Nanoscale

Supplementary Information

Degradation of polypropylene carbonate through plasmonic heating

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Supporting Information (4 pages)

Details of film preparation, data from depolymerization experiments, determination of the extinction coefficient for the films, TEM of the films before and after irradiation, and description of quantum yield measurements.

Details of film preparation

Sample films were prepared by dissolving AuNPs and polypropylene carbonate (PPC) in methylene chloride in nanoparticle:PPC mass ratios of 1:10, 25, 50, 75, 100, 250, 500, and 750. The solutions were always made such that the PPC in methylene chloride was at a concentration of 0.2g/ml. The mixtures were micropipetted on to pre-weighed microscope slides in a volume of 40 μL, and allowed to dry for 24 hours. After drying, the slides were again weighed, and then exposed to 7,000 pulses of a frequency-doubled 532 nm Nd:YAG laser (Quanta Ray 130, 8 ns pulses, 10 Hz). After irradiation, the slides were reweighed and the mass loss recorded.

Data from depolymerization experiments

Below is given the polymer decomposition percentages for different concentrations of gold nanoparticles within the film. Concentrations are reported as mass fraction of nanoparticles within the film. Each film was exposed to 7,000 pulses of 532 nm light, as detailed in the manuscript.

Table S1. Concentrations of light absorber (x) in films (given as mass fraction) and the observed % completion of the PPC film upon exposure to out laser. Also given are the standard deviations in these measurements.

x	[x]	% completion	standard deviation
	mass fraction		
Nanoparticles	9.1E-02	72	5
	3.8E-02	68	10
	2.0E-02	72	9
	1.3E-02	63	12
	9.9E-03	82	4
	4.0E-03	47	4
	2.0E-03	39	2
	1.3E-03	27	1
	0.00	3	1
Sudan IV	9.1E-02	13	1
	9.9E-03	13	1

Determination of the extinction coefficient (ε_{532}) of the films

To determine the extinction coefficient present in the films, a solution of nanoparticles and polypropylene carbonate was made, as if to be deposited on slides to form a 1:100::nanoparticle:PPC (by mass) film. Noted was (*i*) the mass of nanoparticles, (*ii*) the mass of PPC, and (*iii*) the volume of methylene chloride. This solution was then diluted until the absorbance maximum at 532 nm was less than 1 absorption unit when using a quartz cuvette with a 1 cm path length. The extinction coefficient for this solution was then calculated and this value (together with the dilution factor) used to calculate the extinction coefficient of the original solution.

Once the extinction coefficient for the original solution was determined, we then determined the extinction coefficient of the films. This was done by assuming that only the methylene chloride would evaporate in the films, leaving behind the nanoparticles and the PPC. This amounts to further concentration of the film. The loss in volume of the methylene chloride was used to calculate the degree of concentration, which in turn was used to give the extinction coefficient of the nanoparticles in the film. Following this procedure we find: $\varepsilon_{532} = 0.641\ mg_{film}\ mg_{nanopartilce}^{-1}\ \mu m^{-1}$.

Due to the heterogeneity inherent in dealing with nanoparticles, we do not report the extinction coefficient in terms of molarity, rather we report it in terms of mass fraction. It is important to note that this means that this extinction coefficient is only viable for the specific nanoparticles (heptane thiol protected) and polymer (PPC) that we use here. Adaptation to other chemical systems could be done, if the relative densities of the nanoparticles and polymers are known.

Description of quantum yield measurements

Quantum yield measurements were made in the laboratory of Prof. Mark Maroncelli. Steady-state absorption spectra were measured using a Hitachi U-3010 UV/vis spectrophotometer and corrected emission spectra with a Spex Fluorolog F212 fluorimeter. These instruments have been used to successfully measure quantum yields of 10^{-4}. We observed no detectible fluorescence form Sudan IV and so assume the quantum yield must be less than 0.1. This is sufficient to conclude that the vast majority of the energy absorbed by the dye is converted to heat via a non-radiative pathway and supported our choice of Sudan IV as a valid organic dye for comparison of the photothermal effect with that of gold nanoparticles.