Supporting information

Reagents and instruments

Methanol, acrylic acid, methyl acrylate, poly(vinyl pyridine) (PVPy) (Mw=160,000) were purchased from Aldrich. They were used without further purification. Photoacids were synthesized according to a previously-reported procedure.[28]

Transmittance was measured using a Varian Cary 60 Scan UV/Vis spectrophotometer. ^{1}H NMR and ^{13}C NMR spectra were determined in deuterated solvents on a Bruker AV400 NMR spectrometer. The light sources for irradiation were 470 nm LED arrays with 120 LEDs purchased from www.theledman.com. Dynamic light scattering (DLS) measurements were carried out on a SZ-100 Nanopartica Series Instrument manufactured by HORIBA. AFM was conducted using Nanosurf EasyScan 2 AFM.

Preparation of copolymer Poly(acrylic acid-co-methyl acrylate)

Poly(acrylic acid-co-methyl acrylate) (PAA–co–PMA) was prepared by radical polymerization using AIBN as the initiator. In a test tube, 0.2g of acrylic acid and 0.96g of methyl acrylate were dissolved in 1mL of ethanol. Then 3mg of AIBN was added and the solution purged with nitrogen for 30 minutes to remove oxygen. The reaction mixture was heated to 65˚C and kept for 3 hours. After the reaction, the solution was added to diethyl ether dropwise to precipitate out the polymer product and remove unreacted monomers. After the product was dried under vacuum, 0.91g of the polymer was obtained.

Preparation and characterization of the polymer suspension containing mPAH1

The polymer suspension was prepared by noncovalent crosslinking of PAA-co-PMA with PVPy. In a test tube, 12mg of PAA–co–PMA was dissolved in 3mL of methanol. While the solution was stirred vigorously, 0.15mL of PVPy solution in methanol (containing 0.45mg PVPy) was added slowly. An opalescent suspension formed during the addition. (FTIR of a sample prepared by drying the suspension is showing in Figure S1, which indicates hydrogen bonding bewteen pyridine and carboxylic groups of the two polymers.) After all the PVPy solution was added, 3mg of mPAH1 was added to the suspension.

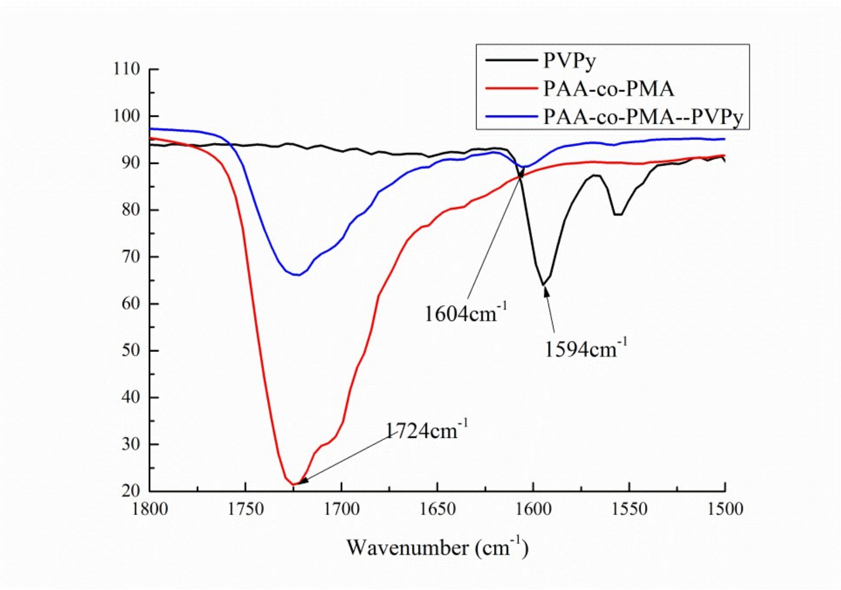

Figure S1. FTIR of the PAA-co-PMA/PVPy mixture in comparison with that of PVPy and PAA-co-PMA obtained using ATR method. (All the samples are solids. The intensity difference is due to different amount of the samples and doesn’t have any quantitative meaning.)

The suspension was irradiated with 470nm LED light with intensity of approximately 20 mW/cm^2. The distance between the solution and the LED light was approximately 5cm. Irradiation time was 3 minutes which is long enough to generate strong acidity in the solution. The size and distribution of the polymer nanoparticle before and after irradiation were measured by dynamic light scattering method. Sunlight is also enough to induce the photoreaction. To demonstrate this, the suspension was kept under outdoor sunlight for 5 minutes and the suspension chnaged to a clear solution. The solution slowly changed back to a cloudy suspension after taken back indoor. (Figure S2)

Just prepared 5 min in sunshine indoor 30 min

Figure S2. Sunlight induced change of the nanoparticle suspension.

For transmittance test, a freshly prepared sample in a quartz cell was first irradiated with 470nm LED light for 3 minutes to convert the milky suspension to a transparent solution. After which, the first scan of transmittance was carried out. As described above, the freshly prepared polymer nanoparticle does not have good size distribution. The transmittance also varied for different samples. Therefore the first measurement started from the transparent solution after the first irradiation. Then the solution was kept in the dark for 2 hours and a transmittance measurement was taken for the resulting suspension. The cycle was repeated for 9 times.

AFM was conducted with a Nanosurf EasyScan 2 AFM using contact mode. TEM was conducted with FEI Tecnai F30 TEM. The supension of nanoparticles was diluted 200 times and dried before TEM. Before irradiation, nanoparticles with expected sizes (~0.2-0.5 nm) were observed together with aggreations and polymers. After irradiation, some aggregations of nanoparticles with smaller sizes was observed (Figure S3). It is worth mentioning that it was difficult to dry the TEM sample quickly due to dilution. Given that nanoparticles were formed by noncovalent interaction, the sample preparation might make the nanoparticles observed by TEM different to that in the suspension.

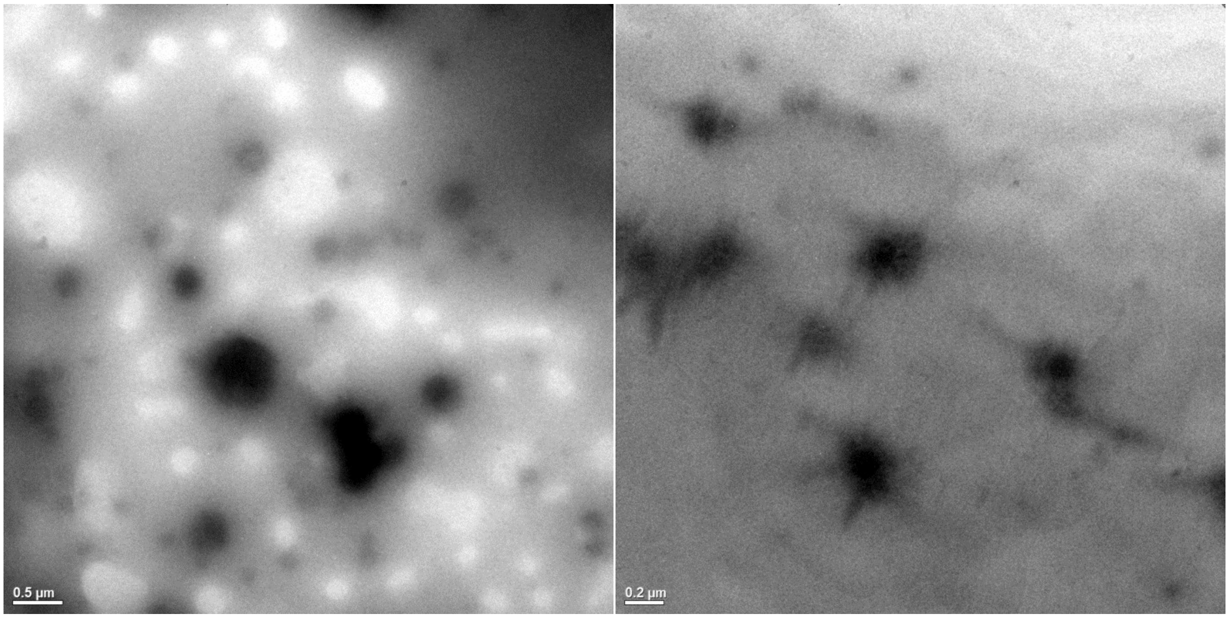

Figure S3. TEM of a diluted nanoparticle suspension before and after irradiatio. (Please note the difference of the scale.)