

Supporting Information

Preparation and application of solid-state upconversion materials based on sodium polyacrylate

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Summary: This file contains 6 pages, 5 figures, 20 equations.

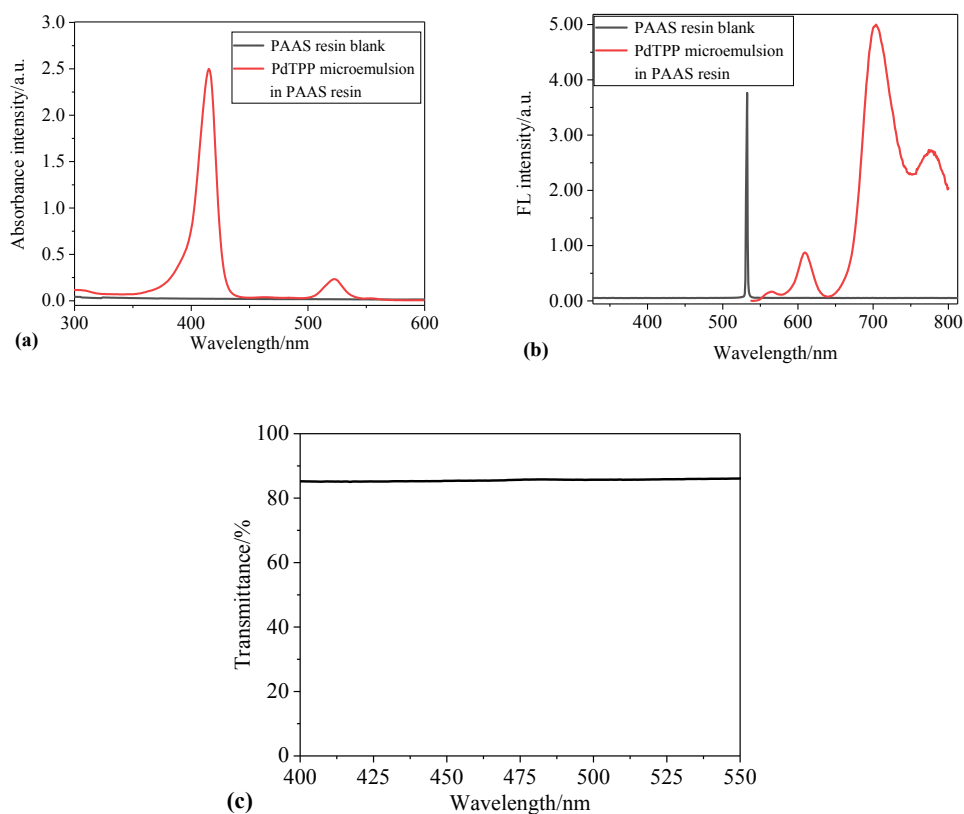
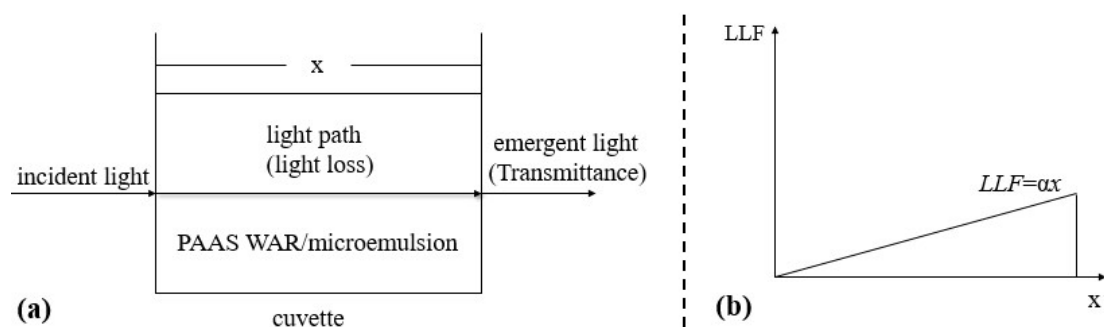


Fig. S1 (a) Absorption spectrum of PAAS resin and PdTPP microemulsion in PAAS resin; (b) Emission fluorescence spectrum of PAAS resin and PdTPP microemulsion in PAAS resin; (c) Transmittance of PAAS WAR/microemulsion system



Scheme 1 (a) The light went across the WAR/microemulsion system; (b) The total light loss (LLF) when the length of light path was x .

First, we calculated the correction coefficients. The PAAS WAR/microemulsion system was loaded in a cuvette, which size is 10 mm length×10 mm width. The light loss includes scattering, reflection and absorption. All these losses could affect the UC efficiencies.

We used the transmittance (T) at different wavelengths to evaluate the valid efficiency of light loss. The transmittance (T) is the percentage of the emergent light that went through the cuvette, so the relationship of the total light loss factor (LLF) and the transmittance (T) was shown in Equation S1.

$$T = 1 - LLF \quad (S1)$$

" α " represented the light loss factor per unit distance. The LLF could be calculated by Equation S2, in which the optical length was set as x .

$$LLF = \alpha x \quad (S2)$$

The light loss was gradually accumulated as the light went across the WAR/microemulsion system. So we can use the average light loss factor (LLF_{avg}) to evaluate the total light loss of the WAR/microemulsion system. The LLF_{avg} could be calculated by Equation S3.

$$LLF_{avg} = \frac{\int_0^x \alpha x}{x} = \frac{1}{2} \alpha x \quad (S3)$$

The correction coefficients (ν) can be calculated by Equation S4.

$$\nu = 1 - LLF_{avg} = \frac{1 + T}{2} \quad (S4)$$

The light loss effect on the UC intensity and laser power density were opposite. The UC intensity was weakened attributed to the scattering when the UC light went across the WAR/microemulsion system. The corrected UC intensity (I'_{UC}) was calculated by the measured raw UC intensity dividing ν (Equation S5).

The actual laser intensity (I'_{LP}) is less than the incident laser power density (I_{LP}), which should be corrected by multiplying ν at 532 nm (Equation S5).

$$\frac{I'_{UC}}{I_{UC}} = \frac{I'_{LP}}{I_{LP}} = \nu \quad (S5)$$

Light transmittance of the WAR/microemulsion system have been measured in Fig. S1c. The light T were 85.4% at 420 nm and 86.0% at 532 nm. The LLF_{avg} was 7.3% at 420 nm and 7% at 532 nm. Therefore, the correction coefficients were 0.927 at 420 nm and 0.93 at 532 nm. The corrected UC intensity (I'_{UC}) and the actual laser intensity (I'_{LP}) can be corrected as follow:

$$I'_{UC} = 1.079 I_{UC} \quad (S6)$$

$$I'_{LP} = 0.93 I_{LP} \quad (S7)$$

After fitting curves by the corrected data in Fig.3a (Relationship of TTA-UC intensity and excitation light power density), the logarithmic plot of TTA-UC intensity versus excitation light power density was also corrected (Fig. 3b). the obtained slop value K_1 and K_2 with three significant digits retained were corrected to 1.89 and 1.19, respectively.

The detection process of water absorbency was as follows: 1 g prepared porous matrix was put into a 500 ml beaker filled with a known volume (V_1) deionized water. The beaker was sealed and stored in room temperature. The porous matrix was soaked long enough to achieve saturated absorption. The remained deionized water was measured as V_2 by a 100 ml measuring cylinder. The water absorbency of the matrix was calculated as Equation S8, where Q represents water absorbency of the matrix; V_1 represents water volume before absorbed by the matrix; V_2 represents water volume after absorbed by the matrix.

$$Q = \frac{V_1 - V_2}{M} \quad (S8)$$

The water absorbency was 400 mL/g calculated through Equation S8.

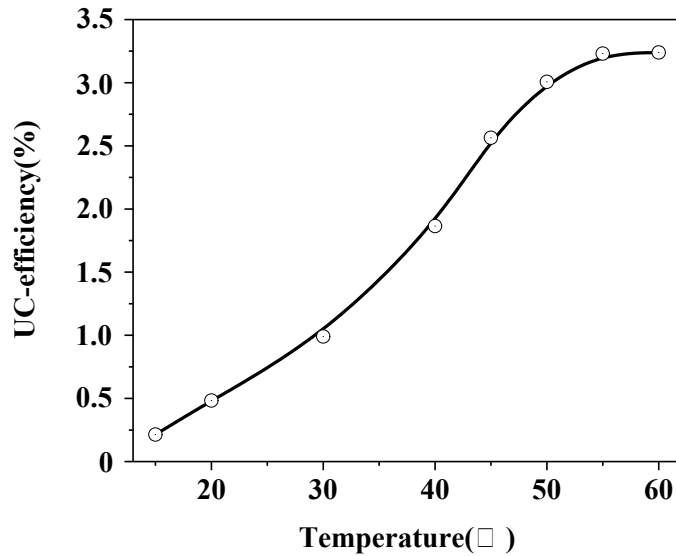


Fig. S2 The temperature-dependent upconversion efficiency of the UC hydrogel in air

TTA-UC efficiency (Φ_{UC}) was calculated by Equation S9, where subscripts “s” and “r” represent sample and reference (Rhodamine B in ethanol was used as standard, $\Phi_r = 65\%$), respectively. Φ_r is the fluorescence quantum yield of reference; A is the absorbance; F is the integrated fluorescence intensity; and η is the refractive index of solvents. The equation is multiplied by a factor of 2, accounting for the fact that two absorbed photons are required to produce one upconverted photon.

$$\Phi_{UC} = 2\Phi_r \left(\frac{A_r}{A_s}\right) \left(\frac{F_s}{F_r}\right) \left(\frac{\eta_s}{\eta_r}\right)^2 \quad (S9)$$

As we discussed that conditions of UC intensity and laser power density affected by light loss were opposite, so the value of F_s should be revived by dividing the correction coefficients at 420 nm and the value of A_s should be revised by multiplying the correction coefficients at 532 nm. Therefore, the corrected TTA-UC efficiency (Φ'_{UC}) should be adjusted with Equation S10.

$$\Phi'_{UC} = 1.16\Phi_{UC} \quad (S10)$$

However, these calculated UC-efficiencies are actually estimated value since the hypotheses were based on that the total light losses are proportional to path lengths. Some complicated factors such as inner filter effects or Mie-scattering were not taken into account.

7-hydroxycoumarin aqueous solution was prepared and fluorescence spectra of DPA and 7-hydroxycoumarin were tested using laser (365 nm), as shown in Fig. S3. Emission characteristic peaks of 7-hydroxycoumarin was at 460 nm while DPA at 413 nm and 435 nm. Fig. 4a of manuscript showed that fluorescence peak at 460 nm increased

as illumination time increasing, while fluorescence peak at 413 nm was nearly constant. Fluorescence peak at 435 nm were actually pulled up by the peak at 460 nm. This phenomenon indicated that 7-hydroxycoumarin aqueous solution should contain DPA that may exudate from the PAAS WAR material, but the quantity of DPA was nearly constant. So DPA didn't cause interference to 7-hydroxycoumarin from either the intensity or the peak position, although their fluorescence peaks were close to each other.

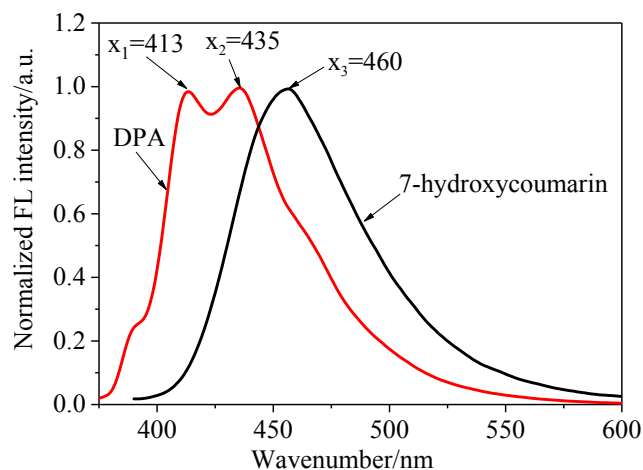


Fig. S3 Normalized fluorescence spectra of DPA and 7-hydroxycoumarin

The efficiency of photocatalytic synthesis of 7-hydroxycoumarin can be obtained by the ratio of quantity (g) of the synthesized 7-hydroxycoumarin and laser power (W/s). The quantity of the synthesized 7-hydroxycoumarin can be obtained through the relationship between fluorescence intensity and concentration of 7-hydroxycoumarin. Linear relationship between fluorescence intensity and concentration of 7-hydroxycoumarin was shown in Fig.S4.

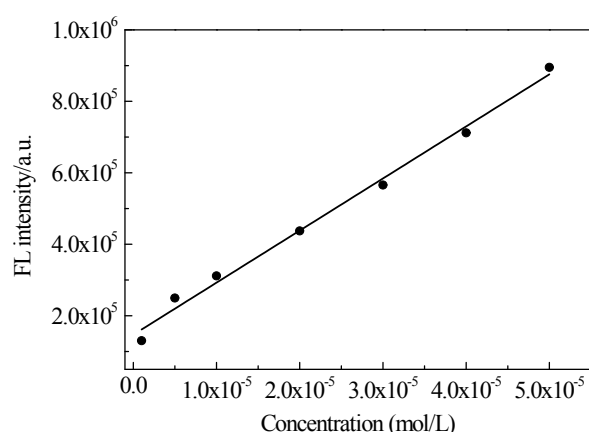


Fig. S4 Fluorescence intensity of 7-hydroxycoumarin under different concentrations

Linear equation was obtained through linear fitting as Equation S11, where y represents fluorescence intensity of 7-hydroxycoumarin and x represents the concentration of 7-hydroxycoumarin.

$$y = 1.46 \times 10^{10} \times x + 1.46 \times 10^5 \tag{S11}$$

Thus, the concentration and quantity of 7-hydroxycoumarin were 6.53×10^{-5} mol/L and 3.07×10^{-5} g within 80 min, which were calculated through the fluorescence intensity in Fig. 4 (a) in the manuscript.

The laser power density is 60 mW/cm² and the laser spot diameter is 0.2 cm, so the actual power of the laser is calculated as 1.88 mW. As a result, the photocatalytic efficiency was calculated by Equation S12, where η is the photocatalytic efficiency, P is laser power, t is photocatalytic time, and y is the quantity of 7-hydroxycoumarin.

$$\eta = \frac{Pt}{y} \quad (S12)$$

The calculated photocatalytic efficiency is 3.41×10^{-6} g/W.

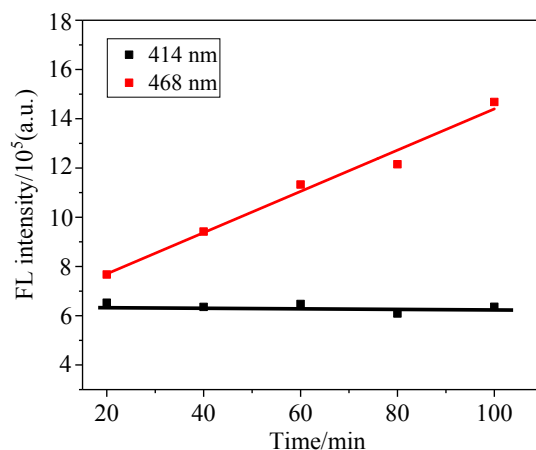
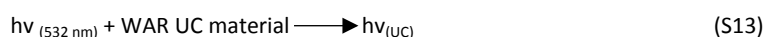


Fig. S5 Fluorescence intensity at 414 nm and 468 nm within 20-100 min.

The hydroxyl radical ($\cdot\text{OH}$) on Pt/WO_3 is mainly generated through the reduction of O_2 as shown the following Equations (S13-S20). Low energy green light was converted into blue light of high energy that matched the band gap of Pt/WO_3 . Then charge carriers of Pt/WO_3 were excited and transferred from valence band to conduction band. The charge carriers on conduction band reacted with dissolved oxygen in solution and generated $\cdot\text{O}_2^-$ radical (Equation S16). Then H_2O_2 was generated by the reaction between $\cdot\text{O}_2^-$ radical and H^+ (Equation S16 and Equation S18). And H_2O_2 was reduced by electrons and split into hydroxy and OH^- (Equation S19). The electron of OH^- can be despoiled by electron hole and also transferred into hydroxy (Equation S20).



The hydroxyl radical on ZnCdS is generated the same way as those on Pt/WO_3 . Charge carriers of ZnCdS were excited and transferred to the surface of ZnCdS , and then the hydroxy was generated from the reactions (Equations S13-S20). And the molecular chain of rhodamine B was gradually destroyed by hydroxy and the degradation began.