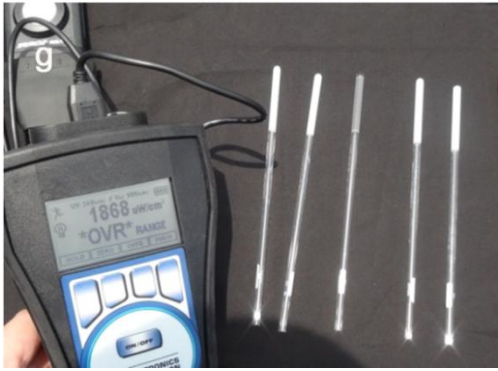
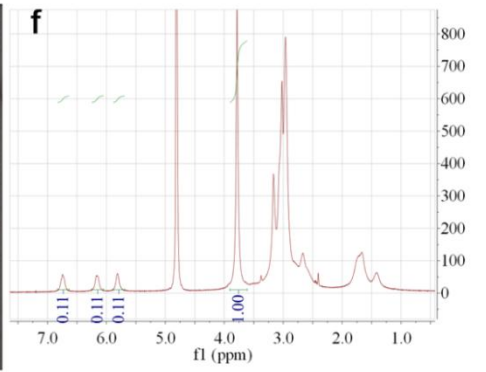
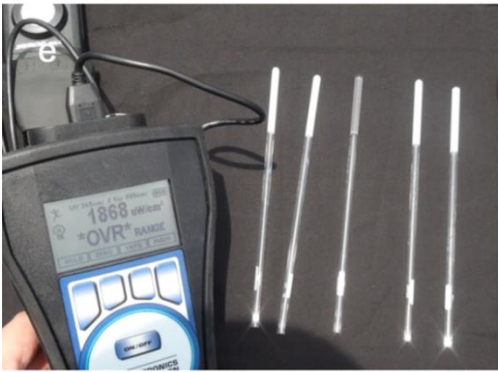
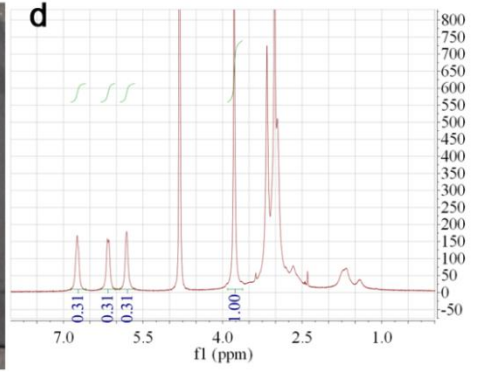
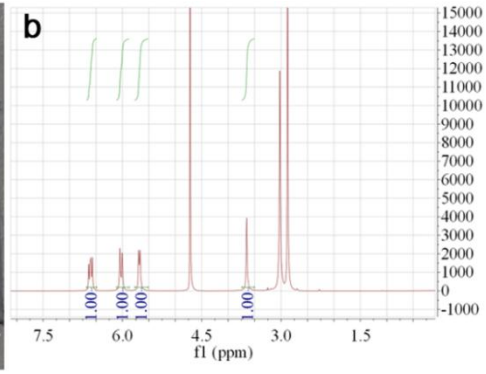
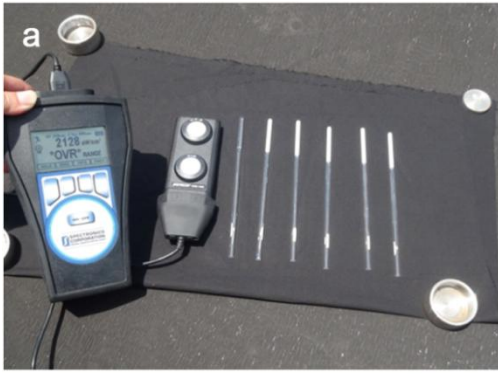


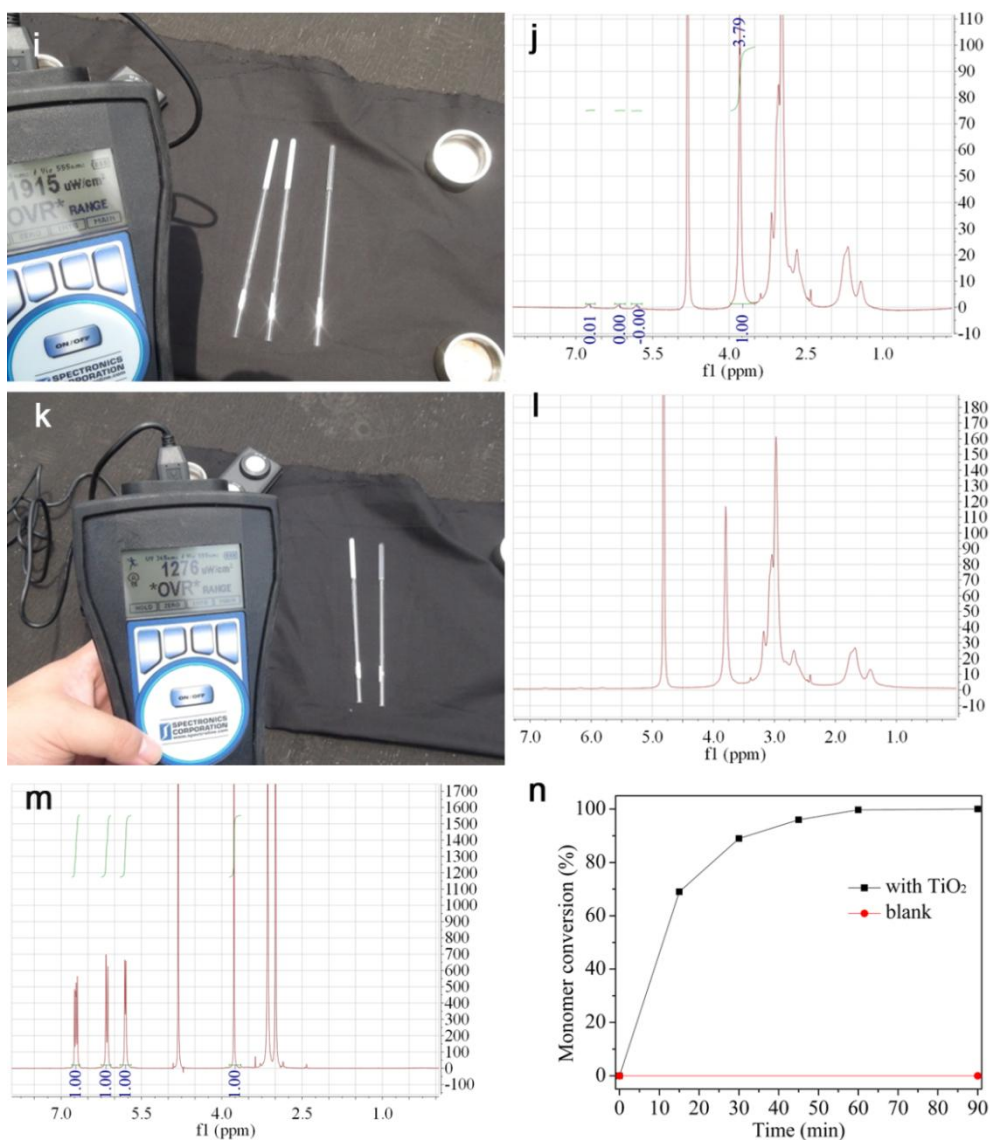
Supplementary Figure S3 | Photographs of CdTe-NC hydrogels (containing 3% DMAA, 3% clay ,94% H₂O and 0.015% CdTe). Original cylindrical hydrogel (a), after 95% strain of compression (b), Original cuboid shaped hydrogel (c), pulled by hands (d).



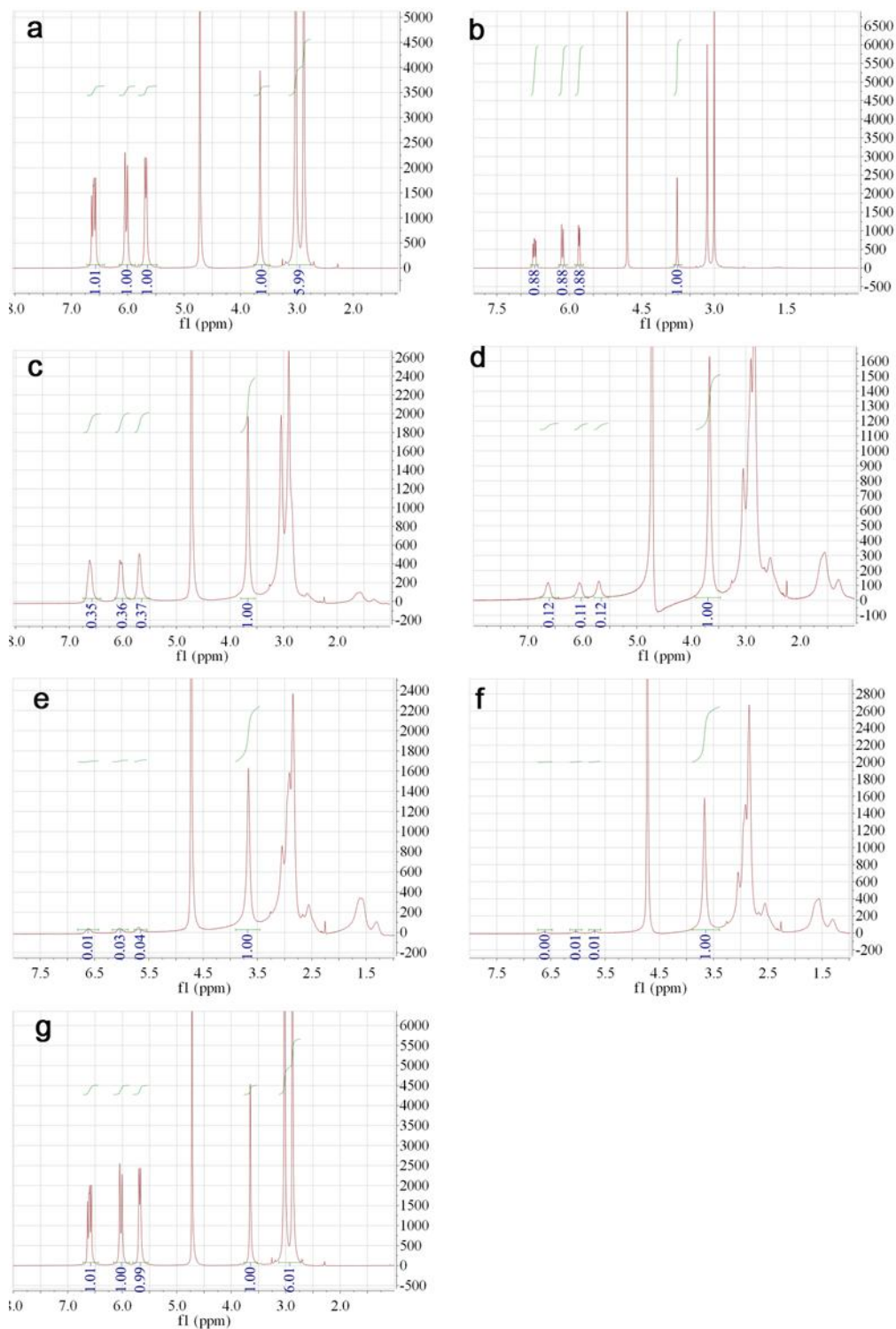


Supplementary Figure S4 | The DRS, XRD, UV-vis and TEM analysis and photographs of various semiconductor nanoparticles: TiO₂ (a, b), ZnO (c, d), SnO₂ (e, f), ZrO₂ (g), Fe₂O₃ (h), CdTe (i), and CdSe (j), and the size of Clay-NS by DLS results (k, l).

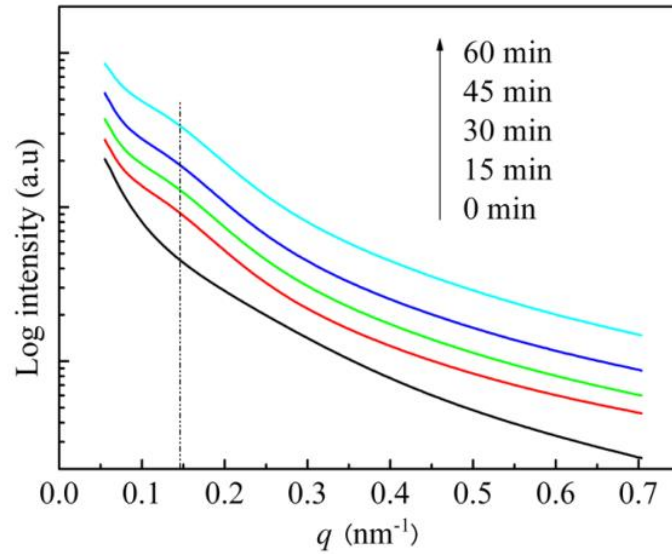




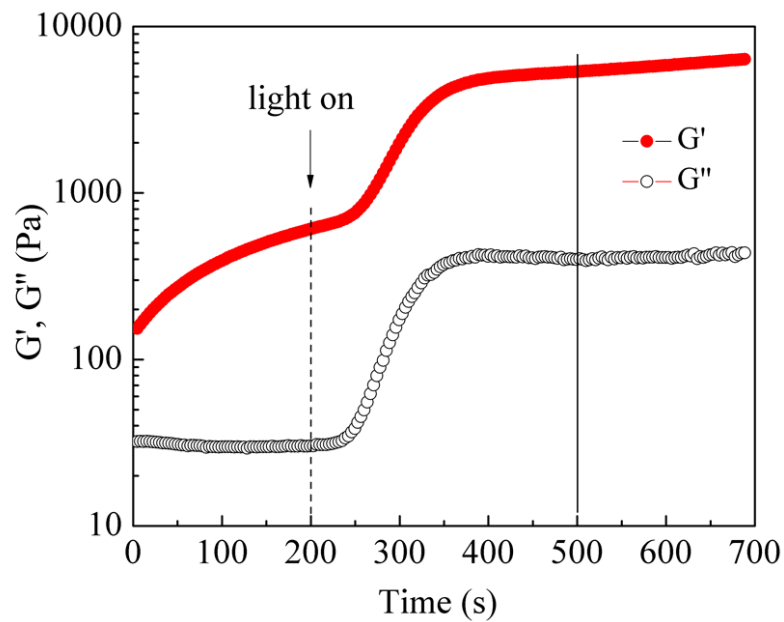
Supplementary Figure S5 | The conversion of monomers under sunlight. Photographs and NMR spectra of the precursor in the presence of 0.2% TiO_2 , under different reaction time: 0 min (a, b); 15 min (c, d); 30 min (e, f); 45 min (g, h); 60 min (i, j); 90 min (k, l); 90 min without TiO_2 (m). The monomer conversion in the hydrogel is calculated using dioxane as internal standard material (n).



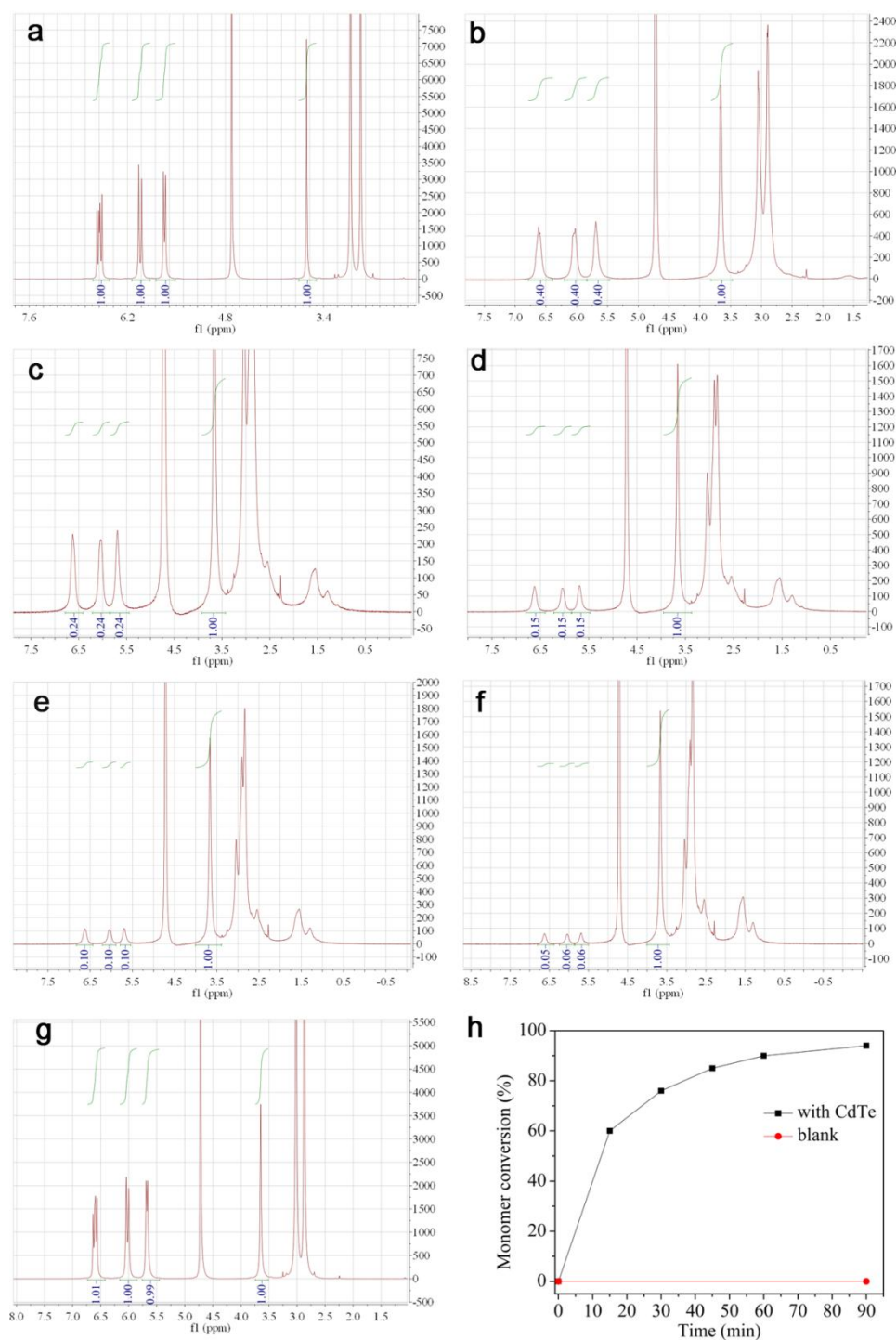
Supplementary Figure S6 | The NMR spectra of samples under Xenon lamp. The precursor was consisted of 3% DMAA, 3% clay ,94% D₂O and 0.1% TiO₂ under different reaction time: 0 min (a); 10 min (b); 15 min (c); 30 min (d); 45 min (e); 60 min (f); without TiO₂ for 60 min (g).



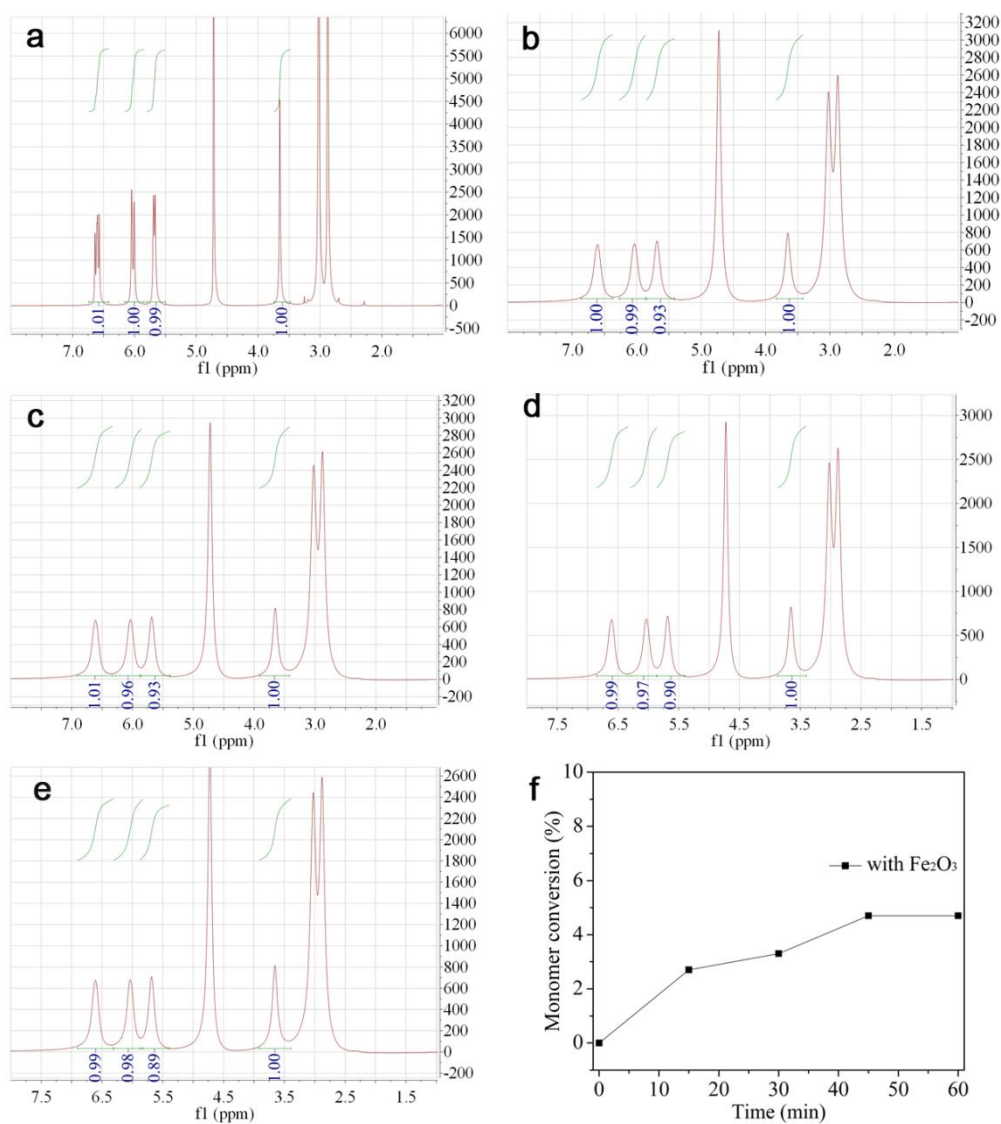
Supplementary Figure S7 | Small-angle X-ray scattering (SAXS) result of samples irradiated by Xenon lamp for different time. The precursor is consisted of 3% DMAA, 3% clay, 94% H₂O and 0.1% TiO₂.



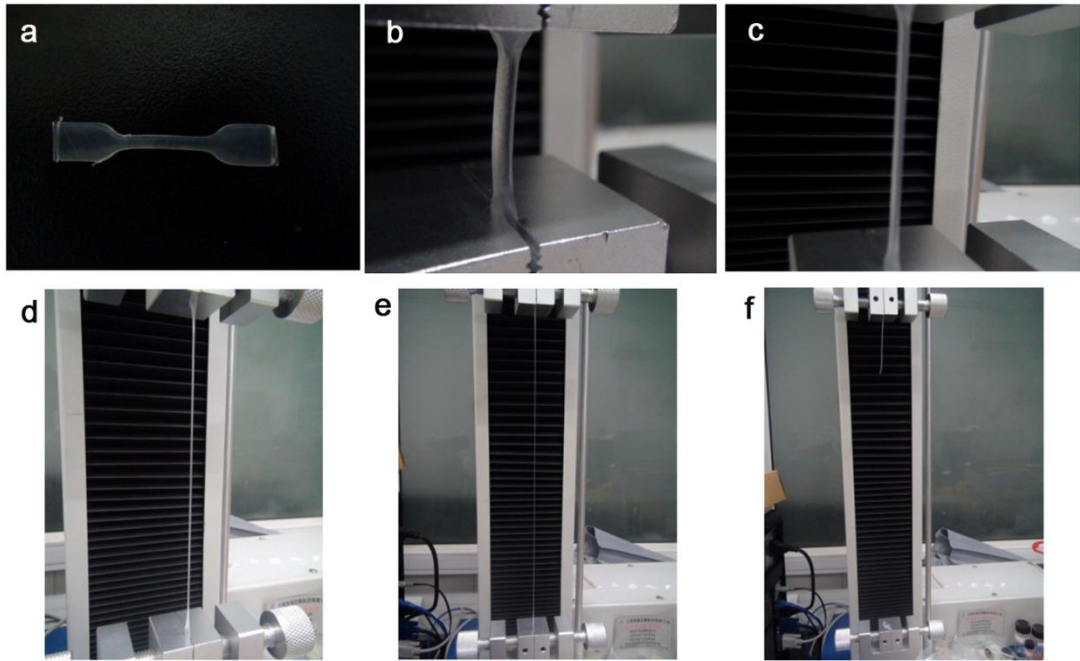
Supplementary Figure S8 | *In situ* rheological measurement irradiated by strong ultraviolet light (UVA=10 mW cm⁻²). The precursor is consisted of 5% DMAA, 5% clay, 90% H₂O and 0.2% ZnO.



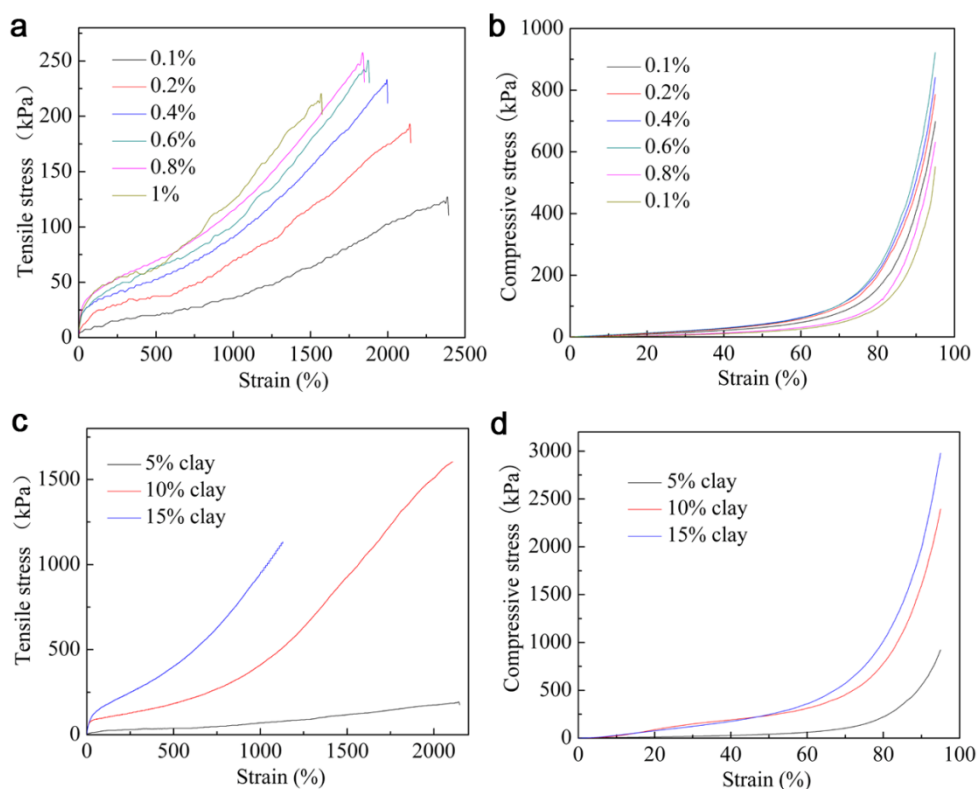
Supplementary Figure S9 | The conversion of monomers under visible light in the present of CdTe. NMR spectra of the precursor containing 3% DMAA, 3% clay ,94% D₂O and 0.015% CdTe, under different reaction time: 0 min (a); 15 min (b); 30 min (c); 45 min (d); 60 min (e); 90 min (f); without CdTe for 90 min (g). The monomer conversion in the hydrogel is calculated using dioxane as internal standard material (h).



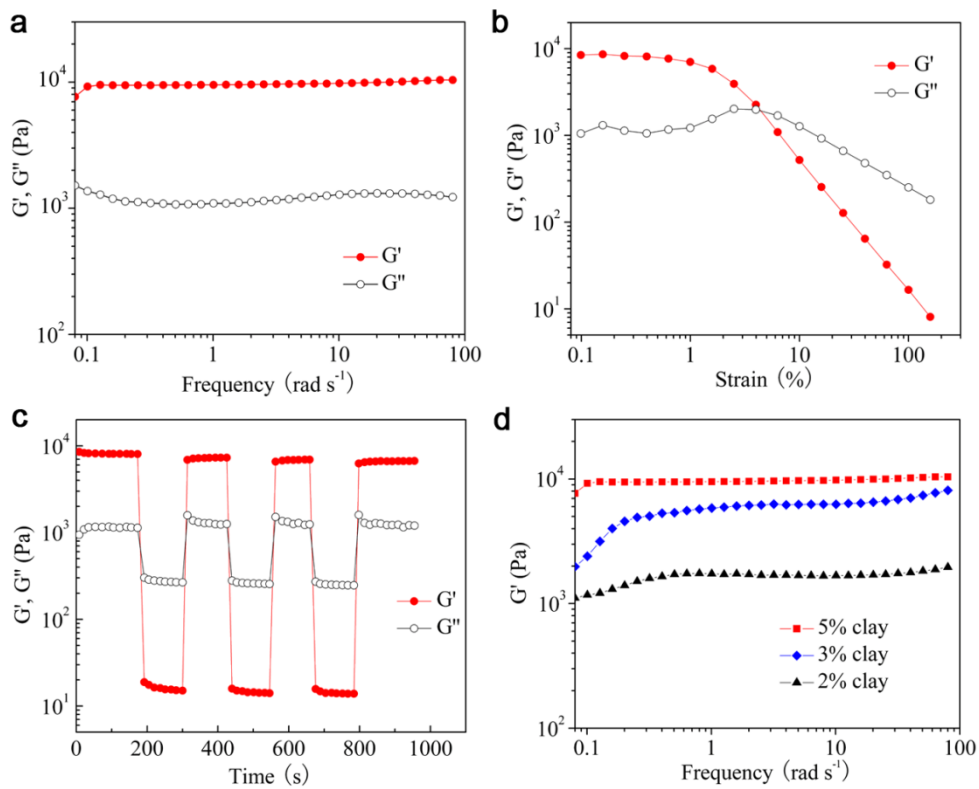
Supplementary Figure S10 | The conversion of monomers under Xenon lamp in the present of Fe_2O_3 . NMR spectra of the precursor containing 3% DMAA, 3% clay ,94% D_2O and 0.2% Fe_2O_3 , under different reaction time: 0 min (a); 15 min (b); 30 min (c); 45 min (d); 60 min (e) and the monomer conversion (f).



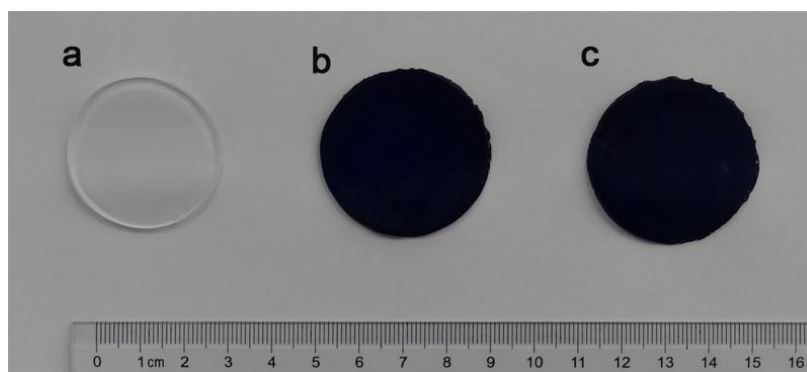
Supplementary Figure S11 | ZnO-NC Hydrogel in tensile process. Sequential photographs of the ZnO-NC hydrogel (a-f) during the tensile process.



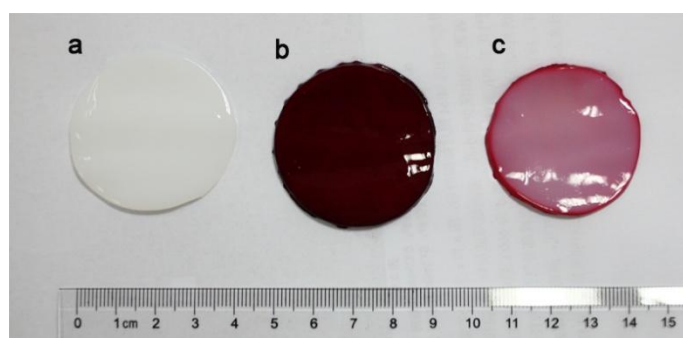
Supplementary Figure S12 | Mechanical and rheological properties of ZnO-hydrogels with different consists. **a**, Tensile properties of ZnO-NC hydrogels containing 5% DMAA, 5% clay, and different ZnO contents. **b**, Compressive properties of ZnO-NC hydrogels containing 5% DMAA, 5% clay, and different ZnO contents. **c**, Tensile properties of ZnO-NC hydrogels containing 0.6% ZnO and different clay contents. **d**, Compressive properties of ZnO-NC hydrogels containing 0.6% ZnO and different clay contents.



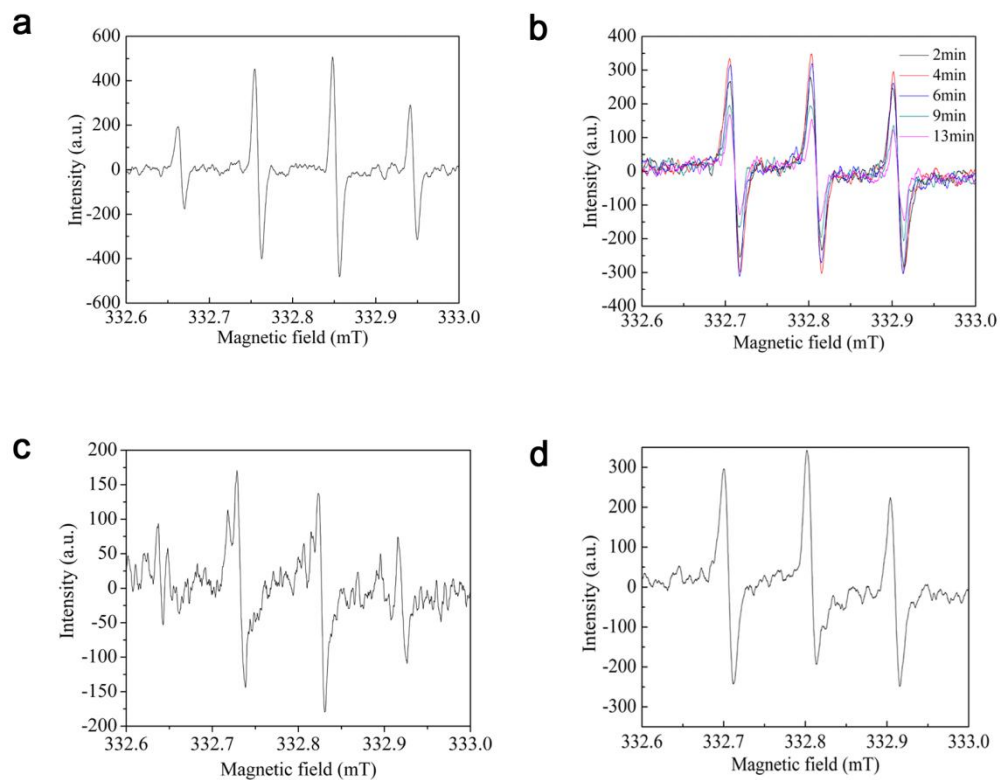
Supplementary Figure S13 | Rheological properties of the ZnO-NC hydrogels. a, G' and G'' values of the ZnO-NC hydrogel (0.2% ZnO, 5% clay, 5% DMAA). **b,** G' and G'' values of the ZnO-NC hydrogel on strain sweep. **c,** G' and G'' values of the ZnO-NC hydrogel (0.2% ZnO, 5.0% clay, 5.0% DMAA) in continuous step strain measurement (γ changes as 1% -100%-1%-100%-1%-100%-1%). **d,** G' values of hydrogels with different contents of clay (5%, 3% and 2%).



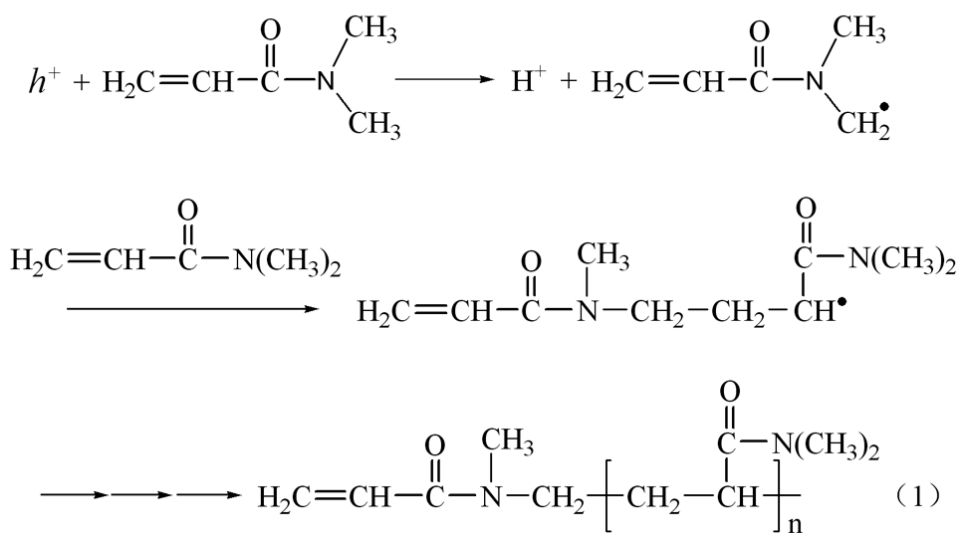
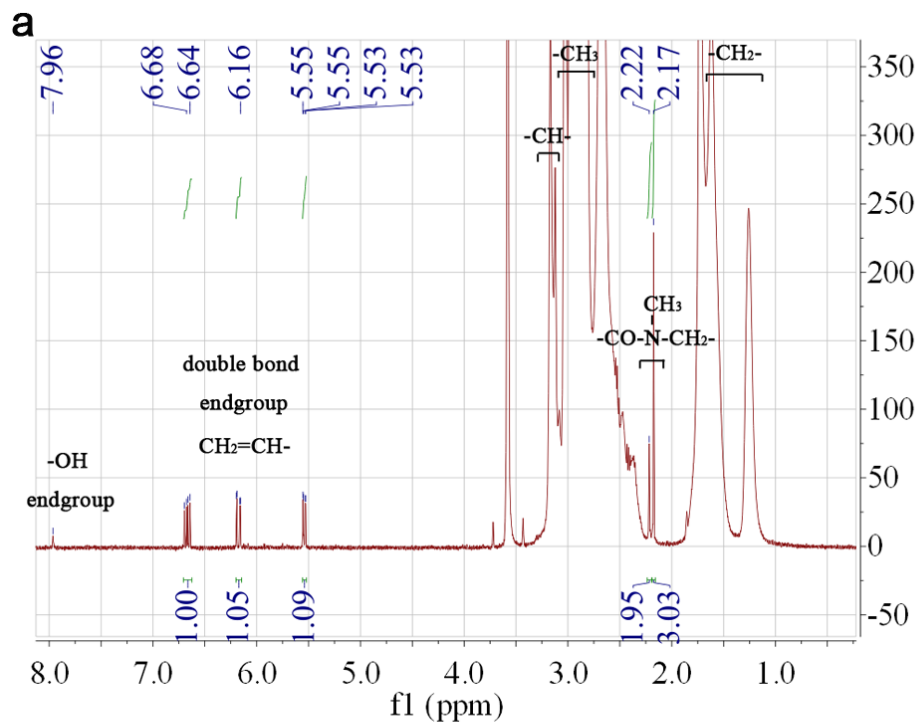
Supplementary Figure S14| The control experiment of NC hydrogel without TiO₂ nanoparticles. Photographs of original NC hydrogel **(a)**, after absorption of methylene blue **(b)** and treated by middle-pressure mercury lamp for 2 h **(c)**. Without TiO₂ in the hydrogel, the organic molecular could not be degraded under UV light.

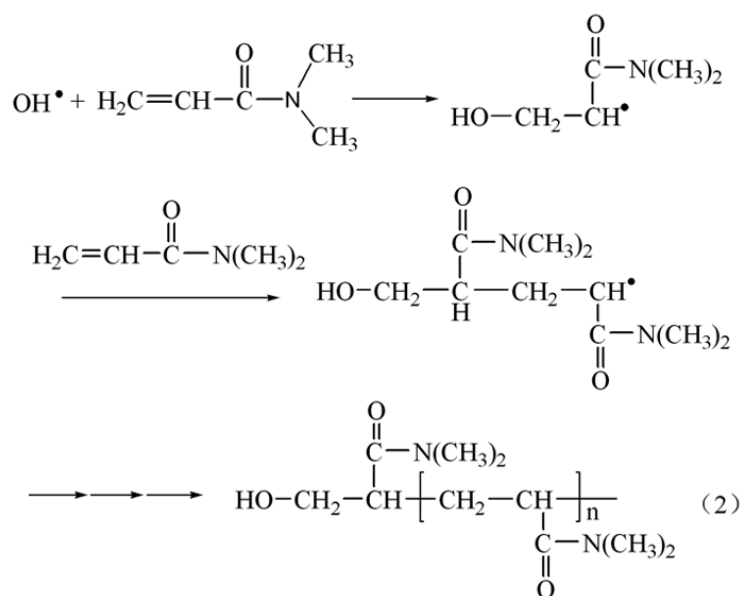
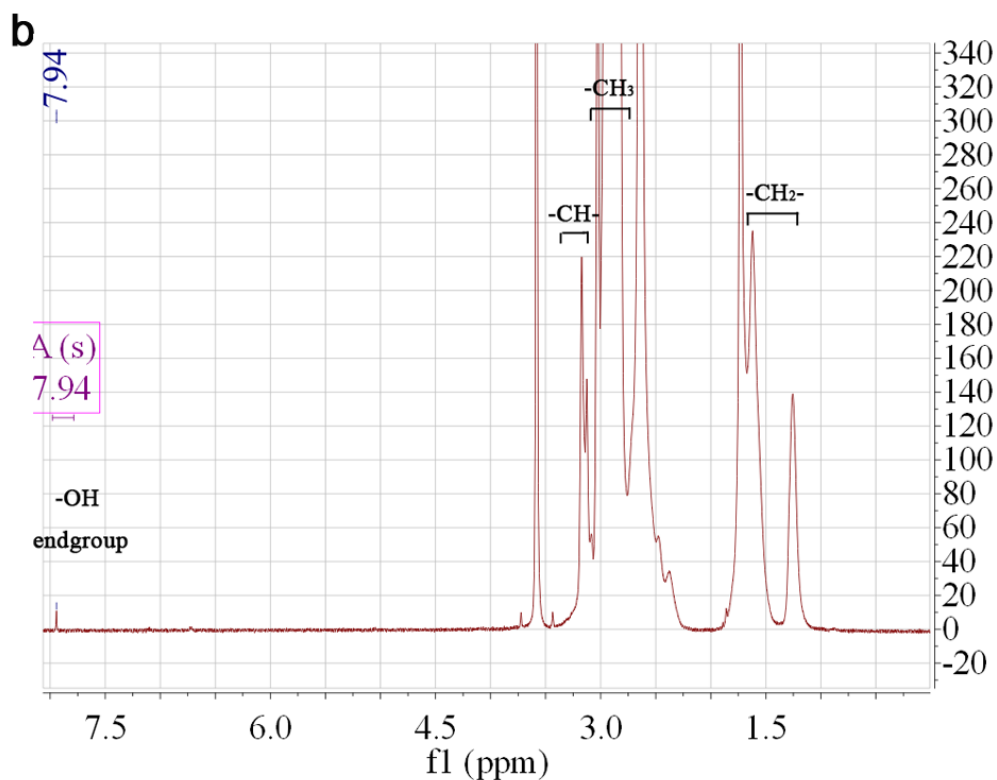


Supplementary Figure S15| The adsorption and degradation properties of functional hydrogel with TiO₂ nanoparticles. Photographs of original TiO₂-NC hydrogel **(a)**, after absorption of Acid fuchsin **(b)** and treated by middle-pressure mercury lamp for 2 h **(c)**.



Supplementary Figure S16 | EPR spectra of the precursors under light irradiation. a, The aqueous solution with TiO_2 and DMPO adduction under UV irradiation. **b,** The time-depended EPR spectra of the aqueous solution of TiO_2 and DMAA under UV irradiation. **c,** The aqueous solution with CdTe and DMPO under visible light (≥ 420 nm) irradiation. **d,** The aqueous solution with CdTe and DMAA under visible light.





Supplementary Figure S17 | The NMR results of polymer products. **a**, NMR spectrum of polymers adsorbed around the TiO₂ nanoparticles. The hole initiated polymerization happened near the surface of TiO₂ and adsorbed DMAA formed surface monomer radical by abstracting hydrogen (equation (1)). **b**, NMR spectrum of the polymers in the solution. The polymerization is most initiated by OH radicals in base condition (equation (2)).

6. Supplementary Movie

The movie (made in 5 July, from 11:00 am to 12:00 noon) shows the preparation process of the ZnO-NC hydrogel under sunlight. Firstly, H₂O (5.28 mL), DMAA monomer (310 μ L) and Clay-NS (300 mg) are mixed to form a clear solution under magnetic stirring for 10 min. Then 120 μ L of ZnO solution (10% in water) was added to the above solution to get a well dispersed suspension. The precursor suspension was taken to roof and placed under sunlight. The intensity at 365 nm was about 1.8 mW cm⁻² at first. After 30 min the intensity at 365 nm changed to 2.2 mW cm⁻². Another 30 min latter, the intensity at 365 nm was about 2.3 mW cm⁻². The elastic ZnO-NC hydrogel was dug out of the bottle. The gel showed little deformation when bearing 100 g weight and could be stretched several times as its original length.

7. Reference:

- [S1] Peng, H., Zhang, L., Kjallman, T. H. M., Soeller, C. & Sejdic, J. T. DNA Hybridization Detection with Blue Luminescent Quantum Dots and Dye-Labeled Single-Stranded DNA. *J. Am. Chem. Soc.* **129**, 3048-3049 (2007).
- [S2] Zhang, J. P. & Gao, L. Hydrothermal synthesis and characterization of SnO₂ nanoparticles. *Acta Chimica Sinica* **12**, 1965-1968(2003).
- [S3] Wang, L., Zhang, C. & Zheng, S. Organic-inorganic Poly (hydroxyether of bisphenol A)s with Double-decker Silsesquioxane in the Main Chains. *J. Mater. Chem.* **21**, 19344-19352 (2011).
- [S4] Shibayama, M. & Norisuye, T. Gel Formation Analyses by Dynamic Light Scattering. *Bull. Chem. Soc. Jpn.* **75**, 641–659 (2002).
- [S5] Haraguchi, K., Farnworth, R., Ohbayashi, A., & Takehisa, T. Compositional Effects on Mechanical Properties of Nanocomposite Hydrogels Composed of Poly(N,N-dimethylacrylamide) and Clay. *Macromolecules* **36**, 5732-5741 (2003).