Electronic Supplementary Material (ESI) for Materials Advances.

Optimization of synthesis conditions of gold nanoparticles – polydimethylsiloxane composite for ultrasound generation

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1. Optical absorption and PA generation experimental set-up

a. Optical absorption

The optical absorption of the samples inserted into a solid sample holder was measured with a UV-Vis spectrometer (TU-1810) as shown in the Supplementary Figure S2. Au-free PDMS is used as a reference sample to calibrate the baseline.

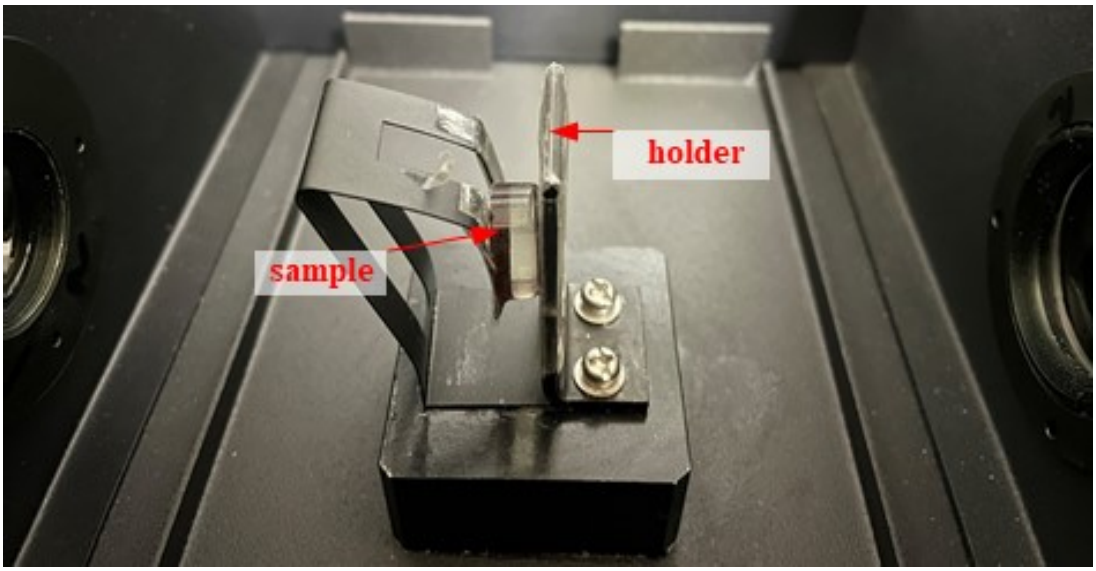

Figure S1 The sample inserted into the solid sample holder of UV-Vis spectrometer

b. Photoacoustic generation

The PA field is measured with a heterodyne Mach-Zehnder Laser Doppler Vibrometer (LDV) [1] as shown in the Figure S2. A He-Ne laser (633 nm) is used as the probe ray of the LDV, which is guided onto the specimen through an optical path system comprising a galvo-mirror to scan the sample, dichroic filter to combine excitation (520 nm) and probe (633 nm) beams and a microscope objective (to increase the spatial resolution of the scan). The PA generation source is a nanosecond pulse laser. It is introduced in the optical path through the dichroic filter and guided to the PA generation layer of the specimen to generate the PA wave.

The specimen is a sandwich structure consisting of the AuNP-PDMS composite at the

top, a thin reflective mylar foil in the middle and an Au-free PDMS at the bottom. The PA wave crosses the mylar foil, which oscillates with the wave. The PA wave is then measured by the probe beam which carries the oscillation of the foil motion and is sent to a high-speed photodiode. All optical components were purchased from Thorlabs.

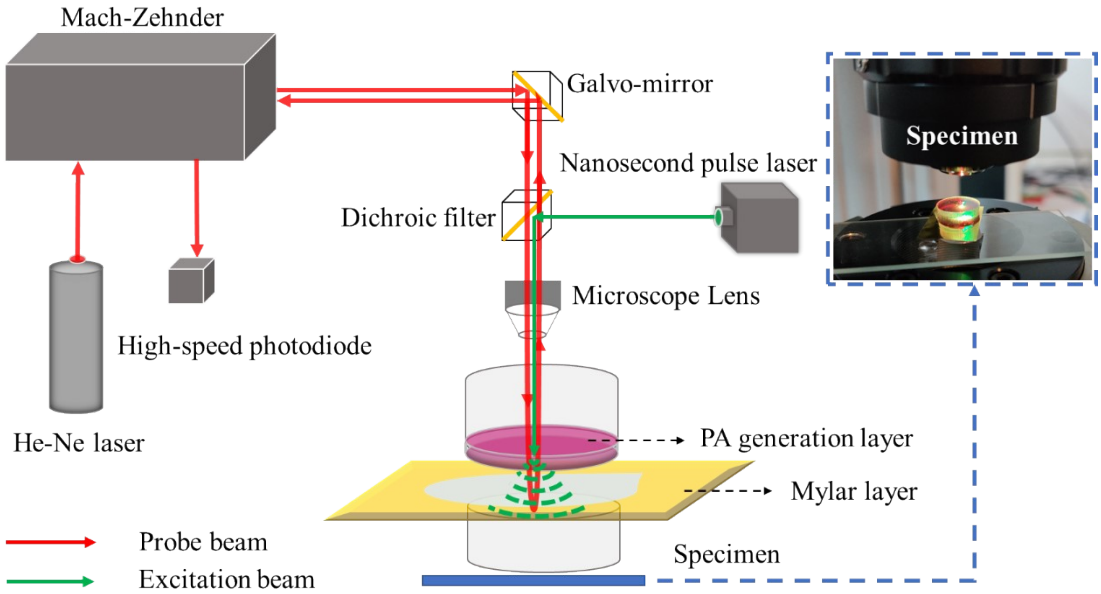

Figure S2 the schematic diagram of the experimental set-up. Note: the distance between generation layer and mylar has been greatly exaggerated in the drawing for clarity, but it is only a few micrometers in the experiment.

2. Scanning electron microscope (SEM) characteristic

Isopropanol sample at 0.013 mol L^{-1} TCA concentration was characterized by SEM (magnification 1000× and 2000×). As shown in Figure S3, the sample surface exhibits aggregates, and the energy dispersive spectrum indicates the presence of Au, confirming that the yellow color in optical images is due to metallic gold.

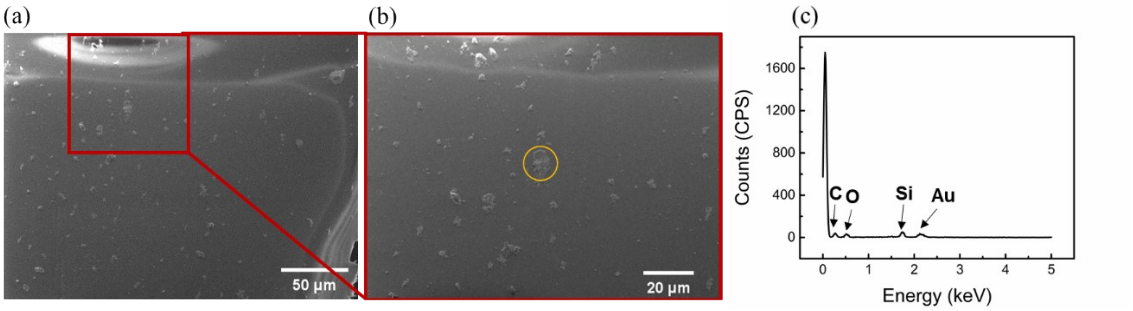

Figure S3 SEM image of isopropanol sample at 0.013 mol L^{-1} TCA concentration at an accelerating voltage of 20 kV. (a) Magnification 1000×. (b) Magnification 2000×. (c) Energy dispersive spectrum. Note: red box indicates the magnified region, and yellow circle displays the gold agglomerations

3. UV-Vis spectrums of DMF, DMSO, the mixture of isopropanol and water

Figure S4 showed the absorbance of the samples using DMF, DMSO and a mixture of isopropanol and water as solvents. The DMF and DMSO samples look nearly transparent and exhibit no absorbance peak near 535 nm. This suggests that nanoparticles were not successfully synthesized with these solvents. The isopropanol-water sample appears purplish red with a maximum absorption at 535 nm, indicating successful synthesis of nanoparticles. The optical absorption of the isopropanol-water sample was only slightly higher than that of water, which suggests that pure isopropanol works best.

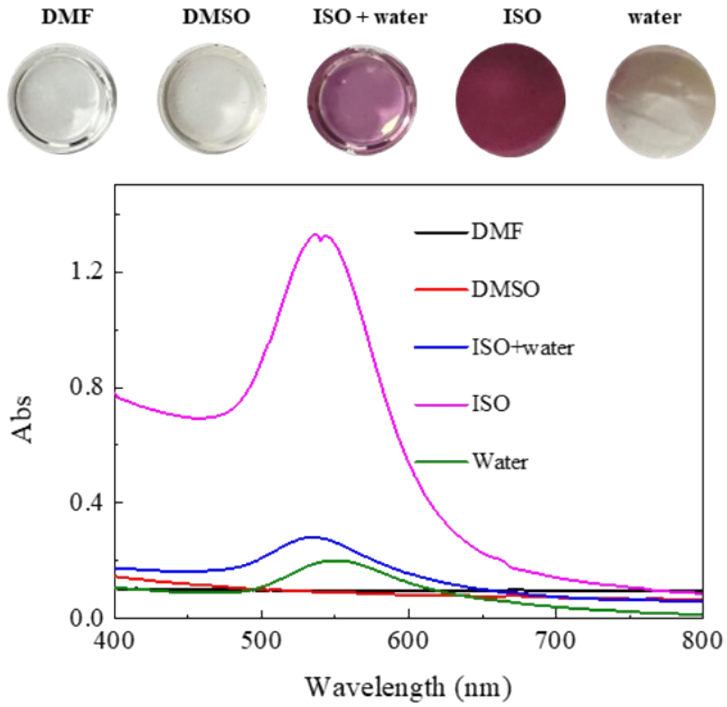

Figure S4 UV-Vis absorption spectrums of solvent samples including DMF, DMSO, mixture of isopropanol (ISO) and water, isopropanol, and water at 0.015 mol L^{-1} of TCA concentration.

4. Effect of solvent characteristics on PA amplitude

The PA amplitude responses of 25 samples to the change of solvent are experimentally studied in Figure S5 (a, b, c, d, e). TCA concentration, solvent dipole moment, pKa of each solvent, Hildebrandt solubility parameter and swelling value S for each solvent are considered. Figure S5 (a) TCA concentration increases contributing to enhance PA amplitude. But at higher TCA concentration, PA signal start to plateau or drop except ethanol. There were similar trends occurred at five solvent samples. Figure S5 (b, c, d, e) show that the trends of PA signal with changes of solvent polarization, pKa, solubility parameter, and S value are similar with those happened in trends of optical absorption.

Figure S5 (f) shows a good linear relationship between experimental result and regression model, and the corresponding regression coefficients of each parameter are shown in Table S1. For the regression model, TCA concentration, the difference of solubility parameter between solvent and PDMS and S value are positively correlated with amplitude, contrarily, polarization and exponential function of pKa negatively correlated. For this regression, the parameters are made dimensionless by comparison with water.

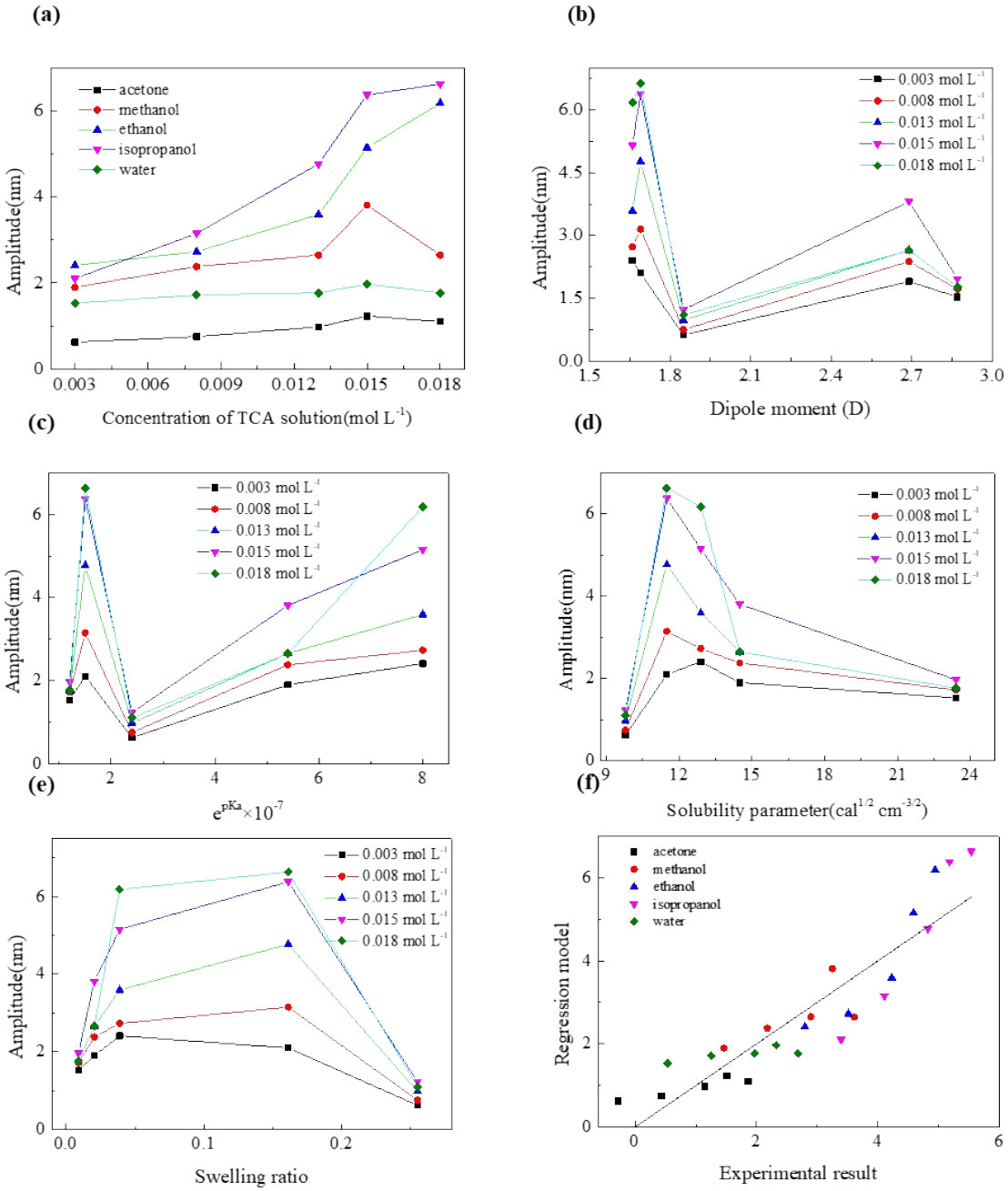

Figure S5. Relationship between solvent property and PA amplitude, (a) TCA concentration for each solvent. (b) dipole moment. (c) pKa, (d) solubility parameter. (e) swelling ratio. (f) linear regression between solvent properties and PA amplitude.

Table S1 parameters and regressed coefficients of the five solvents

Parameter	Normalized parameter	Regressed coefficient
Swelling (S)	$S' = \frac{S}{S_w} - 1$	$\theta_S' = 0.61$
Dipole moment (q)	$q' = \frac{q}{q_w} - 1$	$\theta_q' = -0.47$
Hildebrandt solubility parameter (h)	$h' = \frac{h - h_{pdms}}{h_w} - 1$	$\theta_h' = -1.86$
Acidity constant (pKa)	$pKa' = \frac{pKa}{pKa_w} - 1$	$\theta_{pKa}' = -2.30$
TCA concentration (C) *	$C' = \frac{C}{C_{Zhang}} - 1$	$\theta_C' = 0.77$
Intercept (b)		b' = 0.84

* C_{Zhang} = 0.013 mol L^{-1} is set as standard concentration based on previous studies.

$$u = b' + \theta_C' C' + \theta_S' S' + \theta_q' q' + \theta_h' h' + \theta_{pKa}' pKa'$$

5. Size distribution for 25 samples

Figure S6 show counts size distribution of Au particles by image J. the lower and higher concentration show wide size distribution, which is not beneficial to enhance light absorption and PA amplitude.

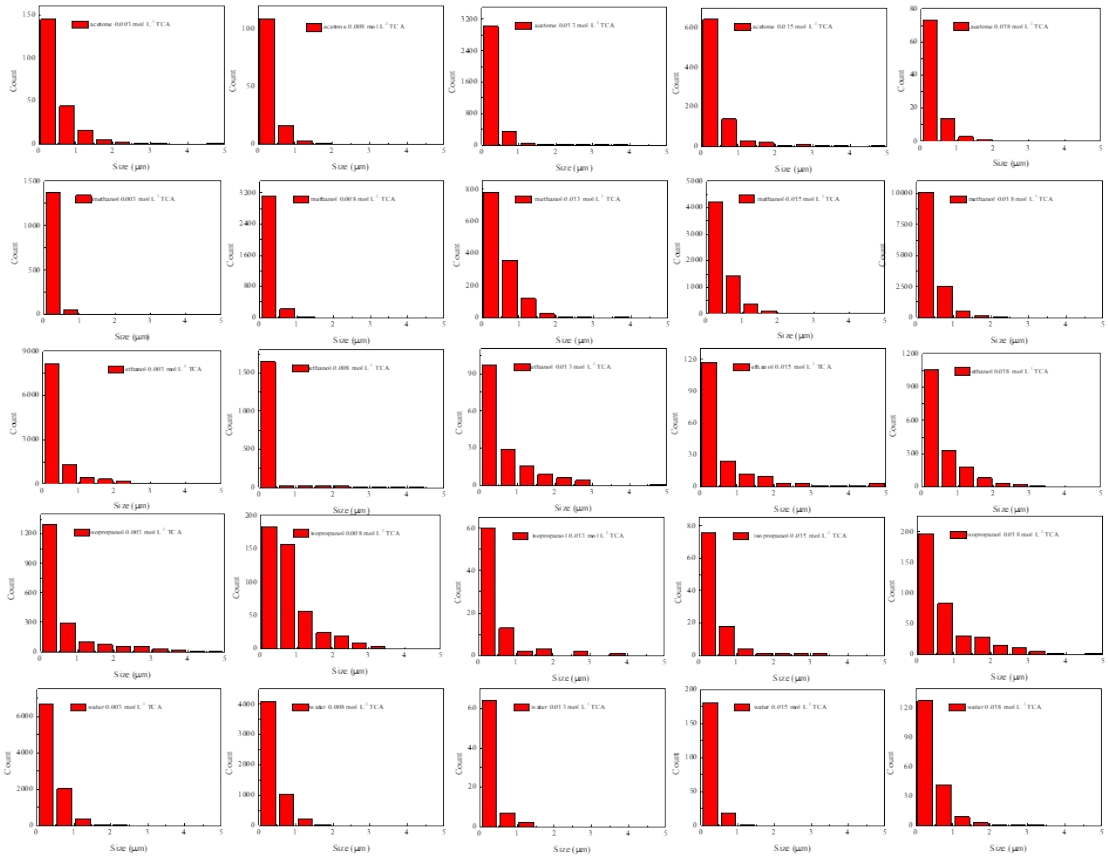

Figure S6. Size distribution diagrams for 25 solvent samples.

Reference

[1] Royer, D., and E. Dieulesaint. "Optical probing of the mechanical impulse response of a transducer." Applied physics letters 49.17 (1986): 1056-1058.