Electronic Supplementary Material (ESI) for Chemical Science.

Supporting Information

Billion-fold Rate Enhancement of Urethane Bond Formation via the Photothermal Effect of Plasmonic Gold Nanoparticles

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Contents

Synthetic Details

Synthesis and characterization of gold nanoparticle

Gold nanoparticles (AuNPs) were synthesized using the Brust 2-phase method,[1] in which 80 ml of a 0.05 M solution of tetraoctylammonium bromide in toluene was mixed with 30 ml of a 0.03 M solution of hydrogen tetrachloroaurate. Once the gold was transferred to the organic layer, the organic layer was then separated, and 0.84 mmol 1-octanethiol was added to the solution. Then, 25 ml of 0.4 M $NaBH_4$ (aq) was added dropwise, and the mixture was stirred for 3 hours. The organic layer containing gold nanoparticles was purified by precipitation with methanol at 0°C overnight. Figure S1 shows the UV-Vis of the resulting particles. As seen in Figure S1, these particles contain a weak plasmon. Figure S2 shows TEM images. The mean diameter of particles before irradiation is 2.1 ± 0.5 nm. We estimate these particles contain 210 gold atoms and 50 octanethiol ligands, leading to an average mass of 4.9×10^4 g mol^{-1}.

Also shown in Figure S1 and S2 are (respectively) the spectra and TEMs of the AuNPs after irradiation. As can be seen, the particles undergo a change in size during irradiation, growing to give a mean diameter of 4.8 ± 5.1 nm. This growth, which appears to be accomplished by the aggregation of smaller nanoparticles, is not complete and we observe both large and small particles within our samples. The presence of the larger particles gives rise to the stronger plasmonic feature shown in Figure S1.

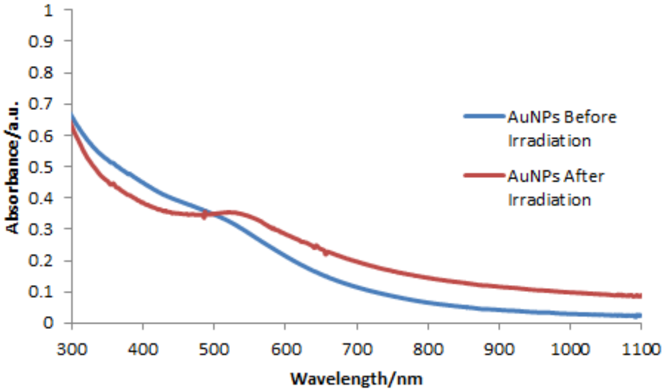

Figure S1. UV-Vis spectrum of AuNPs before and after irradiation

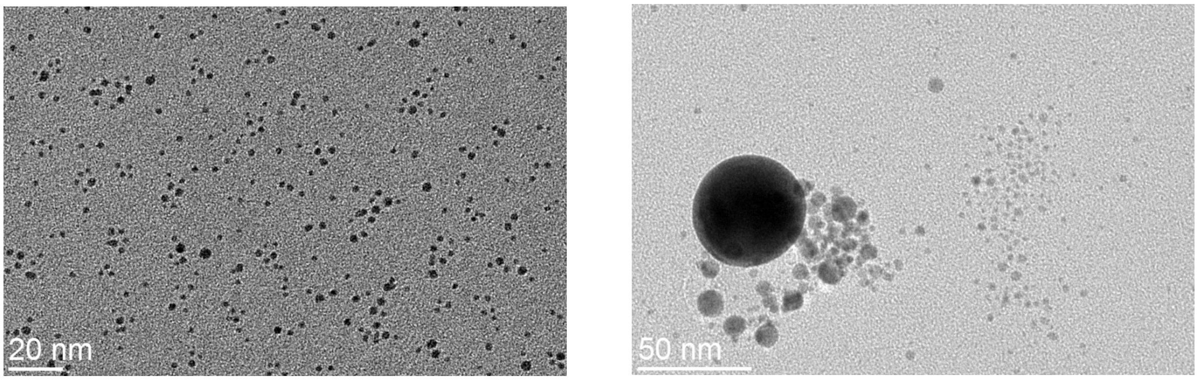

Figure S2. TEM of AuNPs (a) before and (b) after irradiation.

Polyurethane film formation

We prepared separate toluene solutions of (a) hexamethylene diisocyanate (HDI – formulated as Desmodur N3600) and (b) the diester polyol bis(triethylol) heptanedioate (BTEH – formulated as K-FLEX 188) prepared so as to maintain a 0.2 g per ml of toluene mass to volume ratio. AuNPs and/or DBTDL (final concentration 0.08% w/v and 0.07% w/v, respectively) were incorporated into the HDI solutions by dissolution in the toluene used to form the solution .

Polyurethane films were then produced by mixing 0.02 ml of each of the above solutions in a culture tube. Samples were either exposed to periods of irradiation by 532 nm light from QuantaRay 13- Nd:YAG laser (8 ns pulses, 10 Hz) or allowed to proceed under ambient conditions. Spectra were collected over a period of 4 minutes, and the disappearance of the isocyanate peak at 2274 cm^{-1} was monitored. IR spectra were collected using a Perkin Elmer Spectrum 400 FT-IR/FT-NIR spectrometer with a Pike Miracle ATR attachment.

Characterization of DBTDL

Dibutyltin dilaurate (DBTDL) was incorporated into appropriate HDI solutions at a loading of 0.07% w/v. UV-Vis characterization is presented in Figure S3. At the concentrations we used there is no appreciable UV-visible absorption.

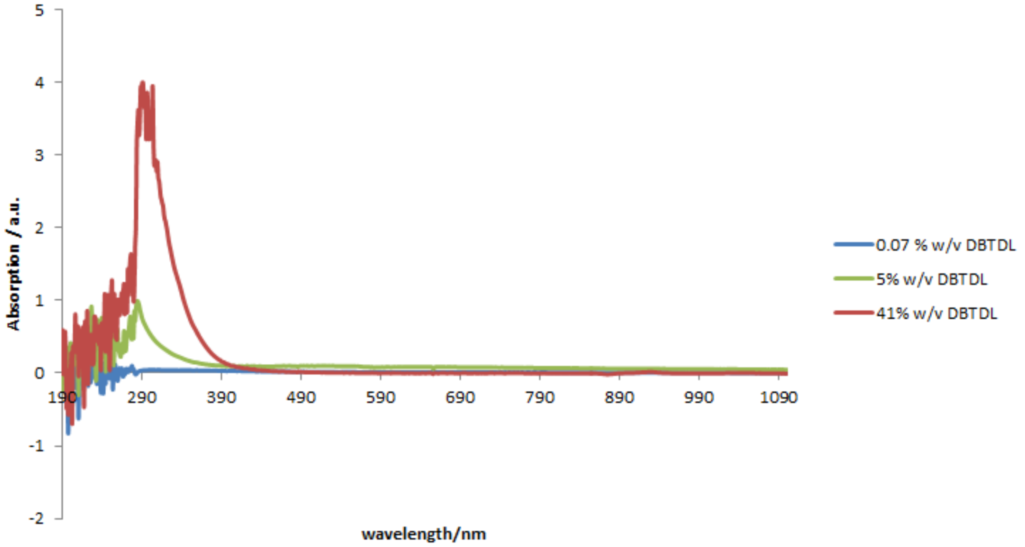

Figure S3. UV-Vis spectrum of 0.07% w/v solution of DBTDL in toluene.

Temperature calibration of polyurethane film formation

In order to determine the impact of bulk-scale heating, we followed the course of the reaction between HDI and BTEH in vials immersed in oil baths held at 50 °C, 75 °C, and 100 °C. The reaction was followed using the same infrared markers as described above and in the manuscript. For each temperature, we fit the early time kinetics and used the slopes to calculate the enhancement of the reaction rate, with respect to that at room temperature (25 °C). This gives us an understanding of the kinetic impact of bulk heating and plotting these data (Figure S4) allows us to estimate the temperatures that would be required to obtain the kinetic enhancements realized by the photothermal effect (Table 1 in manuscript).

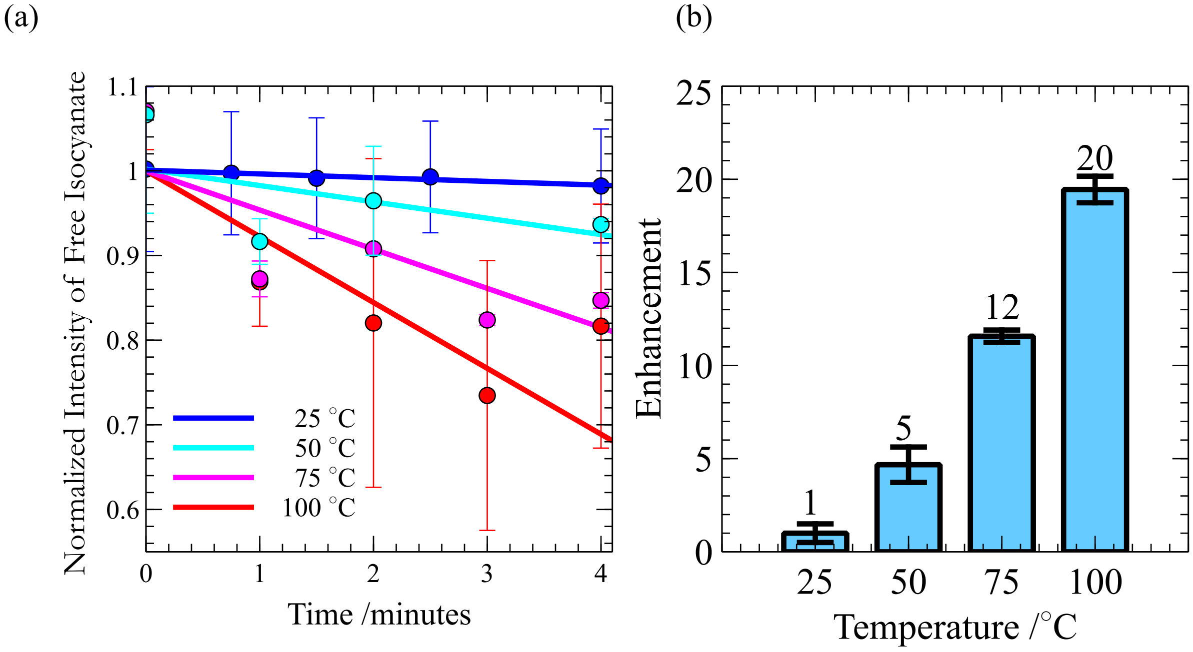

Figure S4. (a) Early time kinetics of polyurethane film formation over time at various temperatures. (b) The enhancement of the kinetics at these temperatures, relative to the room temperature rate.

Billion-fold rate enhancement

Because we know that the photothermal enhancement requires the pulsing of light, we assume that the rate enhancement only occurs when the particles are hot. However, the particles are only hot for a small fraction of the ‘real’ elapsed time (4 minutes).

What this also means is that the reaction rate must be running extremely fast during those times when the AuNPs are hot. That is, the rate that we calculate for the ‘real’ time (4 minutes) cannot be the rate that is actually occurring during the fraction of time that the particles are hot ('irradiated time'). In fact, the ratio of the 'irradiated time' rate (during which the particles are hot) to the 'real time' rate (4 minutes, or 240 seconds), must be equal to the ratio of the 'real time' to the 'irradiated time'. And these are both equal what we might call an 'additional enhancement factor' – that is the amount of additional enhancement that results when we take into account that the particles are only hot for a small fraction of time.

$$additional\ enhancement\ factor = \left(\frac{k_{irradiated\ time}}{k_{real\ time}}\right) = \left(\frac{t_{real\ time}}{t_{irradiated\ time}}\right) \quad (1)$$

Calculating this additional enhancement then becomes simple. We already know the real time (4 minutes). If we knew the 'irradiated time' (the time during which the particles are hot) we could calculate this 'additional enhancement.' This is made simple by assuming the particles are only hot for the duration of the laser pulse. The reason we can assume this is that, for 2 nm particles, the time it takes to cool down is ~10 ps. Because, we use 8 ns pulses, 10 ps is negligible and we make the simplifying assumption that the particles are only hot during the 8 ns pulses.

We run the reaction for 4 minutes in 'real' time. But the laser is operating at 10 Hz. So, the total irradiated time (what we are calling 'irradiated' time) is given by:

$$Irradiated\ time = 4\ minutes \left(\frac{60\ seconds}{1\ minute}\right)\left(\frac{10\ pulses}{1\ second}\right)\left(\frac{8\ ns}{1\ pulse}\right) = 19200\ ns\ \approx 20\ \mu s \quad (2)$$

And we are now ready to calculate the additional enhancement factor:

$$additional\ enhacenment\ factor = \left(\frac{240\ seconds}{2\times10^{-5}\ seconds}\right) = 1.2 \text{ x } 10^7 \quad (3)$$

When we multiply the 'real time' enhancements (Figure 2b in the manuscript) by this number, we obtain billion-fold enhancement of the rate.

MALDI of polyurethane samples

In order to ensure that we were making cross-linked (high molecular weight) polymers, we acquired MALDI of polyurethane films cured under both photothermal and traditional means. These are shown in Figure S5. These results demonstrate that the only substantial difference between the two means of curing is a higher proportion of high-mass products for the photothermally cured samples, indicating that there is a larger proportion of cross-linking within the photothermally cured samples.

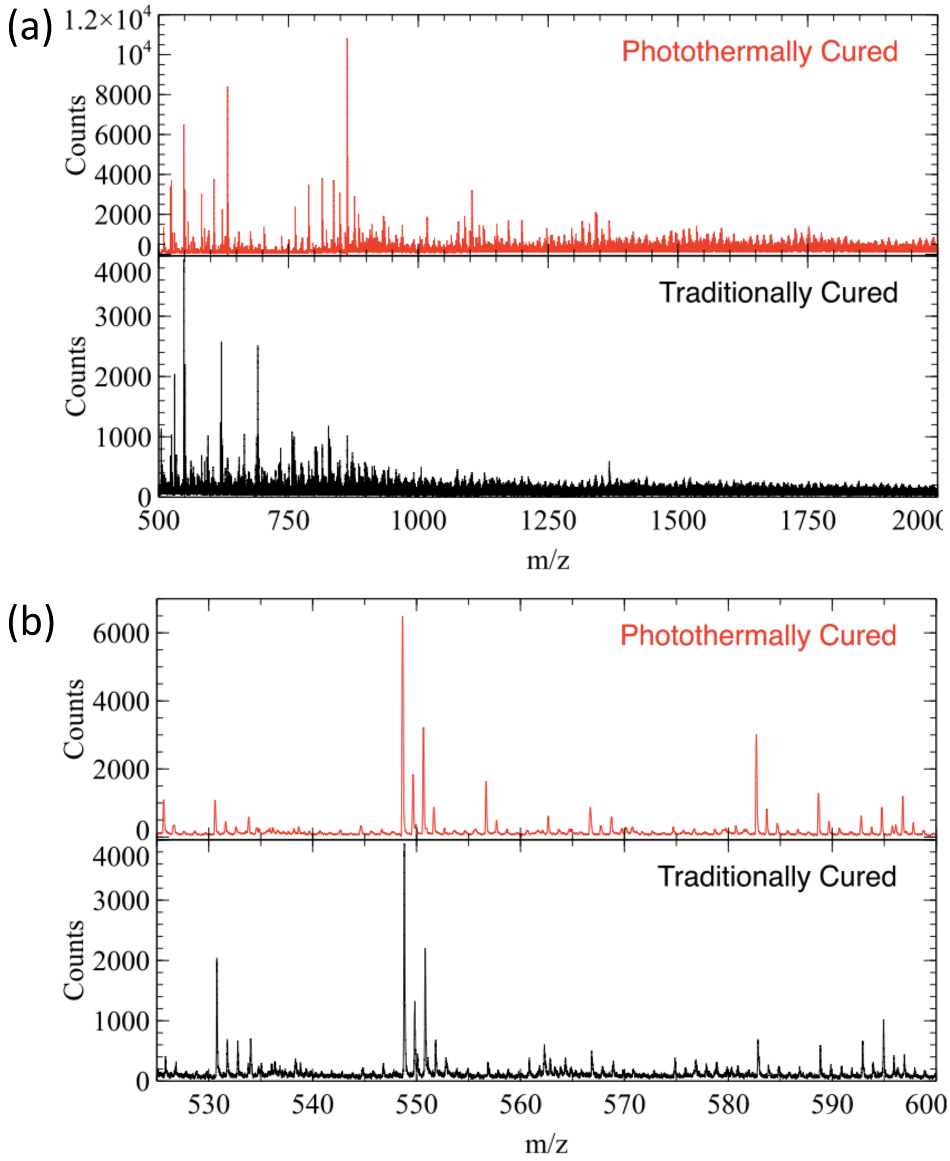

Figure S5. MALDI spectra for polyurethane films that have been photothermally cured and traditionally cured (bulk heating). Shown are (a) a large range of masses detected, and (b) a zoom in on the masses associated with the alcohol-isocyanate dimer. Similar peaks are found in all cases.

References

1. Brust, M., Walker, M., Bethell, D., Schiffrin, D. J. & Whyman, R. *Journal of the Chemical Society, Chemical Communications* **1994**,*7*, 801.