Plasmon enhanced triplet-triplet annihilation upconversion of post-modified polymeric acceptors

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Materials and Syntheses

Synthesis of poly[(methyl methacrylate)-*co*-(glycidyl methacrylate)] (PMMA-*co*-GMA)

Material preparations:

S-1-dodecyl-S'-(α,α'-dimethyl-α"-acetic acid)trithiocarbonate (DDMAT) was synthesized according to the procedure described in Lai *et al*,[1] with some additions to the procedure. A round bottom flask was purged with nitrogen gas and left with a positive nitrogen atmosphere for the rest of the reaction, to which Aliquot 336 (tricaprylylmethylammonium chloride, 1.50 mL, 3.3 mmol) had been added. To this, acetone (49.00 mL, 0.6665 mol) and 1-dodecanethiol (19.40 mL, 81.0 mmol) were injected, and the mixture was cooled to less than 10° C. Next 50% (w/v) NaOH aqueous solution (7.00 mL, 87.5 mmol) was added dropwise, which produced a frothy, white foam. The mixture was left to stir and cool for 15 minutes. Then anhydrous carbon disulfide (5.00 mL, 83.0 mmol) was added to a second aliquot of acetone (10.00 mL, 0.1360 mol) and the solution was added dropwise to the round bottom flask mixture over 10 minutes, which produced a yellow color initially, but turned a transparent darker orange/red color. Chloroform (10.00 mL, 0.1243 mol) was added in one portion, followed by a second aliquot of 50% NaOH solution (18.00 mL, 0.2250 mol) dropwise over 10 minutes. The reaction was left to stir overnight at ambient temperature, under the nitrogen atmosphere. The following day, a dark orange/brown crust had formed at the surface of the reaction, which was exposed to air and ultrapure water (100 mL) was added with vigorous stirring to break up the chunks. Concentrated HCl (24 mL) was added dropwise, which dissolved the chunks and returned the solution to a dark orange color. The solution was purged with a flow of compressed air with stirring for about four hours to remove residual acetone, which was ceased when light orange precipitate balls formed at the surface of the nearly clear solution. The precipitate was filtered out and broken apart, and then stirred with 200 mL of isopropanol. The isopropanol solution was concentrated to dryness under reduced pressure and the residual dark orange solid was recrystallized in hexanes twice. This produced the bright yellow crystalline DDMAT, with characterization similar to the published method.

General procedure for polymerization:

As an example of the synthesis of PMMA-*co*-GMA, the following is the procedure for the 28% GMA copolymer. A mol ratio of 24/76 GMA to MMA was used in the feed. A round bottom flask was charged with GMA (0.327 mL, 2.40 mmol), MMA (0.809 mL, 7.60 mmol), DDMAT (36.5 mg, 0.1 mmol), AIBN (1.6 mg, 0.01 mmol), and tetrahydrofuran (THF) (5.00 mL). The mixture was chilled in an ice bath and purged with nitrogen gas for 15 minutes to remove molecular oxygen, and then cannulated to a microwave reaction flask with septum cap. The mixture was reacted in a microwave reactor at 120° C for 28 minutes under nitrogen pressure. The polymerization was stopped by exposure to air. The polymer solution was condensed and precipitated in cold methanol twice to remove unreacted starting materials. The resulting light yellow solids were air dried. The other copolymers were synthesized in a similar fashion, however with appropriate mol ratios of GMA and MMA, listed in Table S1.

Table S1: Feed and Actual Ratios of PMMA-*co*-GMA copolymers

Polymer	5% GMA	6% GMA	10% GMA	16% GMA	28% GMA	40% GMA	52% GMA
Feed Ratio	2/98	4/96	8/92	12/88	24/76	36/64	48/52
Actual Ratio	5/95	6/96	10/90	16/84	28/72	40/60	52/48

Synthesis of poly[(methyl methacrylate)-*co*-(2-hydroxypropyl-9-anthroate methacrylate)] (polyACA)

Using the ratio of GMA per polymer and the solid mass, each GMA monomeric unit was treated as one mol equivalent. A representative synthesis of 28% ACA polyACA follows, adapted from Khalafi-Nezhad *et al*.[2] 28% GMA PMMA-*co*-GMA (0.1435 g polymer, 0.35 mmol GMA units), 9-anthracene carboxylic acid (ACA) (0.1507 g, 0.70 mmol), TBAB (22.5 mg, 0.07 mmol), TEA (9.73 µL, 0.07 mmol) and sodium sulfate-dried *N,N*-dimethylformamide (DMF) (5.00 mL) were added to a microwave reaction vessel. The mixture was reacted in a microwave reactor at 150° C for 25 minutes. The mixture started a light yellow color, but after the reaction, turned a dark orange/brown color. The solution was condensed and precipitated in cold methanol to remove unreacted starting materials. The resulting beige solid polyACA was air dried. The other polyACA copolymers were synthesized in a similar fashion, however with appropriate mol ratios of 1/2 GMA unit to ACA.

Synthesis of polyACA-grafted silver nanoparticles (Ag@polyACA)

Material preparations:

Silver nanoparticles were synthesized following a modified Turkevich method,[3] using a sodium borohydride solution for reduction of a silver salt solution.[4] Briefly, $AgNO_3$ aqueous solution (1 mL, 0.01 M) and trisodium citrate dihydrate aqueous solution (1 mL, 0.03 M) were added to ultrapure water (97 mL) with stirring. To the stirring mixture, $NaBH_4$ aqueous solution (1 mL, 1.79 mg mL^{-1}) was added dropwise. The reaction almost immediately turned a grey color, but further addition of the $NaBH_4$ solution turned the reaction mixture yellow, which continued to deepen over time, which indicated nanoparticle growth. The nanoparticle solution was left to stir at ambient temperature for an hour, before aliquots of the solution were stabilized with Tween-20 for reaction with thiol-terminated polyACA.

Thiol-terminated polyACA were prepared by reduction of the trithiocarbonate end-group of the copolymers to a thiol using a $NaBH_4$ reduction method for RAFT chain transfer agent-terminated polymers.[5] As a representative synthesis, 28% ACA polyACA (10.0 mg) was dissolved in 1.00 mL of THF. Then $NaBH_4$ aqueous solution (9.0 mg/0.200 mL) was added dropwise to the stirring polyACA solution, and the reaction was left to stir at ambient temperature overnight. The following day, THF was removed, and the aqueous reaction emulsion was dissolved in dichloromethane (DCM) and washed with saturated ammonium chloride aqueous solution. The aqueous layer was further extracted twice more by DCM and the DCM layers were combined, dried over sodium sulfate, filtered, and the filtrate was concentrated to dryness under reduced pressure. The residual polymer was precipitated in cold methanol and the resulting off-white solid was thiol-terminated polyACA.

General polymer grafting procedure:

To a portion of prepared silver nanoparticles (5.00 mL), polyACA solution (1.00 mL) was added dropwise, and the mixture was left to stir for four hours. The mixture turned from a transparent yellow color to a slightly turbid yellow/orange solution with a slight sheen. The polyACA solution was prepared with THF

to obtain an approximate 5-fold more concentrated solution than the nanoparticle solution, so that upon mixing, an approximate 1/1 mol ratio of polyACA to nanoparticle would be obtained. After the reaction completed, the nanocomposites were centrifuged, washed with 1/1 ultrapure water and THF twice, and then the supernatant was replaced with THF.

Methods and Spectroscopic Measurements

Spectroscopic measurements

Photoluminescence (PL) spectra were obtained using a home-built setup illustrated in Figure S1. The setup consists of a 532 nm DPSS laser (85-GCB-020, Melles Griot), some optical elements (including shutter, attenuator, microscopic objective and optical fibers), a monochromator (Acton Research) and a photon counting PMT (Hamamatsu R928P), data acquisition elements and software (NCL and SpectraSense, Acton Research), and a PC. A 532 nm notch filter was placed in front of the monochromator entrance to reduce laser stray-light.

The laser beam was focused onto the polished end of a 400-µm silica step-index optical fiber (NA = 0.22, RoMack, Inc.) with a microscope objective (10x, NA = 0.25, Newport). The shutter and the variable neutral density filter (Newport) were used to adjust the laser intensity at the samples. Laser power was adjusted to 0.8 mW (or as noted in the figures), measured at the tip of the optical fiber and focused on a 1 mm diameter spot. Samples were contained in septum-capped glass vials and placed directly in front of the optical fiber. The shutter was used to only expose the samples to the laser during data acquisition. All measurements were carried out at ambient temperature. Samples were prepared in the following manner. PolyACA or Ag@polyACA and PtOEP were dissolved separately in THF, and then mixed together at the final desired concentrations, as noted in the figures. The solutions were kept in an ice bath and deoxygenated by nitrogen gas purge for 15 minutes directly before PL measurements.

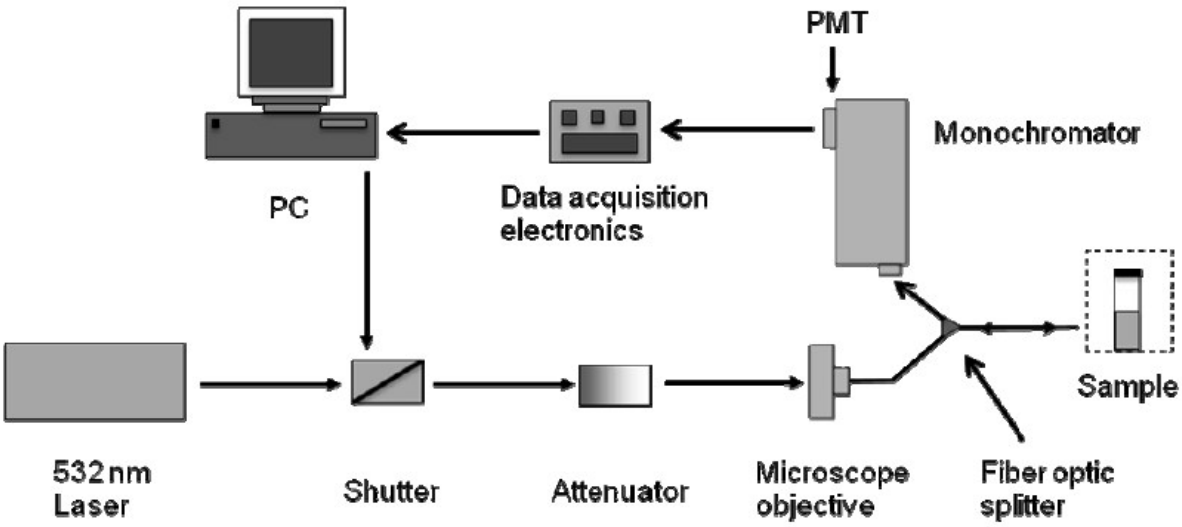


Figure S1. Schematic illustration of PL instrument setup.

Fluorescence emission spectra were obtained using a QM-40 spectrometer (PTI) equipped with PMT (PTI). The light source was a xenon arc lamp, and all measurements were done in a quartz cuvette, held

in a light-tight chamber (PTI) and the samples were prepared in THF. Spectra were collected using FelixGX software and analyzed using OriginLab software.

Estimation of nanoparticle concentration

The [Ag atoms] is known, based on the [$AgNO_3$] added to the nanoparticle solution. Assuming a spherical volume, with radius of 0.160 nm,[6] a single Ag atom occupies $4\pi r^3$ volume = 0.0515 nm^3. Next, the mean particle size was determined from the size distribution of the unmodified silver nanoparticles. Assuming a spherical volume again, with an average diameter = 10.213 nm and therefore average radius of 5.106 nm, the average volume of a single nanoparticle = 1,673.4 nm^3. Next the volume of one nanoparticle was divided by the volume of a Ag atom to get the average number of Ag atoms per nanoparticle = 32511 atoms/particle. The [Ag atoms] was divided by the average number of Ag atoms per nanoparticle to give the average number of nanoparticles in the solution. This was converted to molarity, and was found to be 1.23E-9 M.

Determination of quantum yields

TTA-UC quantum yields (QY) of the samples was determined by using Eq. S1, and following previously described procedures.[7]

Eq. S1

$$\phi_{unk} = 2\phi_{std}\left(\frac{A_{std}}{A_{unk}}\right)\left(\frac{I_{unk}}{I_{std}}\right)\left(\frac{\eta_{unk}}{\eta_{std}}\right)^2$$

Here, ϕ, A, I, and η represent the QY, absorbance, integrated upconversion intensity from the spectra, and refractive index, respectively. The subscript std refers to a reference fluorophore with known QY and subscript unk refers to the sample to be determined. Rose Bengal (RB) was used as the reference fluorophore. RB has ϕ_{std} = 0.11 in ethanol at room temperature under excitation = 532 nm.[8] The refractive indices of THF and ethanol are η_{THF} = 1.407 and η_{EtOH} = 1.361.[9] All measurements were taken under the same experimental settings and solutions were prepared as described.

Characterization

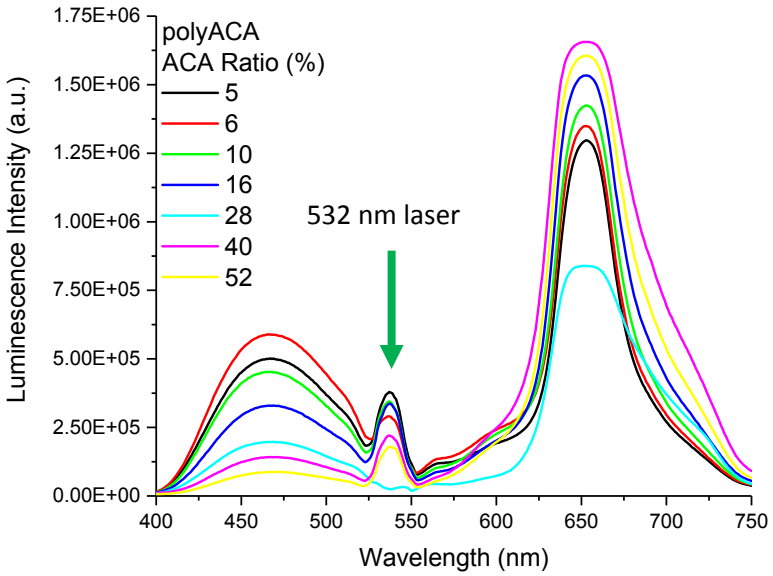


Figure S2. Photoluminescence spectra of polyACA TTA-UC samples with the entire wavelength range shown. The green arrow indicates the laser excitation, where the peak represents slight stray laser light. The upconversion range is between 400-530 nm and the PtOEP phosphorescence range is between 600-750 nm.

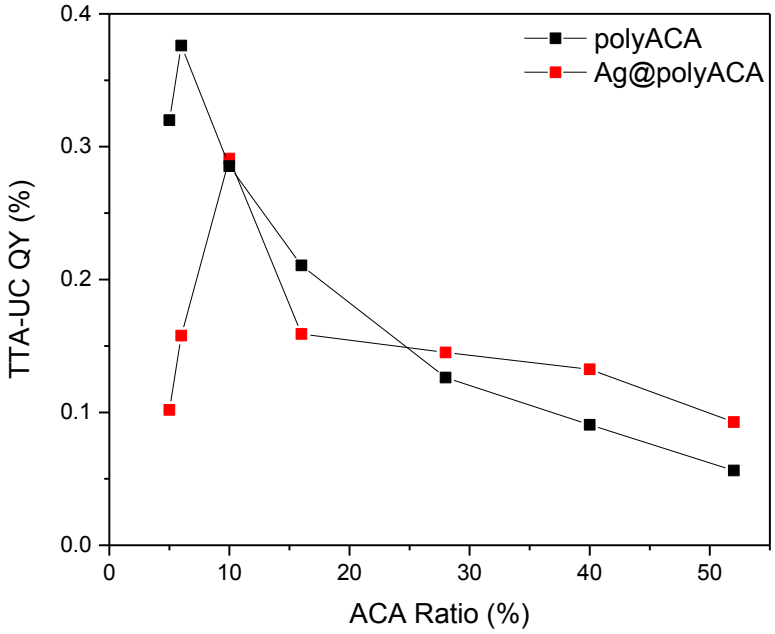
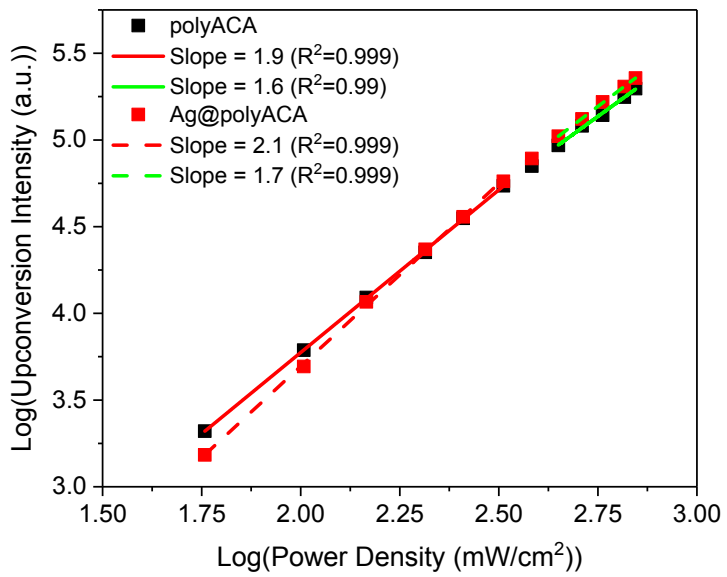


Figure S3. QY of polyACA (black squares) and Ag@polyACA (red squares) using Rose Bengal as the reference and Eq. S1 to calculate. Excitation power density was 254.6 mW/cm^2.

A



B

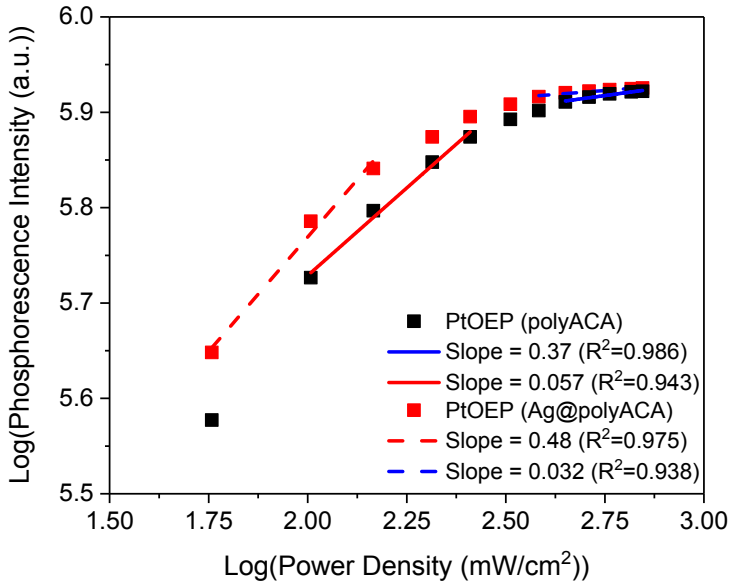


Figure S4. (A) Power dependence log-log plot of the upconversion intensity versus the excitation power density for polyACA (black squares) with quadratic range (solid red line) and linear range (solid green line), and Ag@polyACA (red squares) with quadratic range (dashed red line) and linear range (dashed green line). Extrapolation to the intersection of the two lines for each set gives the threshold intensity (I_{th}). For polyACA, I_{th} = 352.5 mW/cm^2 and for Ag@polyACA, I_{th} = 341.3 mW/cm^2. (B) Power dependence log-log plot of the PtOEP phosphorescence intensity versus the excitation power density for polyACA samples (black squares), and Ag@polyACA samples (red squares). This plot is typically linear, however, the slope of these plots are much smaller than one, indicating a more efficient radiative pathway for PtOEP by phosphorescence.

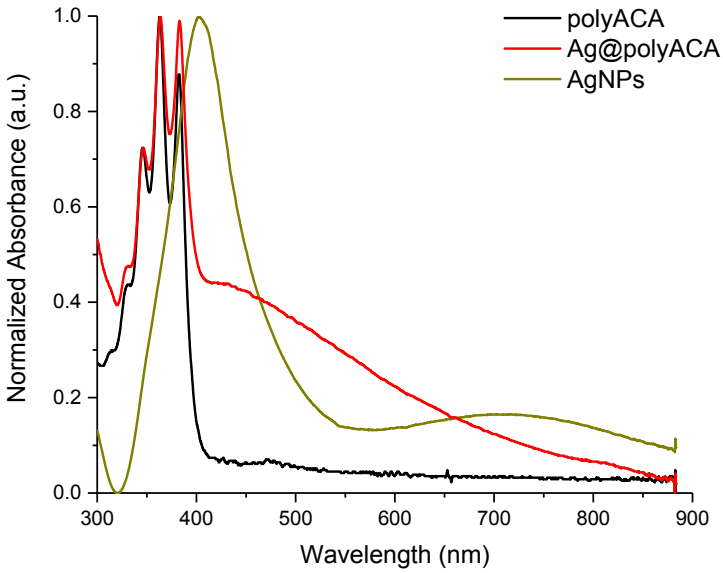
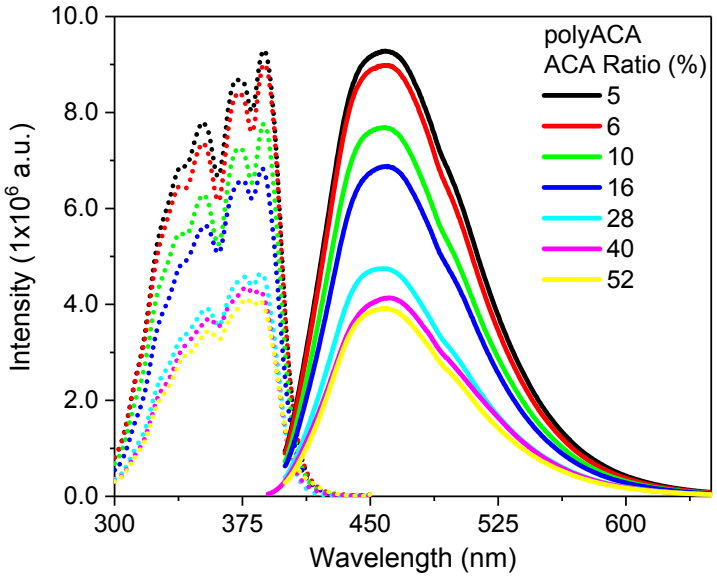


Figure S5. Normalized UV-visible spectra of polyACA (black), Ag@polyACA nanocomposite (red), and unmodified silver nanoparticle (AgNPs) (green) in THF solutions. The characteristic anthracene absorbance is between 320-420 nm, while the nanoparticle plasmon band is between 320-550 nm. There is another band in the nanoparticle sample between 550-900 nm, which indicates some aggregation of the particles. Aggregation was observed in the unmodified nanoparticle samples when dispersed in THF, which was used in order to replicate the conditions for the other samples. Aggregation was not observed when the nanoparticles were dispersed in water, however, aggregation was observed for the modified nanoparticles when dispersed in water.

A



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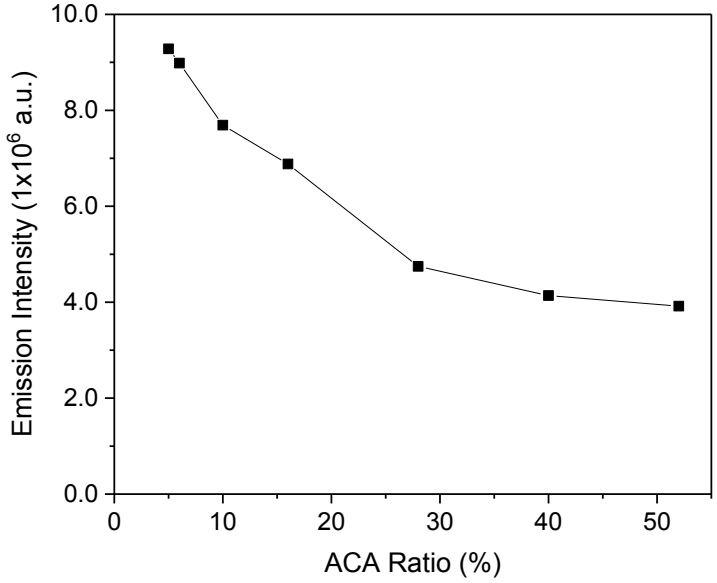

Figure S6. (A) Fluorescence emission (solid lines) and excitation (dotted lines) of the polyACA series, with specified ACA ratios: 5% ACA (black), 6% ACA (red), 10% ACA (green), 16% ACA (blue), 28% ACA (cyan), 40% ACA (magenta), and 52% ACA (yellow). (B) The relationship between fluorescence emission intensity (excitation at 380 nm) and the ACA ratio.

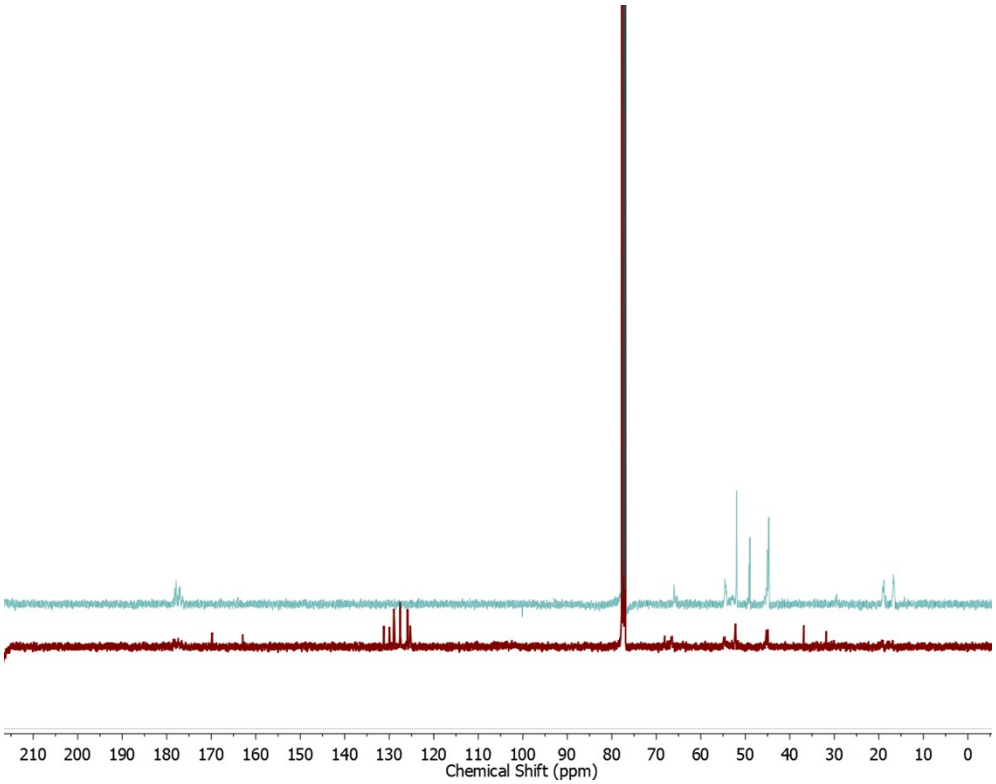

Figure S7. ^{13}C NMR spectra of PMMA-*co*-GMA (teal trace) and polyACA (maroon trace).

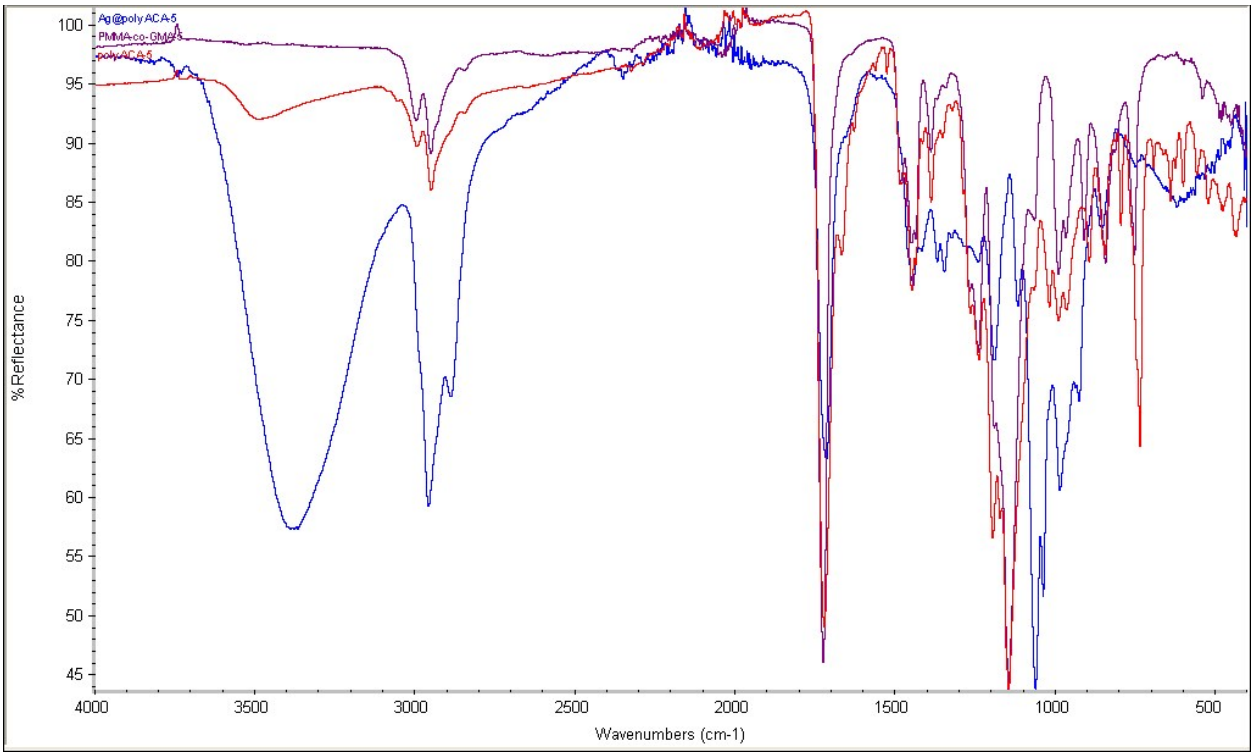

Figure S8. FTIR spectra of PMMA-*co*-GMA (purple trace), polyACA (red trace), and Ag@polyACA (blue trace).

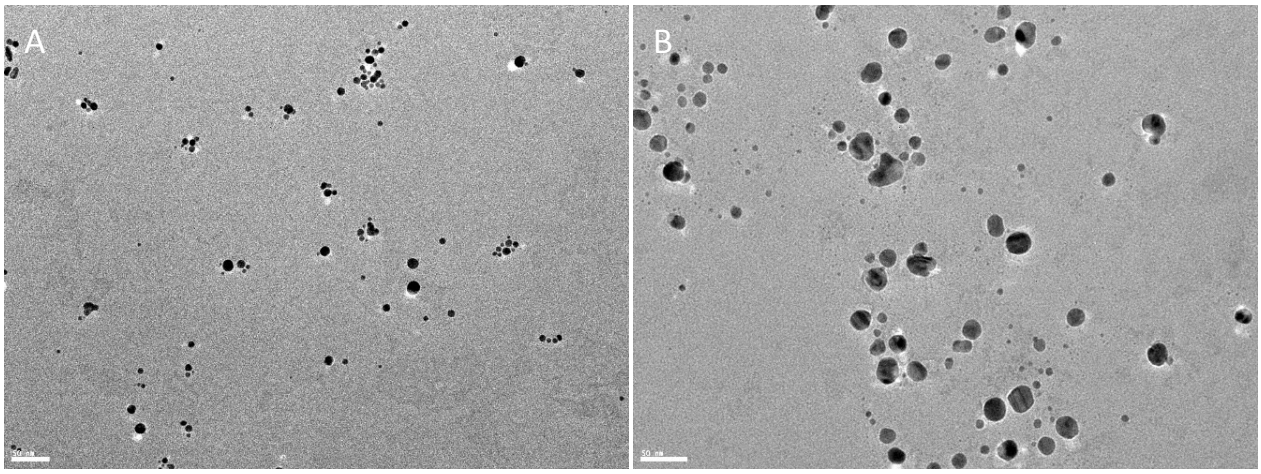

Figure S9. TEM micrographs of unmodified silver nanoparticles (A) and Ag@polyACA nanocomposites (B). Scale bar is 50 nm.

Using ImageJ software, the diameters of 130 nanoparticles were measured for both the unmodified silver nanoparticles and the Ag@polyACA nanocomposites. Mean values were obtained, along with standard deviation and polydispersity of the samples. The unmodified silver nanoparticles had an average diameter of 10.2 ± 4.0 nm with a PDI of 0.151, which indicates intermediate polydispersity. For representation, the 28% ACA Ag@polyACA had an average diameter of 18.0 ± 10.3 nm with a PDI of 0.330, indicating polydispersity. It is evident that some of the nanocomposites were increased in size due to the polyACA grafting, however not all of the nanoparticles were reacted with, resulting to a wider range of distribution.

References

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