## 1. General Methods

All reagents were obtained from Sigma-Aldrich, or Key Organics and used as received. Water for nanoparticle synthesis and hydrogen evolution experiments was purified using an ELGA LabWater system with a Purelab Option S filtration and ion exchange column ($\rho$ = 15 MΩ cm) without pH level adjustment. The UV-visible absorption spectra of the polymers were recorded on a Shimadzu UV-2550 UV-Vis spectrometer and fluorescence spectra were measured with a Shimadzu RF-5301PC fluorescence spectrometer at room temperature. The bulk were measured as powders in the solid state whilst the emulsion particles were measured as suspensions. Imaging of the polymer morphology was achieved on a Hitachi S4800 Cold Field Emission SEM, with secondary electron, backscatter and transmission detectors. Dynamic light scattering measurements were performed on a Malvern Zetasizer Nano Particle Sizer, at 25 °C, in aqueous solutions or with the addition of triethylamine (TEA), methanol (MeOH) or triethanolamine (TeOA) as described. Three measurements, each of 12 scans, were taken for each sample and the average calculated. Polymer refractive index of 1.59 and absorbance of 0.01 was used for all samples. Measurements in aqueous solution were fitted using the Malvern 'Generic latex' standard operating procedure with solvent refractive index of 1.330 and viscosity 0.8872 cP. Measurements in Water/MeOH/TEA mixture were fitted with a modified operating procedure with solvent refractive index of 1.337 and viscosity 1.646 cP. Measurements in a 10% TeOA mixture were fitted with a modified operating procedure with solvent refractive index 1.013 and viscosity of 1.347 cP. Static light scattering measurements were performed on a Malvern Mastersizer 3000 Particle Sizer, polymers were dispersed in water/methanol/triethylamine (1:1:1) mixture by 10 minutes of ultrasonication and the resultant suspensions were injected into a stirred Hydro SV quartz cell, containing more of the water/methanol/triethylamine (1:1:1) mixture, to give a laser obscuration of 2 – 8%. Particle sizes were fitted according to Mie theory, using the Malvern 'General Purpose' analysis model, for non-spherical particles with fine powder mode turned on. A polymer refractive index of 1.59, polymer absorbance of 0.1 and solvent refractive index of 1.337 were used for fitting. Palladium content was determined via ICP-OES by the University of Liverpool Analytical Services for emulsion particles and by ICP-MS (Perkin Elmer ICP MS NexION 2000) for bulk samples. Thermogravimetric analysis was performed on an EXSTAR6000 over the temperature range 40 to 800 °C in platinum pans under air with a heating rate of 10 °C $min^{-1}$. Surface areas were measured by nitrogen adsorption and desorption at 77.3 K. Powder samples were degassed offline at 110 °C for 15

hours under dynamic vacuum ($10^{-5}$ bar) before analysis. Isotherms were measured using Micromeritics 2420 volumetric adsorption analyzer. Surface areas were calculated in the relative pressure ($P/P_0$) range from 0.07 to 0.35 of the adsorption branch.

## 2. Synthesis

**Synthesis of bulk polymers:** Me-CMP, S-CMP1 and P10 were synthesised according to literature procedures.[1–3]

**Synthesis of 3,7-Dibromodibenzo[*b*,*d*]thiophene sulfone**: Dibenzo[*b,d*]thiophene sulfone (20.0 g, 92.5 mmol) in sulfuric acid (98%, 600 mL) was heated in a nitrogen purged flask to 70 °C. In the dark *N*-bromosuccinimide (35.6 g, 200 mmol) was added in several portions and the solution stirred for 24 h. The mixture was carefully added to water with cooling and then extracted with chloroform, washed with brine, dried with magnesium sulfate and filtered. After evaporation a mixture of 3,7-dibromodibenzo[*b,d*]thiophene sulfone and 3-bromodibenzo[*b,d*]thiophene sulfone was obtained. 3,7-dibromodibenzo[*b,d*]thiophene sulfone was isolated by re-crystallisation from chlorobenzene as a white powder (22.5 g, 60.2 mmol, 65%).

**Synthesis of 3,7-Dibenzo[*b*,*d*]thiophene sulfone diboronic acid bis(pinacol) ester:** 3,7-Dibromodibenzo[*b,d*]thiophene sulfone (935 mg, 2.5 mmol), bis(pinacolato)diboron (1.50 g, 5.9 mmol), potassium acetate (586 mg, 6.0 mmol) and [Pd(DPPF)$Cl_2$] (27.4 mg, 0.038 mmol, 1.5 mol%) were added to a dried flask, dried under vacuum for 5 mins and then purged with $N_2$. *N*,*N*-Dimethylformamide (25 mL) was added via syringe and the solution was stirred under nitrogen at 90 °C overnight. The solution was added to water (100 mL) and the product extracted with ethyl acetate. The organic phase was washed with hydrochloric acid (1 M, 50 mL), dried with magnesium sulfate and filtered. After evaporation the crude product was recrystallized from acetonitrile to give light brown crystals of 3,7-dibenzo[*b,d*]thiophene sulfone diboronic acid bis(pinacol) ester (564 mg, 1.2 mmol, 48%).

**Representative synthesis of mini-emulsion particles:**[4] The monomers were dissolved in toluene (16 mL) and degassed by nitrogen bubbling for 30 minutes. An aqueous solution (144 mL) of sodium *n*-dodecyl sulfate (10 mg $mL^{-1}$) and sodium carbonate (3.5 mg $mL^{-1}$) was

degassed by nitrogen bubbling for 30 minutes. [$Pd(PPh_3)_4$] (5 mg, 6.83 μmol) was added to the organic phase followed by the aqueous solution. The mixture was sonified with a Branson 550 W digital sonifier at 40% power for 2 minutes. The emulsion was then degassed for a further 10 minutes before heating to 90 °C for 16 hours. The emulsion was filtered through paper (Whatman® general use) and nanoparticles were used as synthesised.

**ME-CMP-e:** Monomers: 1,3,5-phenyl triboronic acid tri(pinacol) ester (40.1 mg, 0.88 mmol) and 4,4'-dibromobiphenyl (41.2 mg, 0.132 mmol).

**S-CMP1-e:** Monomers: 1,3,5-phenyl triboronic acid tri(pinacol) ester (40.1 mg, 0.88 mmol) and 3,7-dibromodibenzo[*b,d*]thiophene sulfone (49.4 mg, 0.132 mmol).

**P10-e:** Monomers: 3,7-dibenzo[*b,d*]thiophene sulfone diboronic acid bis(pinacol) ester (51.5 mg. 0.11 mmol) and 3,7-dibromodibenzo[*b,d*]thiophene sulfone (41.2 mg, 0.11 mmol).

## 3. Dynamic Light Scattering

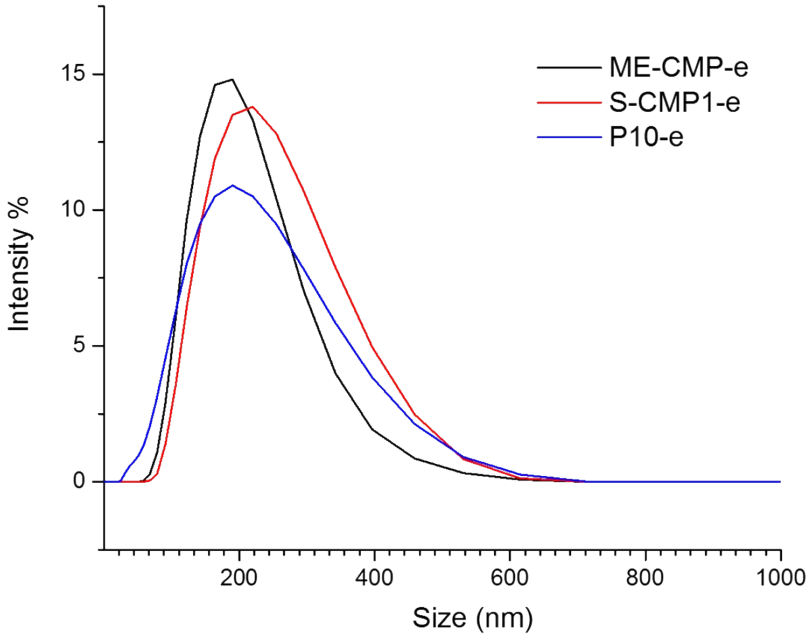


**Figure S1:** Distribution of particle sizes for the emulsion particles as synthesised.

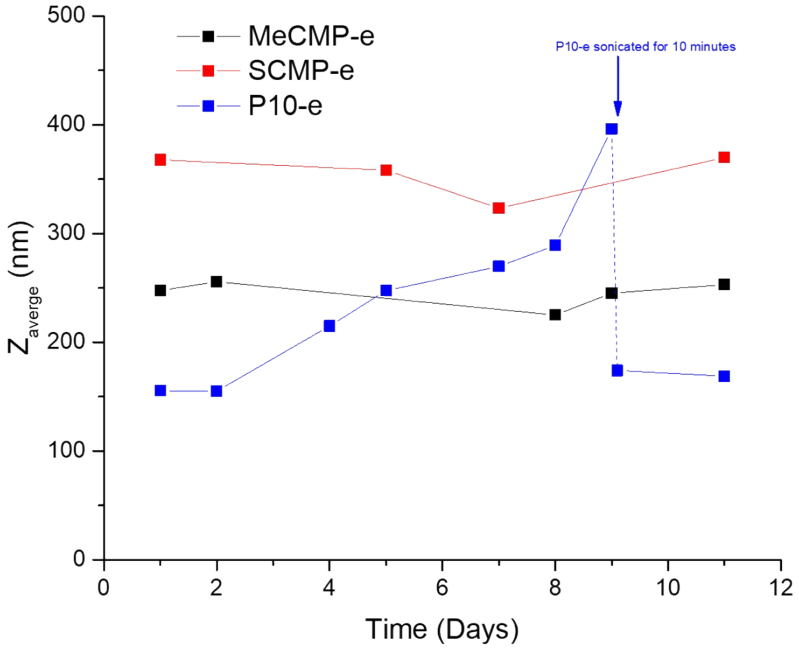


**Figure S2:** Emulsion particle size over time when left without stirring. P10-e sample was sonicated on day 9 for 10 minutes.

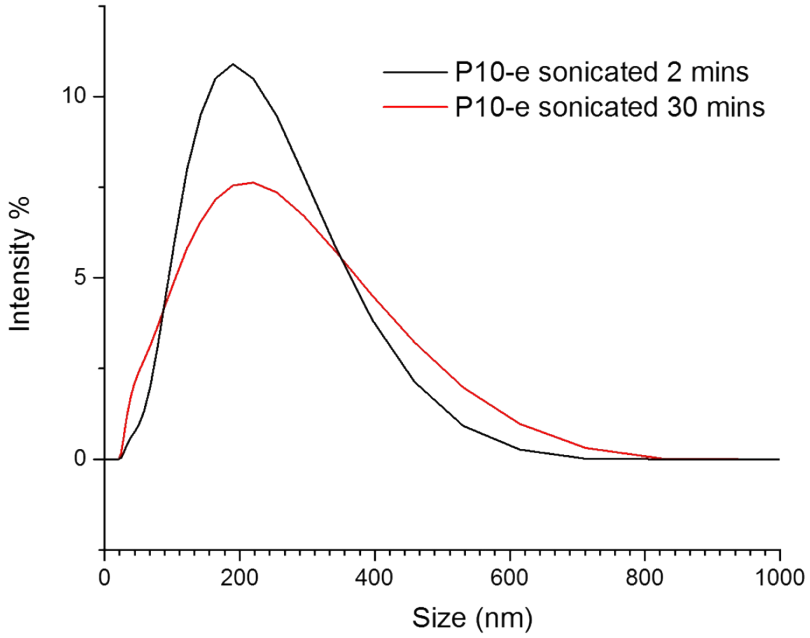


**Figure S3:** P10-e batches synthesised using different lengths of sonication before heating.

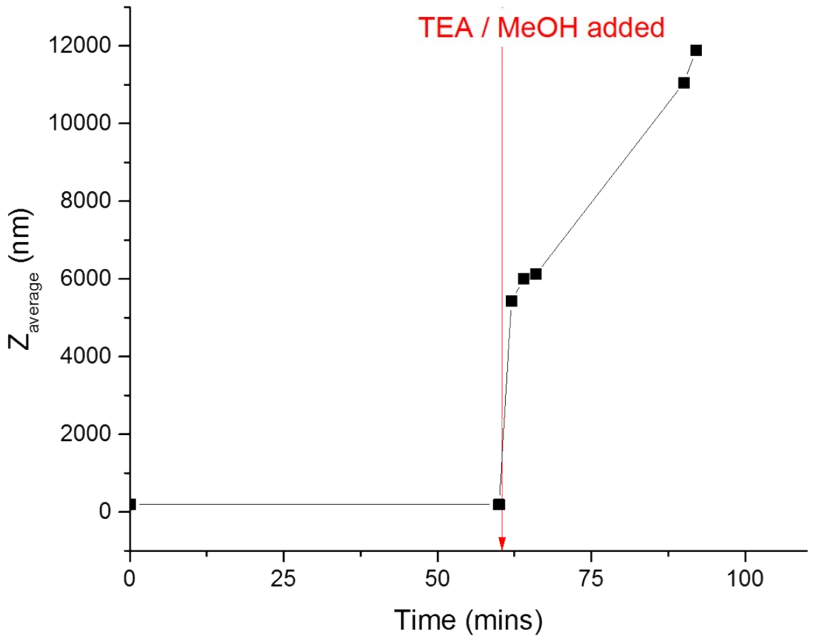


**Figure S4:** Aggregation of ME-CMP-e particles upon addition of TEA (1 mL) and MeOH (1 mL) to the aqueous nanoparticle solution (1 mL).

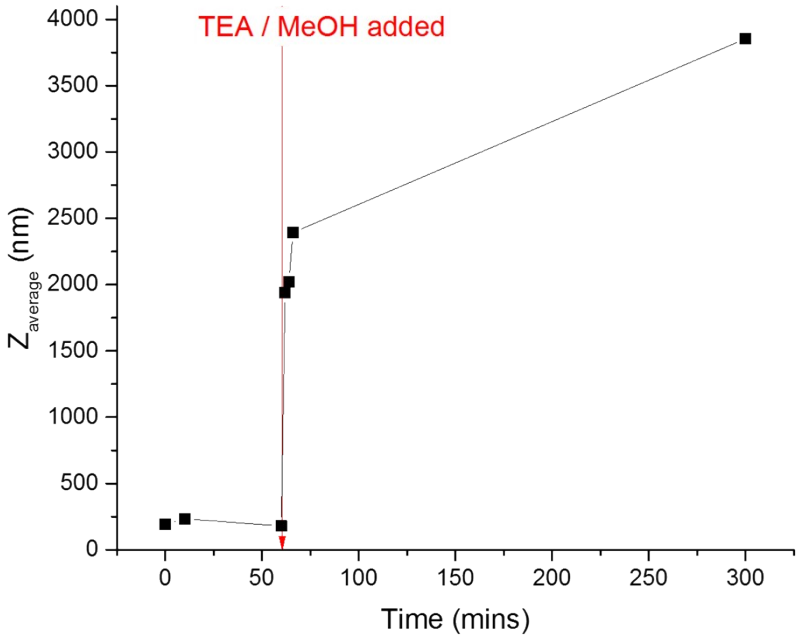


**Figure S5:** Aggregation of S-CMP-e particles upon addition of TEA (1 mL) and MeOH (1 mL) to the aqueous nanoparticle solution (1 mL).

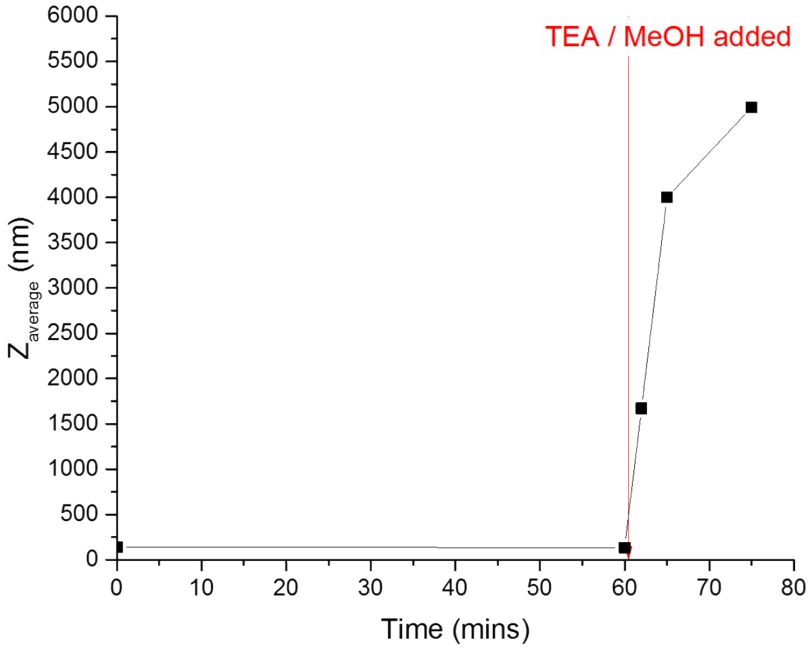


**Figure S6:** Aggregation of P10-e particles upon addition of TEA (1 mL) and MeOH (1 mL) to the aqueous nanoparticle solution (1 mL).

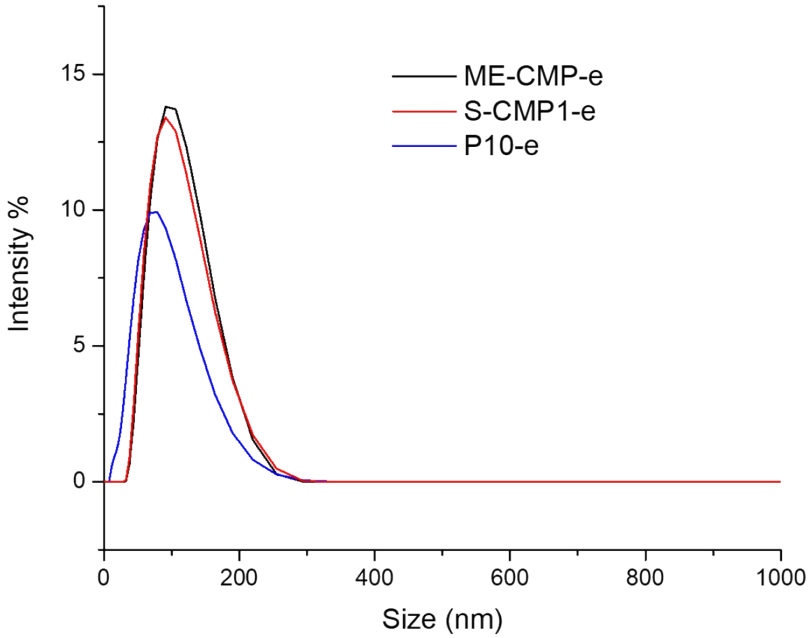


**Figure S7:** Emulsion particle sizes in 10% TeOA aqueous solution.

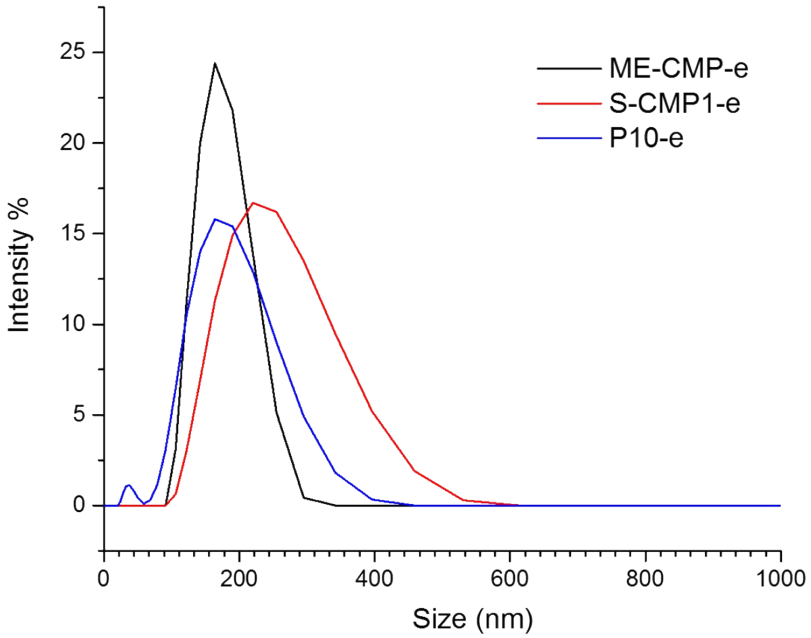


**Figure S8:** Particle sizes in 0.1 M ascorbic acid.

## 4. Static Light Scattering

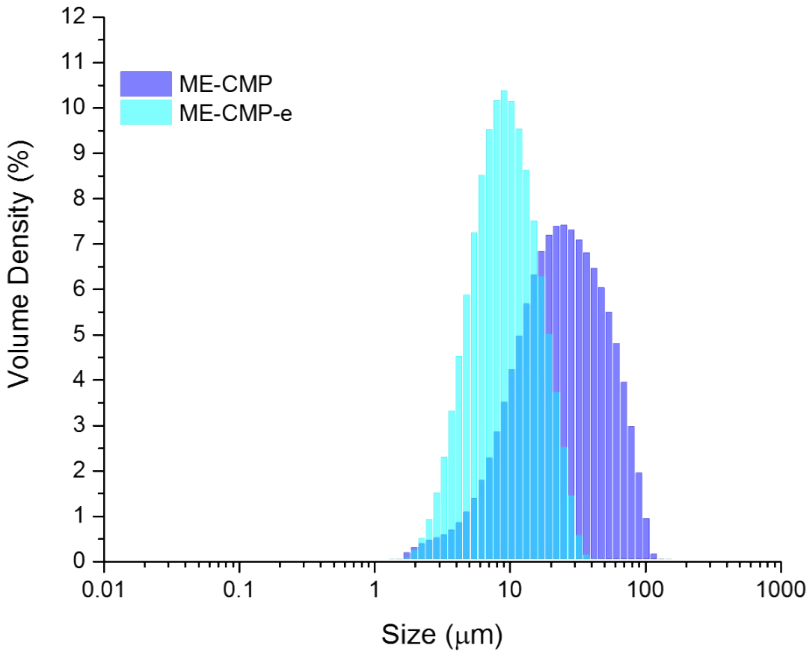


**Figure S9:** Particle size distribution of ME-CMP-e and ME-CMP in 33% TEA, 33% MeOH, 33% aqueous photocatalytic mixture.

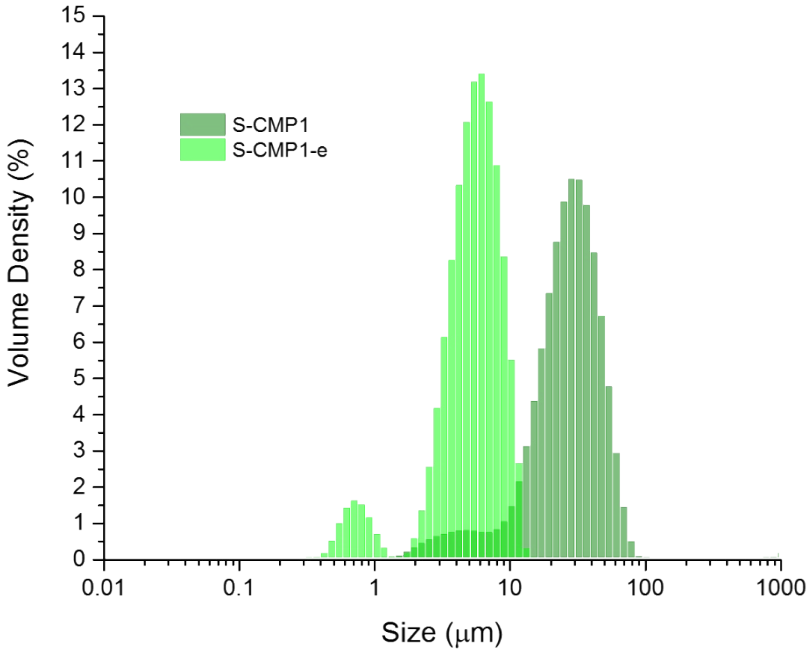


**Figure S10:** Particle size distribution of S-CMP1-e and S-CMP1 in 33% TEA, 33% MeOH, 33% aqueous photocatalytic mixture.

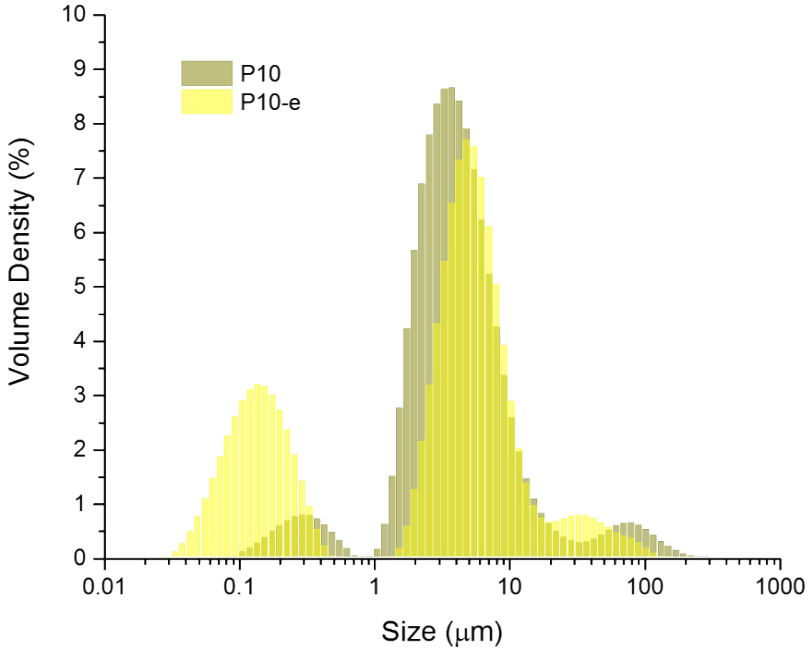


**Figure S11:** Particle size distribution of P10-e and P10 in 33% TEA, 33% MeOH, 33% aqueous photocatalytic mixture.

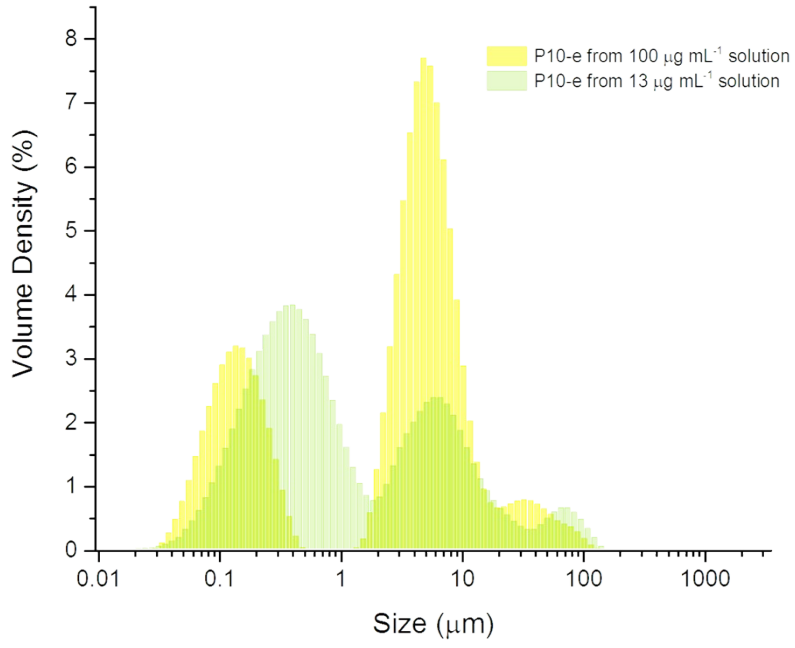


**Figure S12:** Particle size distribution of P10-e from different concentration 33% TEA, 33% MeOH, 33% aqueous photolysis mixtures

$$D[3,2] = \frac{\sum_{1}^{n} D_{iv_i}^{3}}{\sum_{1}^{n} D_{iv_i}^{2}}$$

**Equation 1**

Sauter mean diameter, *D*[3,2], gives the diameter of a sphere that has the same volume : surface area ratio as the entire distribution.[5,6]

## 5. Scanning and Transmission Electron Microscopy

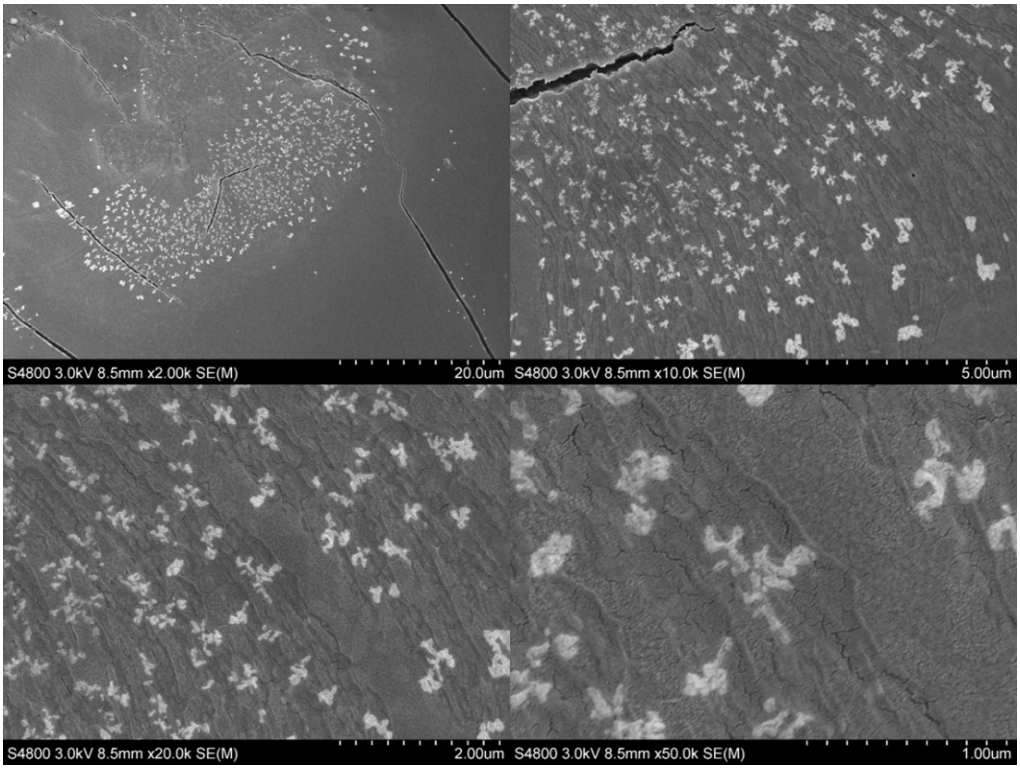


**Figure S13:** SEM images of ME-CMP-e as synthesized.

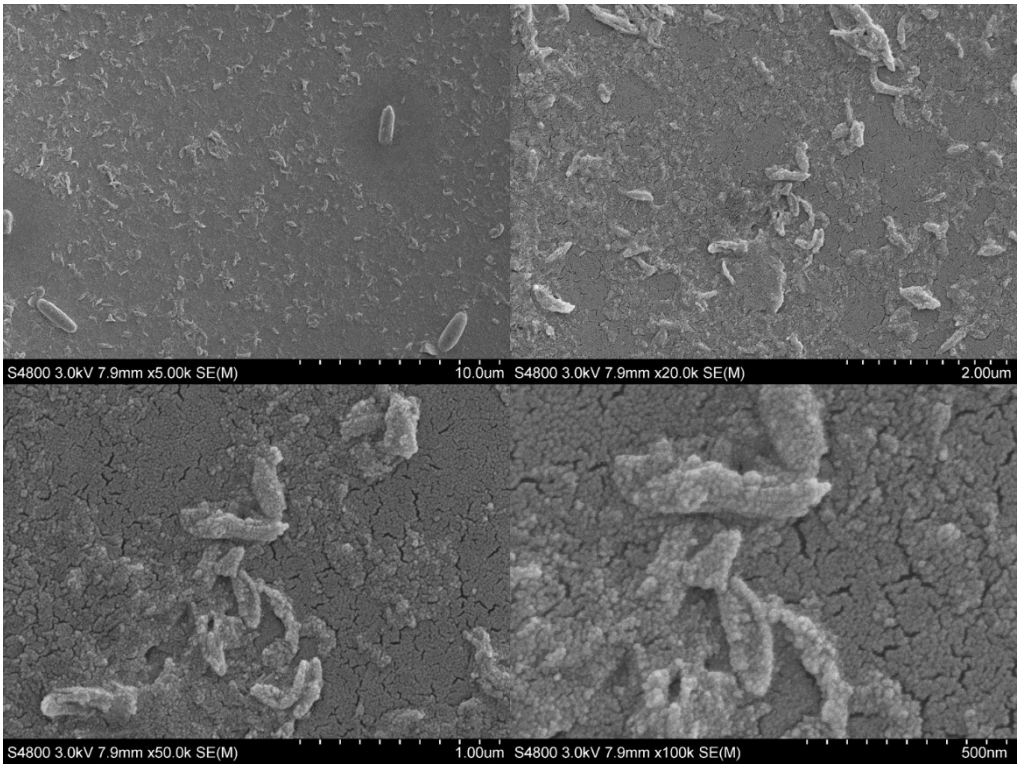


**Figure S14:** SEM images of S-CMP1-e as synthesized.

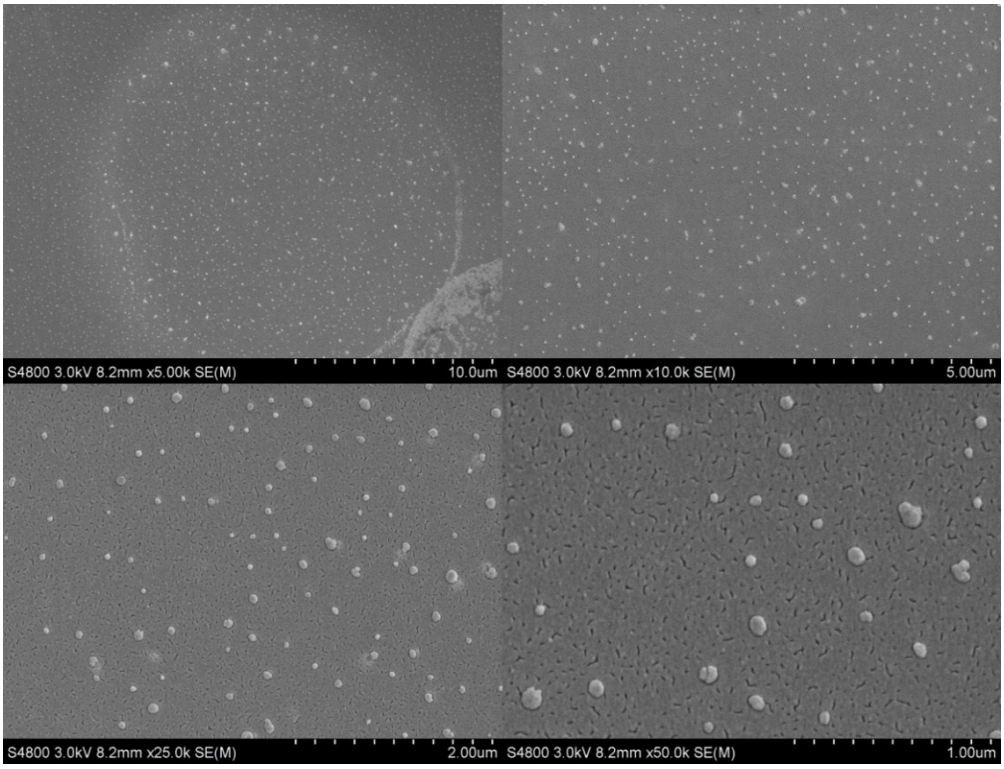


**Figure S15:** SEM image of P10-e as synthesized.

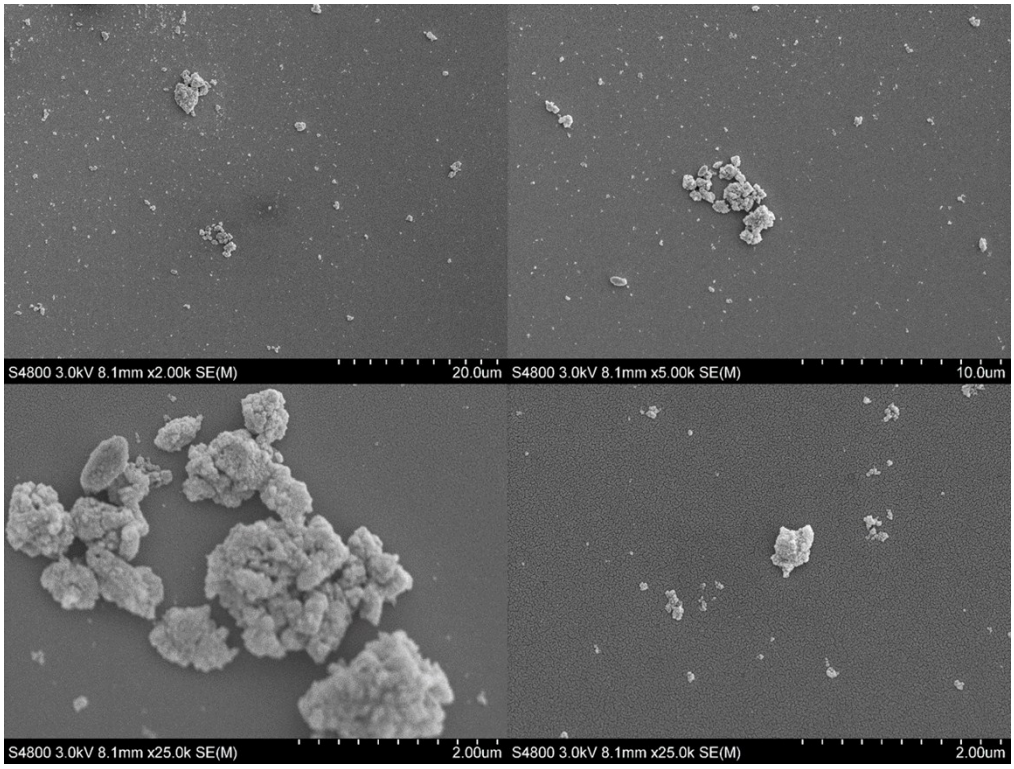


**Figure S16:** SEM images of ME-CMP-e collected from photolysis mixture after 5 hours of irradiation.

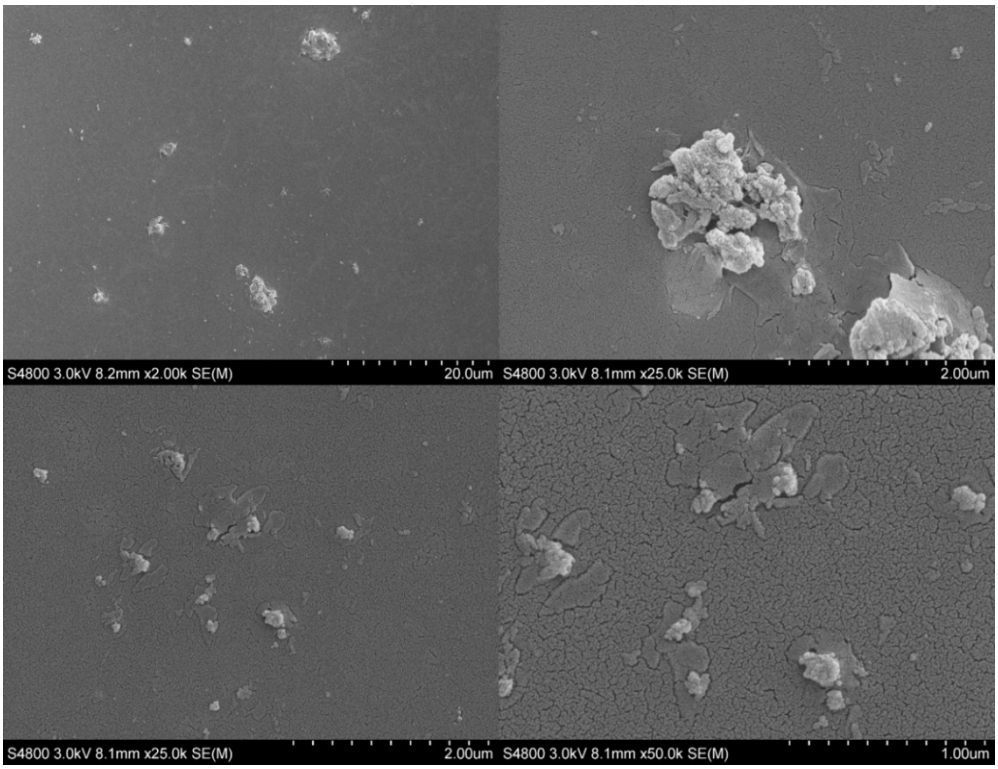


**Figure S17:** SEM images of S-CMP1-e collected from photolysis mixture after 5 hours of irradiation.

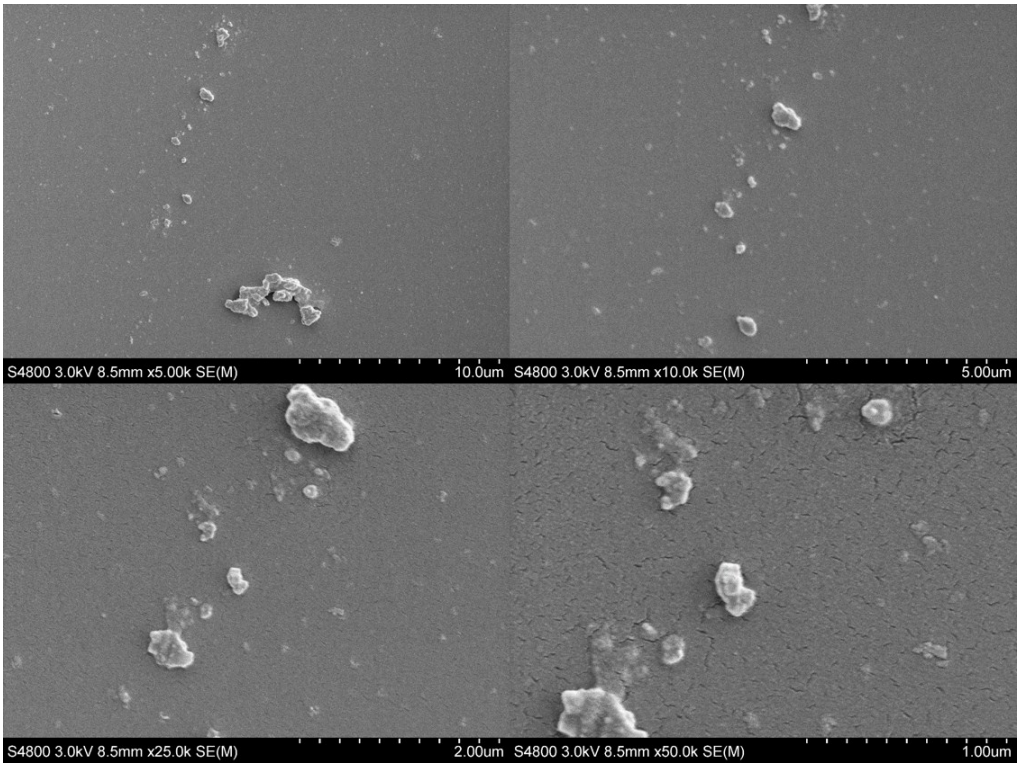


**Figure S18:** SEM images of P10-e collected from photolysis mixture after 5 hours of irradiation.

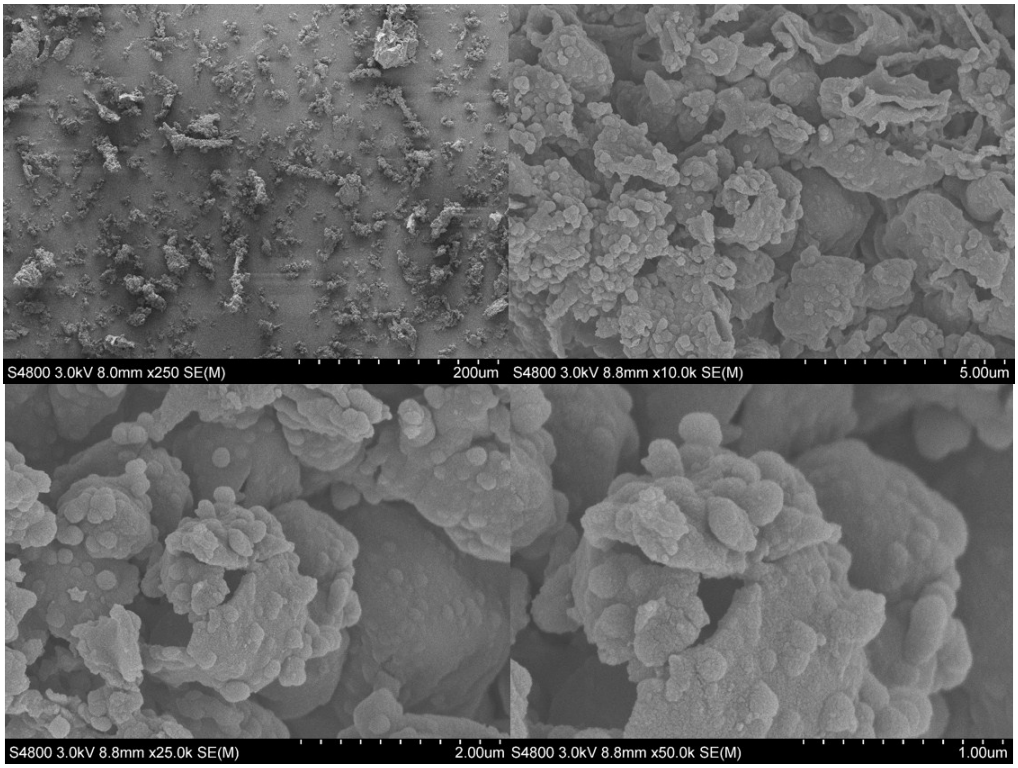


**Figure S19:** SEM images of bulk ME-CMP.

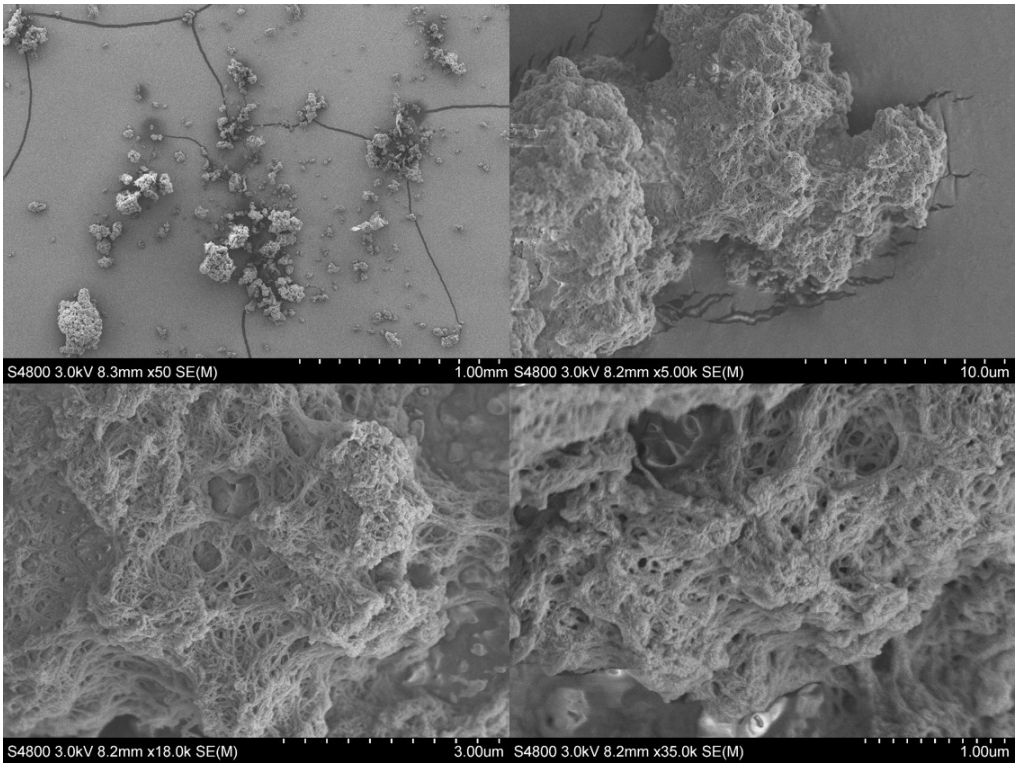


**Figure S20:** SEM images of bulk S-CMP1.

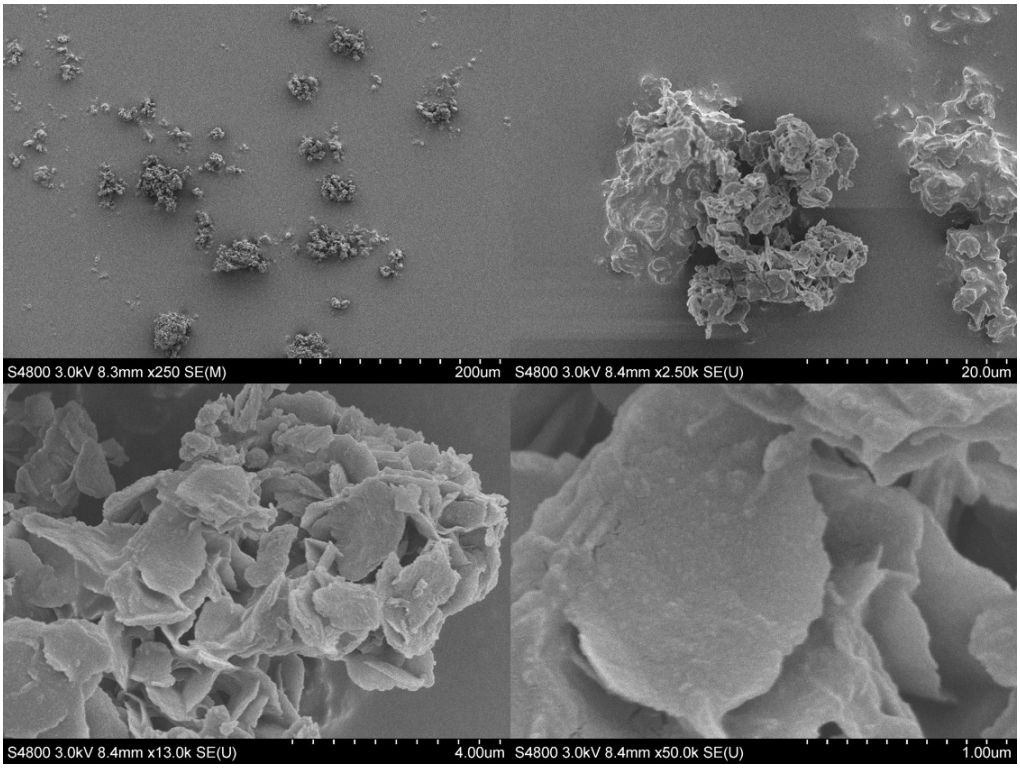


**Figure S21:** SEM images of bulk P10.

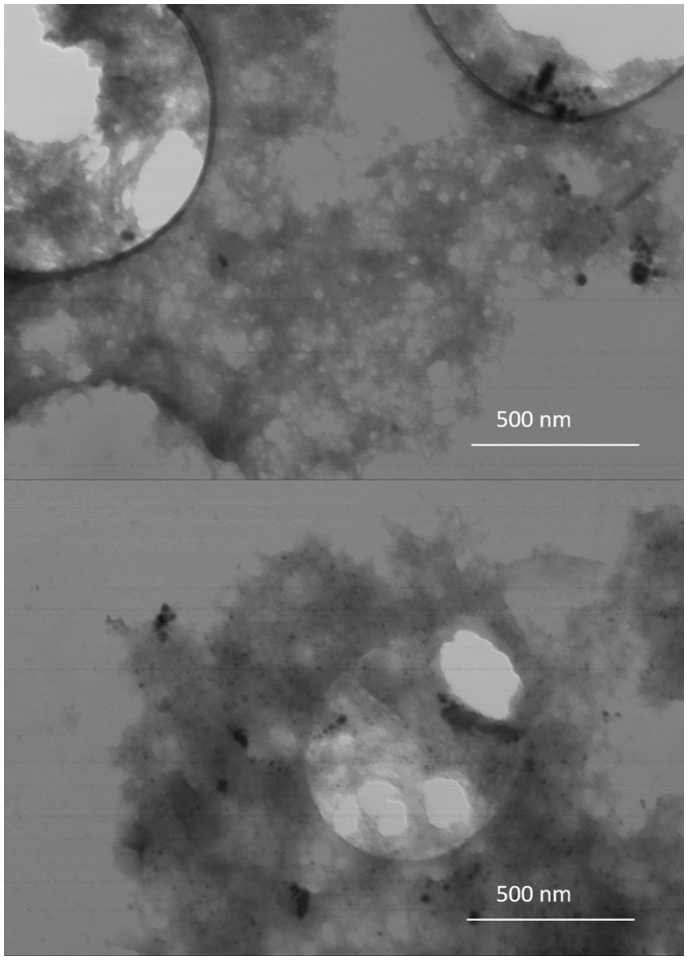


**Figure S22:** TEM images of P10-e with (bottom) and without (top) 3wt% Pt. Both samples also contain > 10 nm particles of residual pallidum from synthesis. Pt loaded from $K_2PtCl_6$ (aq) by insitu photodeposition in the photocatalytic mixture.

## 6. UV-Vis Spectroscopy

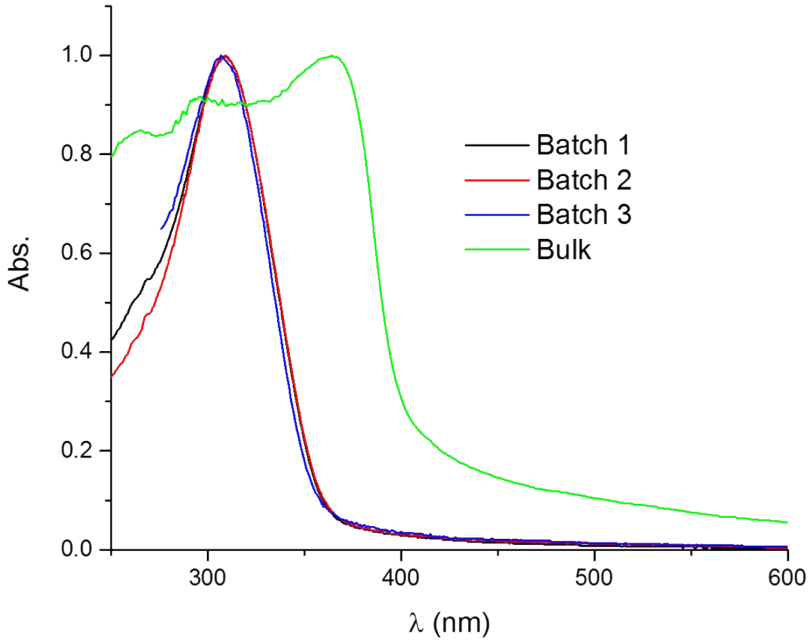


**Figure S23:** UV-Vis spectra of ME-CMP-e batches in suspension and ME-CMP as bulk powder.

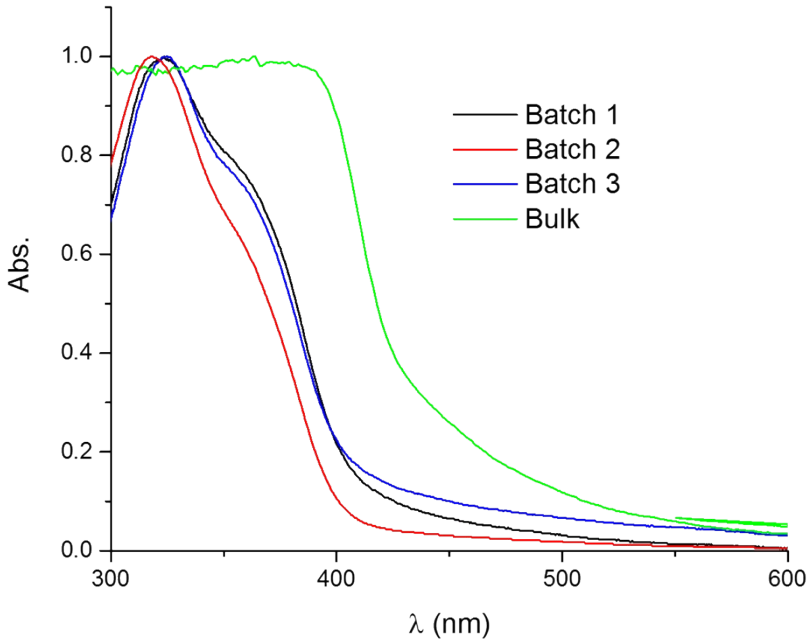


**Figure S24:** UV-Vis spectra of S-CMP1-e batches in suspension and S-CMP1 as bulk powder.

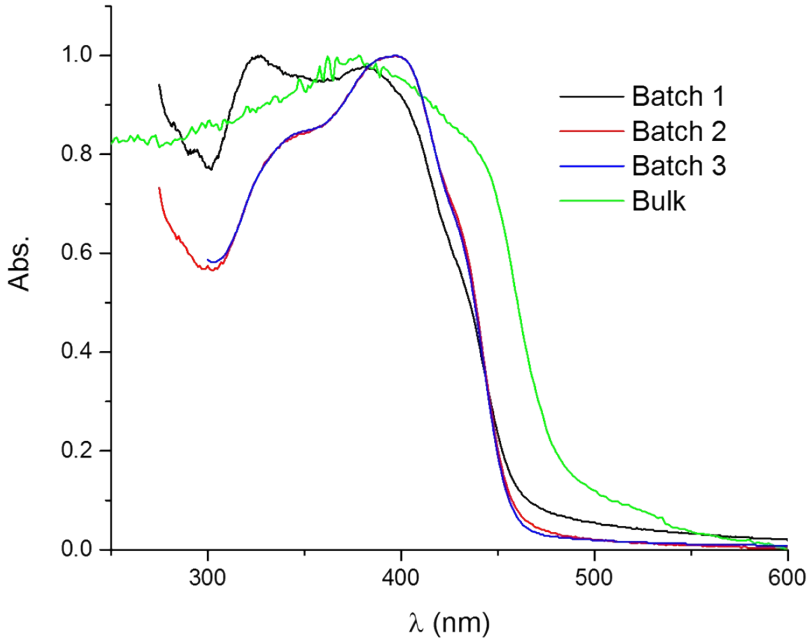


**Figure S25:** UV-Vis spectra of P10-e batches in suspension and P10 as bulk powder.

## 7. PL Spectroscopy

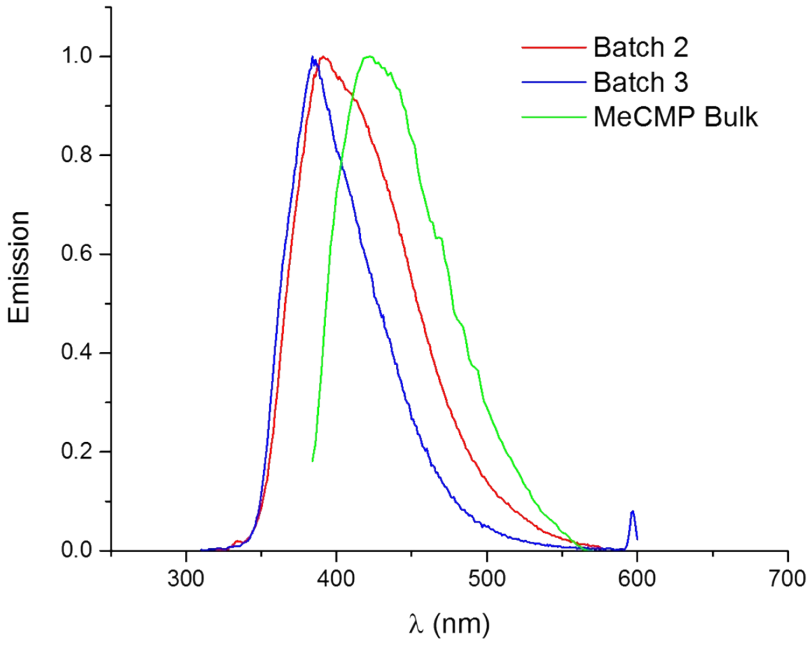


**Figure S26:** PL spectra, excited at 300 nm, of ME-CMP-e batches in suspension and ME-CMP as bulk powder.

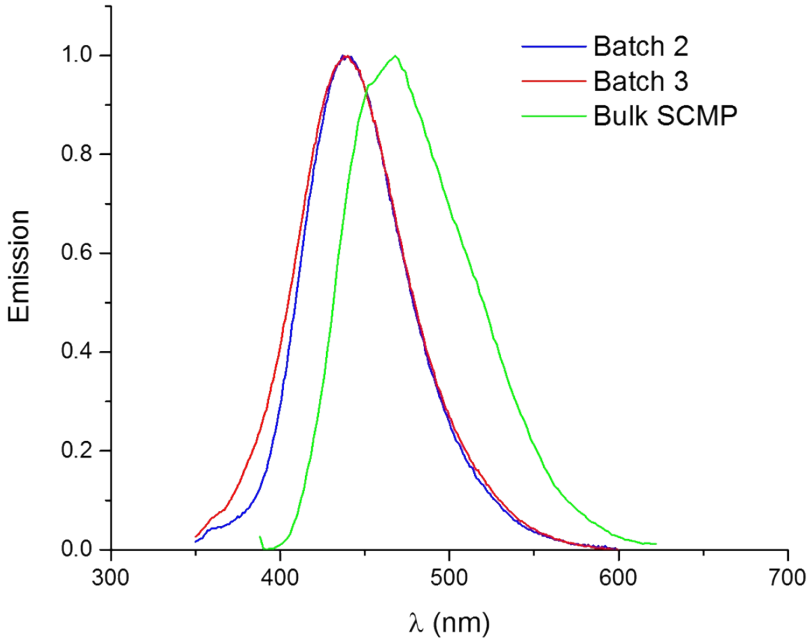


**Figure S27:** PL spectra, excited at 320 nm, of S-CMP1-e batches in suspension and S-CMP1 as bulk powder.

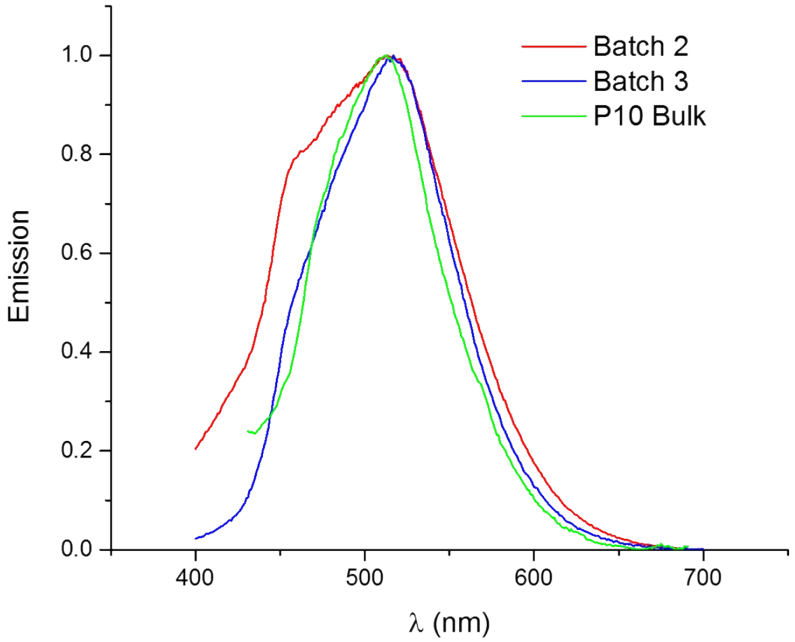


**Figure S28:** PL spectra, excited at 380nm, of P10-e batches in suspension and P10 as bulk powder.

## 8. Thermogravimetric Analysis

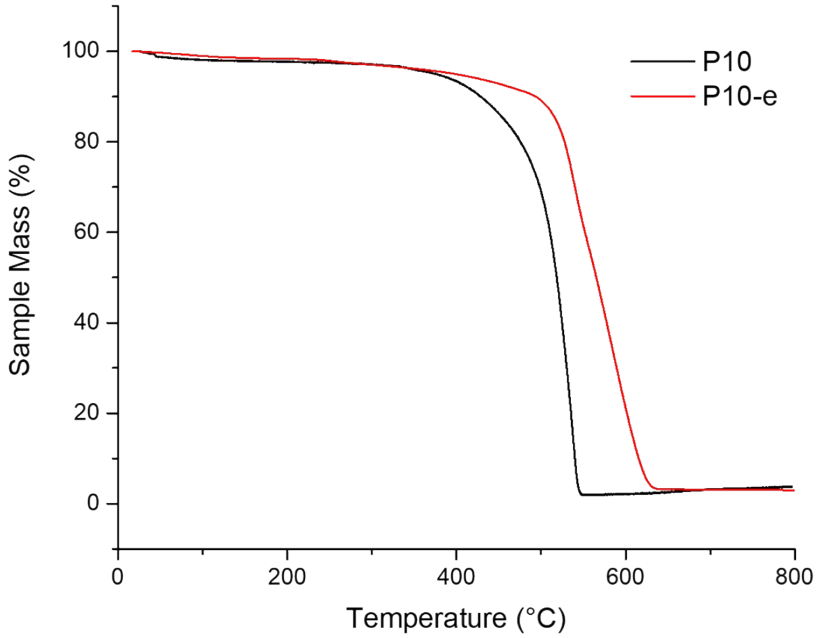


**Figure S29:** Thermogravimetric analysis of P10 and P10-e heated at 10 °C $min^{-1}$ in air.

## 9. BET Isotherm

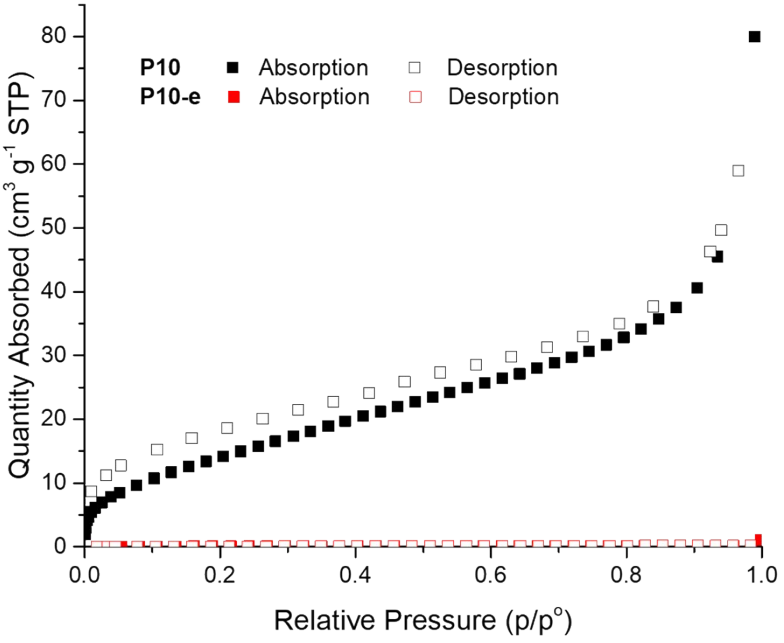


**Figure S30:** Nitrogen sorption isotherms for polymers P10 and P10-e measured at 77.3 K and up to 1 bar (desorption curves shown as open symbols). The BET surface areas were calculated to be $SA_{BET}$ = 56 $m^2$ $g^{-1}$ for P10, $SA_{BET}$ = 7 $m^2$ $g^{-1}$ for P10-e.

## 10. Hydrogen Evolution Experiments

A quartz flask was charged with the catalyst and sacrificial donor and sealed with a septum. The resulting suspension was ultrasonicated until the photocatalyst was dispersed before degassing by $N_2$ bubbling for 30 minutes. For standard measurements the reaction mixture was illuminated with a 300 W Newport Xe light-source (Model: 6258, Ozone free) for the time specified. The lamp was cooled by water circulating through a metal jacket. Gas samples were taken with a gas-tight syringe, and run on a Bruker 450-GC gas chromatograph equipped with a Molecular Sieve 13X 60-80 mesh 1.5 m × ⅛" × 2 mm ss column at 50 °C with an argon flow of 40.0 mL $min^{-1}$. Hydrogen was detected with a thermal conductivity detector referencing against standard gas with a known concentration of hydrogen. Hydrogen dissolved in the reaction mixture was not measured and the pressure increase generated by the evolved hydrogen was neglected in the calculations.

### 10.1. Hydrogen evolution experiments using TEA / MeOH

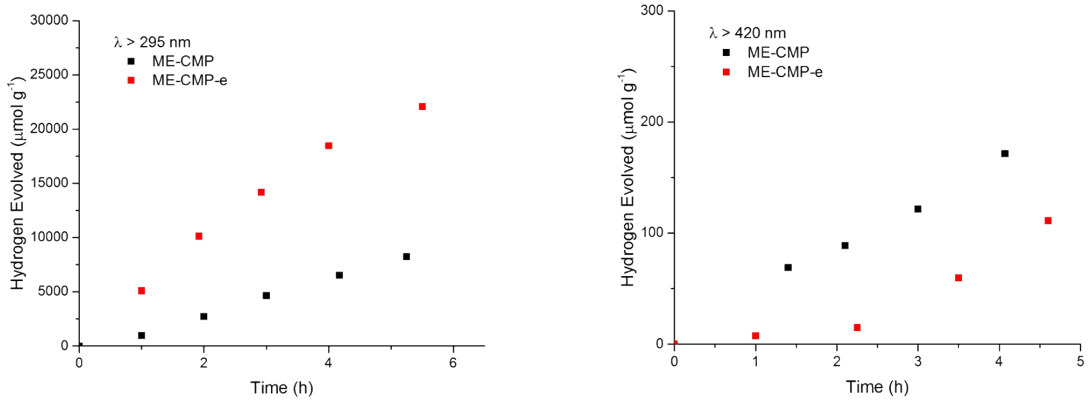


**Figure S31:** Hydrogen evolution of ME-CMP-e (red) and ME-CMP (black) in 25 mL aqueous/methanol/triethylamine (1:1:1) (aqueous phase containing water: toluene (9:1), SDS surfactant 10 mg $mL^{-1}$ and $Na_2CO_3$ 3.5 mg $mL^{-1}$) and polymer concentrations of 0.06 mg $mL^{-1}$. Irradiated by a 300 W Xe lamp fitted with a λ > 295 nm (left) or λ > 420 nm (right) cut off filter.

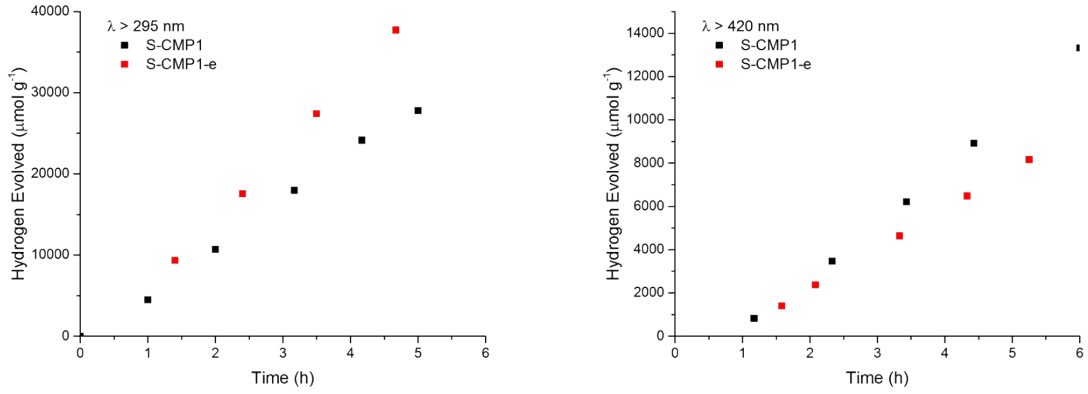


**Figure S32:** Hydrogen evolution of S-CMP1-e (red) and S-CMP1 (black) in 25 mL aqueous/methanol/triethylamine (1:1:1) (aqueous phase containing water: toluene (9:1), SDS surfactant 10 mg $mL^{-1}$ and $Na_2CO_3$ 3.5 mg $mL^{-1}$) and polymer concentrations of 0.07 mg $mL^{-1}$. Irradiated by a 300 W Xe lamp fitted with a λ > 295 nm (left) or λ > 420 nm (right) cut off filter.

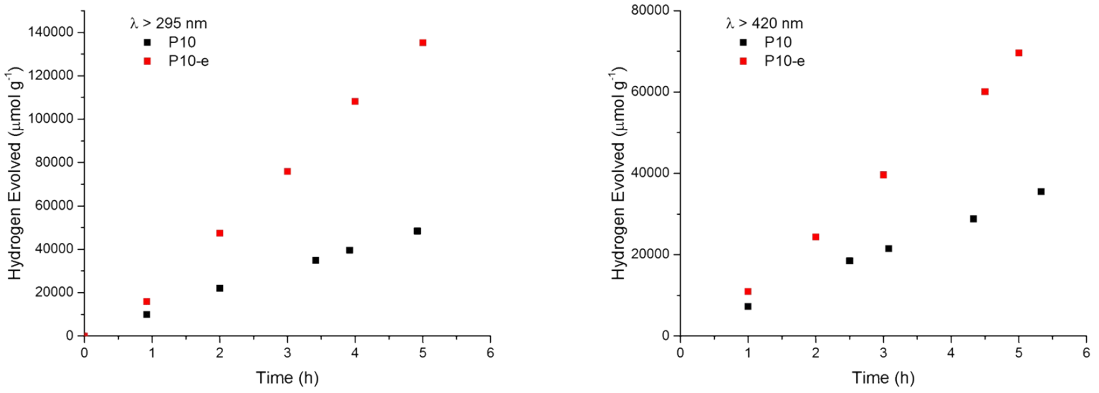


**Figure S33:** Hydrogen evolution of P10-e (red) and P10 (black) in 25 mL aqueous/methanol/triethylamine (1:1:1) (aqueous phase containing water: toluene (9:1), SDS surfactant 10 mg $mL^{-1}$ and $Na_2CO_3$ 3.5 mg $mL^{-1}$) and polymer concentrations of 0.1 mg $mL^{-1}$. Irradiated by a 300 W Xe lamp fitted with a λ > 295 nm (left) or λ > 420 nm (right) cut off filter.

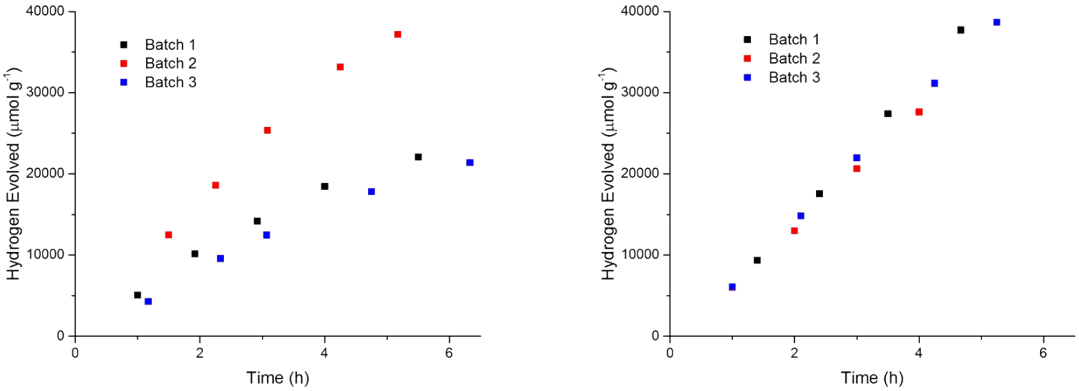


**Figure S34:** Hydrogen evolution of repeat batches of ME-CMP-e (left) and S-CMP1-e (right) in 25 mL aqueous/methanol/triethylamine (1:1:1) (aqueous phase containing water: toluene (9:1), SDS surfactant 10 mg $mL^{-1}$ and $Na_2CO_3$ 3.5 mg $mL^{-1}$) and polymer concentrations of 0.06 mg $mL^{-1}$ and 0.07 mg $mL^{-1}$ respectively. Irradiated by a 300 W Xe lamp fitted with a $\lambda > 295$ nm cut off filter.

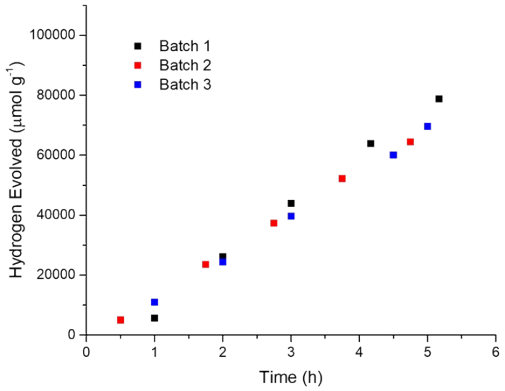


**Figure S35:** Hydrogen evolution of repeat batches of P10-e in 25 mL aqueous/methanol/triethylamine (1:1:1) (aqueous phase containing water: toluene (9:1), SDS surfactant 10 mg $mL^{-1}$ and $Na_2CO_3$ 3.5 mg $mL^{-1}$) and polymer concentration of 0.1 mg $mL^{-1}$. Irradiated by a 300 W Xe lamp fitted with a $\lambda > 420$ nm cut off filter.

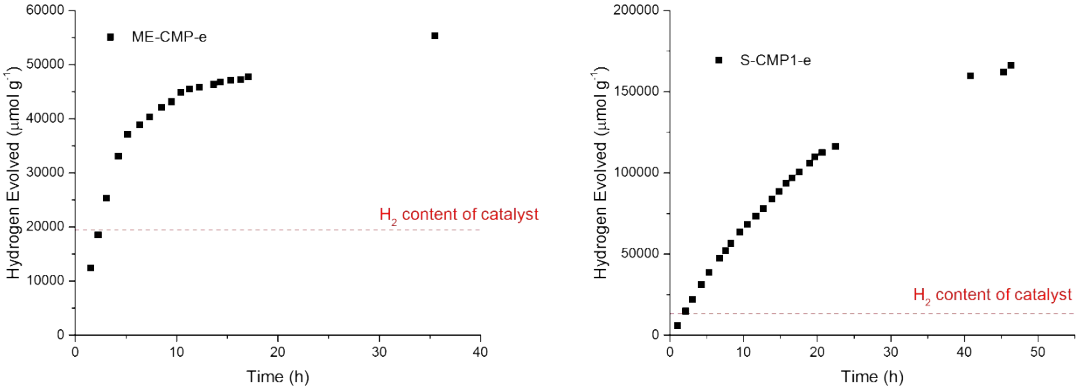


**Figure S36:** Extended hydrogen evolution of ME-CMP-e (left) and S-CMP1-e (right) in 25 mL aqueous/methanol/triethylamine (1:1:1) (aqueous phase containing water: toluene (9:1), SDS surfactant 10 mg $mL^{-1}$ and $Na_2CO_3$ 3.5 mg $mL^{-1}$) and polymer concentrations of 0.06 mg $mL^{-1}$ and 0.07 mg $mL^{-1}$ respectively. Irradiated by a 300 W Xe lamp fitted with a $\lambda > 295$ nm cut off filter.

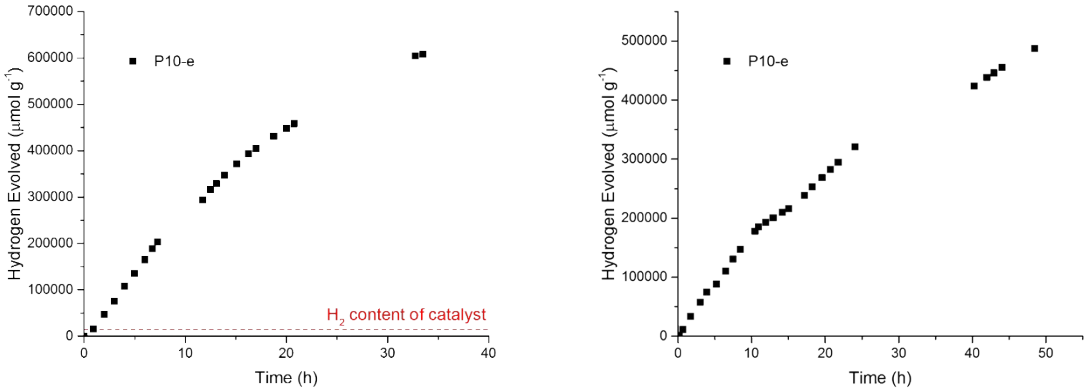


**Figure S37:** Extended hydrogen evolution of P10-e in 25 mL aqueous/methanol/triethylamine (1:1:1) (aqueous phase containing water: toluene (9:1), SDS surfactant 10 mg $mL^{-1}$ and $Na_2CO_3$ 3.5 mg $mL^{-1}$) and polymer concentration of 0.1 mg $mL^{-1}$. Irradiated by a 300 W Xe lamp fitted with a λ >295 nm (left) or a λ > 420 nm (right) cut off filter

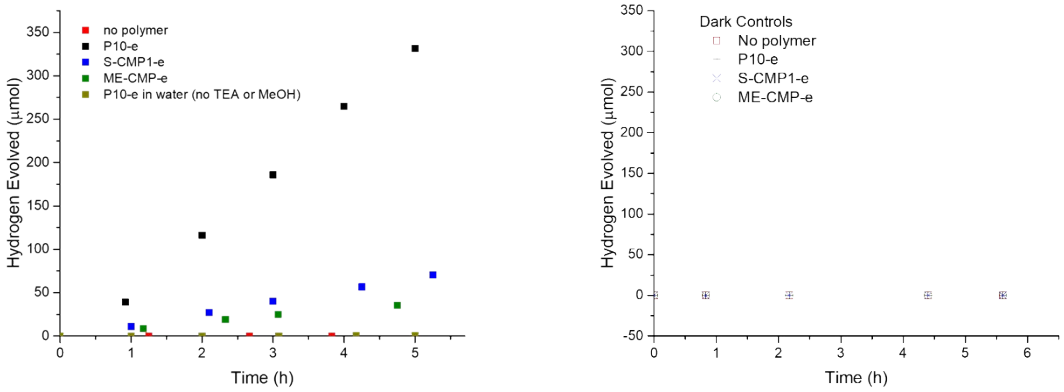


**Figure S38:** Control reactions. (Left) hydrogen evolution of no polymer (red) and emulsion particles (black, blue, green) in 25 mL aqueous/methanol/triethylamine (1:1:1) (aqueous phase containing water: toluene (9:1), SDS surfactant 10 mg $mL^{-1}$ and $Na_2CO_3$ 3.5 mg $mL^{-1}$) as well as P10-e without triethylamine sacrificial electron donor (yellow). Irradiated by a 300 W Xe lamp fitted with a λ > 295 nm cut off filter. (Right) emulsion particles) in 25 mL aqueous/methanol/triethylamine (1:1:1) (aqueous phase containing water: toluene (9:1), SDS surfactant 10 mg $mL^{-1}$ and $Na_2CO_3$ 3.5 mg $mL^{-1}$) and no irradiation.

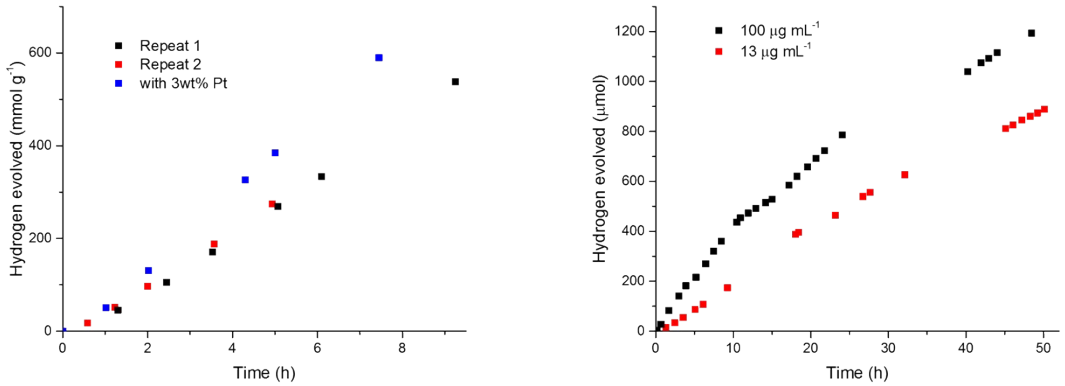


**Figure S39:** Hydrogen evolution of P10-e at low concentration (13 μg $mL^{-1}$). 325μg in 25 mL aqueous/methanol/triethylamine (1:1:1) (aqueous phase containing water: toluene (98.56 : 1.44), SDS surfactant 1.3 mg $mL^{-1}$ and $Na_2CO_3$ 0.5 mg $mL^{-1}$). Irradiated by a 300 W Xe lamp fitted with a $\lambda > 420$ nm filter.

### 10.1.2. External Quantum Efficiency

For determining the external quantum efficiency, P10-e and P10 in equal parts water/methanol/triethylamine with 3.3 mg $mL^{-1}$ SDS surfactant, 1.25 mg $mL^{-1}$ $Na_2CO_3$ and polymer concentrations as described in Table S1, were irradiated by a λ = 420 nm LED (67.7 mW $cm^{-2}$) controlled by an IsoTech IPS303DD Power Supply. Light intensity was measured with a ThorLabs S120VC photodiode power sensor controlled by a ThorLabs PM100D Power and Energy Meter Console. The apparent quantum yields were estimated using Equation (2):

$$\Phi_{H_2} = 2 \times \frac{moles\ of\ hydrogen\ evolved}{moles\ of\ incident\ photons} \qquad (Equation\ 2)$$

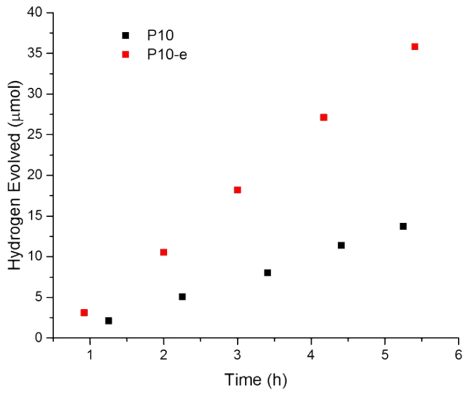


**Figure S40:** $H_2$ evolution experiments under λ = 420 ± 5 nm illumination using a LED.

**Table S1: External quantum efficiencies**

| Photocatalyst | Polymer concentration ( mg $mL^{-1}$) | Path Length (cm) | Light intensity (mW $m^{-2}$) | External Quantum Efficiency[a] |
|---|---|---|---|---|
| P10 | 0.01 | 1.0 | 2.04 | 2.3 ± 0.1 % |
| P10-e | 0.01 | 1.0 | 1.98 | 5.8 ± 0.2 % |
| P10-e | 1.0 | 1.0 | 1.84 | 12.7 ± 0.8 % |
| P10-e | 0.01 | 2.0 | 1.80 | 10.5 ± 1.0 % |
| P10-e | 0.01 | 5.0 | 2.93 | 14.2 ± 0.2 % |
| P10-e | 1.0 | 5.0 | 2.21 | 20.4 ± 0.4 % |

[c]Calculated using Equation 2.

## 10.2. Sacrificial Donor Screening

### 10.2.1 Hydrogen evolution experiments using an ascorbic acid donor

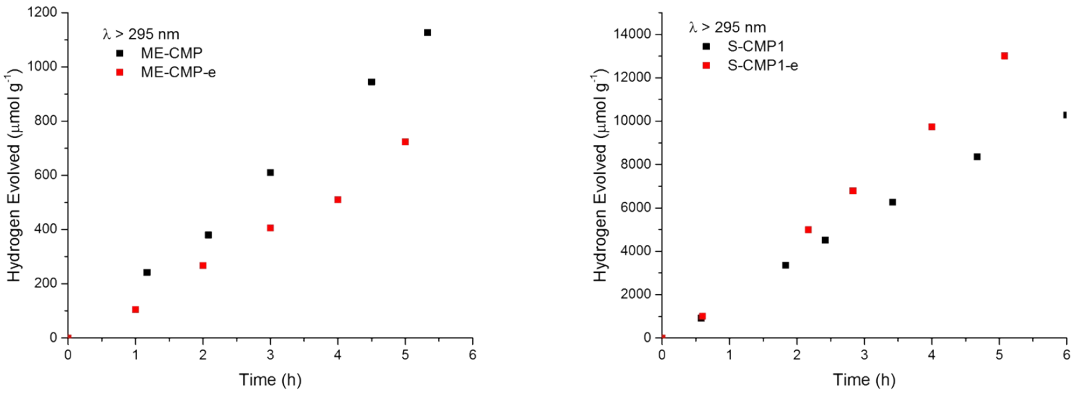


**Figure S41:** Hydrogen evolution of ME-CMP-e (red left), ME-CMP (black left), S-CMP1-e (right red) and S-CMP1 (black right) in 25 mL 0.1 M Ascorbic Acid including 8.3 mL water: toluene (9:1), SDS surfactant 10 mg $mL^{-1}$ and $Na_2CO_3$ 3.5 mg $mL^{-1}$. Polymer concentrations of 0.06 mg $mL^{-1}$ and 0.07 mg $mL^{-1}$ respectively. Irradiated by a 300 W Xe lamp fitted with a λ > 295 nm cut off filter.

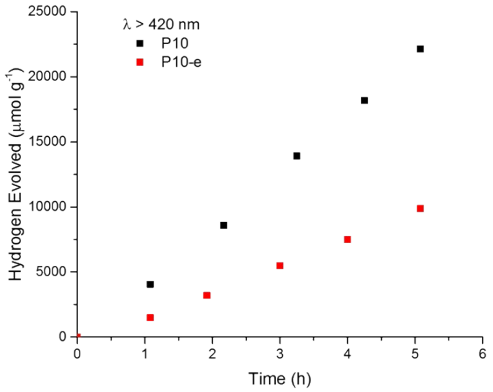


**Figure S42:** Hydrogen evolution of P10-e (red) and P10 (black) in 25 mL 0.1 M Ascorbic Acid including 8.3 mL water: toluene (9:1), SDS surfactant 10 mg $mL^{-1}$ and $Na_2CO_3$ 3.5 mg $mL^{-1}$. Polymer concentrations of 0.1 mg $mL^{-1}$. Irradiated by a 300 W Xe lamp fitted with a λ > 420 nm cut off filter.

## 10.2.2 Hydrogen evolution experiments using a TeOA donor

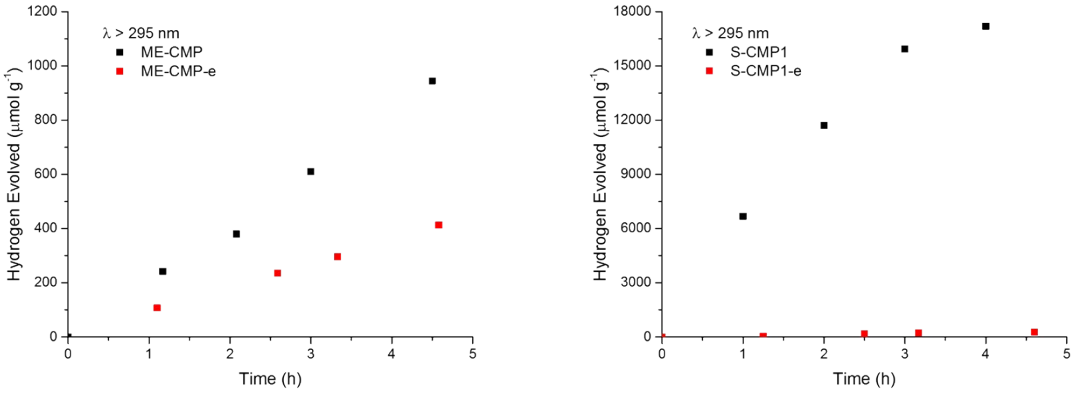


**Figure S43:** Hydrogen evolution of ME-CMP-e (red left), ME-CMP (black left), S-CMP1-e (right red) and S-CMP1 (black right) in 25 mL, containing 2.5 mL TeOA, 14.2 mL water and 8.3 mL water: toluene (9:1), SDS surfactant 10 mg $mL^{-1}$ and $Na_2CO_3$ 3.5 mg $mL^{-1}$. Polymer concentrations of 0.06 mg $mL^{-1}$ and 0.07 mg $mL^{-1}$ respectively. Irradiated by a 300 W Xe lamp fitted with a $\lambda > 295$ nm cut off filter.

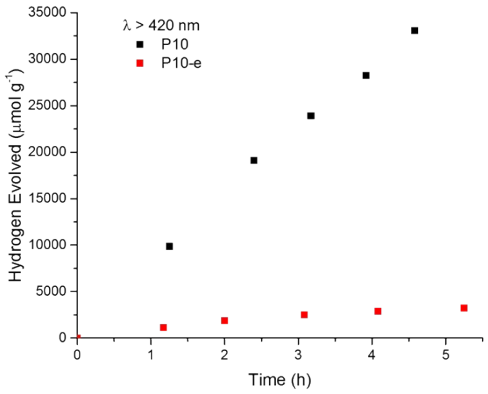


**Figure S44:** Hydrogen evolution of P10-e (red) and P10 (black) in 25 mL, containing 2.5 mL TeOA, 14.2 mL water and 8.3 mL water: toluene (9:1), SDS surfactant 10 mg $mL^{-1}$ and $Na_2CO_3$ 3.5 mg $mL^{-1}$. Polymer concentrations of 0.1 mg $mL^{-1}$. Irradiated by a 300 W Xe lamp fitted with a $\lambda > 420$ nm cut off filter.

### 10.2.3 Salt induced aggregation

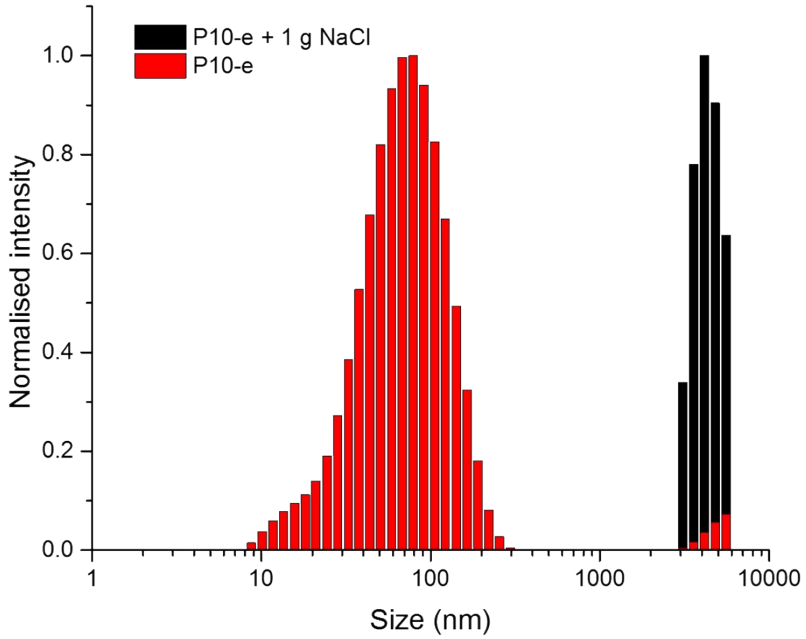


**Figure S45:** Particle size distribution by DLS of P10-e in 10 vol. % TeOA before and after addition of 1 g NaCl.

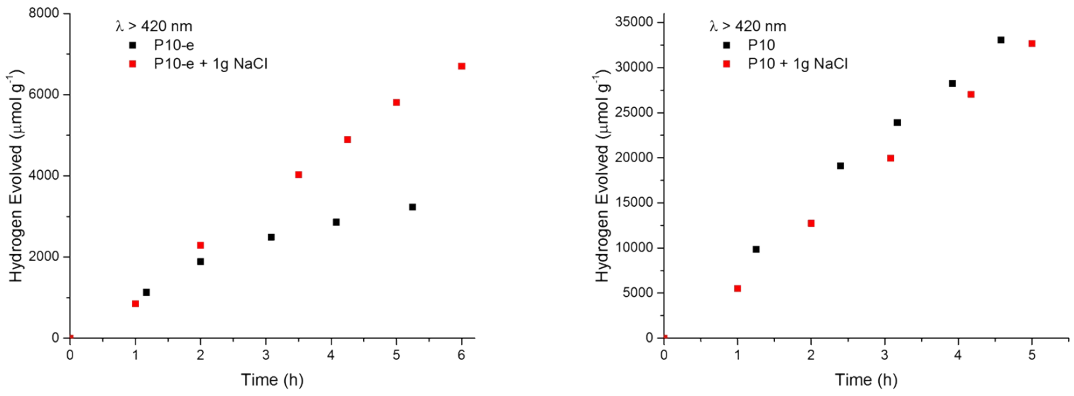


**Figure S46:** Hydrogen evolution of P10-e with salt (red left) and without (black left), polymer concentration of 0.1 mg $mL^{-1}$. Hydrogen evolution of P10 with salt (red right) and without (black right) polymer concentration 0.1 mg $mL^{-1}$. All in 25 mL, containing 2.5 mL TeOA, 14.2 mL water and 8.3 mL water: toluene (9:1), SDS surfactant 10 mg $mL^{-1}$ and $Na_2CO_3$ 3.5 mg $mL^{-1}$. Irradiated by a 300 W Xe lamp fitted with a λ > 420 nm cut off filter.

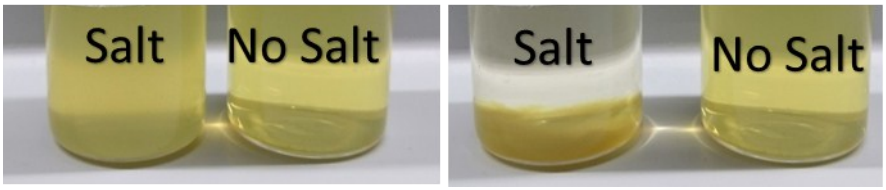


**Figure S47:** Photograph of P10-e in 10 % TeOA solution with and without 1 g NaCl. 5 minutes after addition of salt (left) and after leaving to sit for one hour (right)

### 10.2.4 Removal of toluene and deposition onto silica

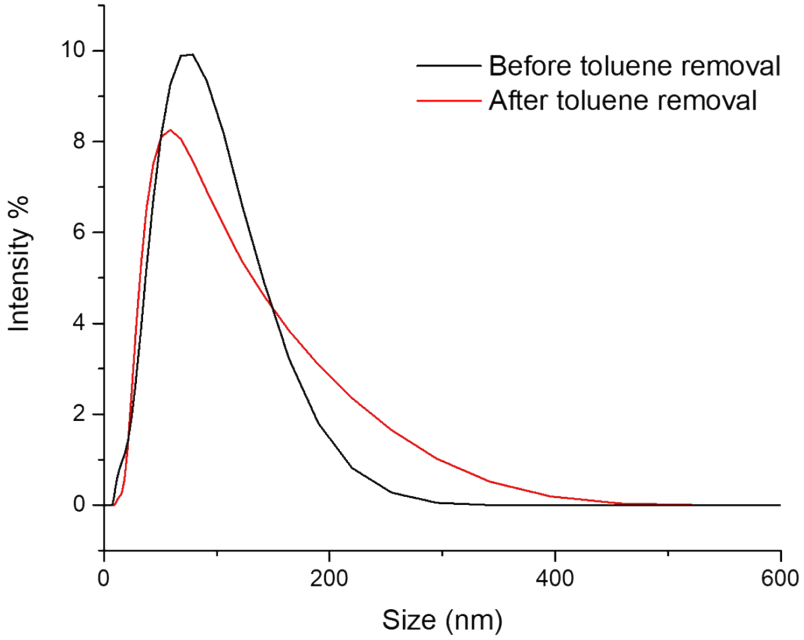


**Figure S48:** Particle size by DLS of P10-e in 10 % TeOA before and after removal of residual toluene.

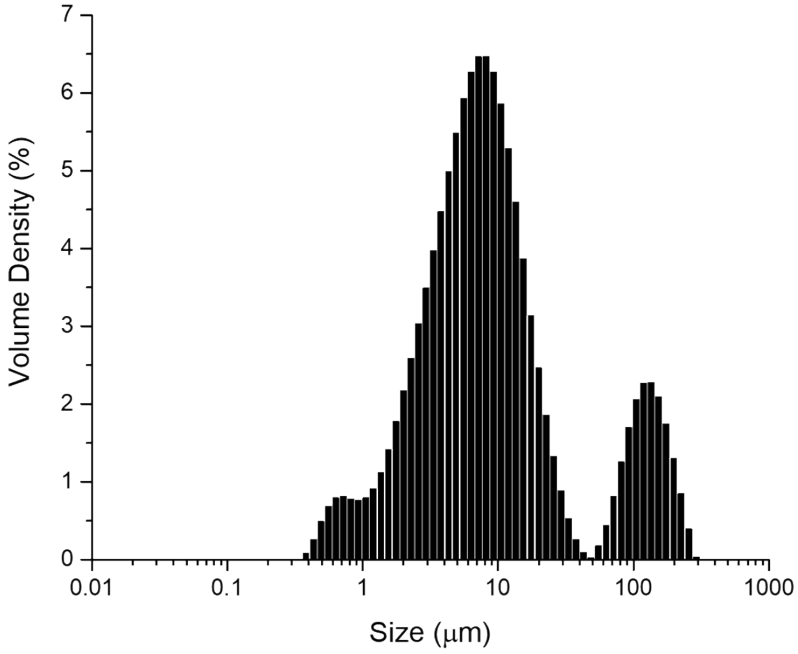


**Figure S49:** Particle size by SLS of P10-e deposited onto silica colloids.

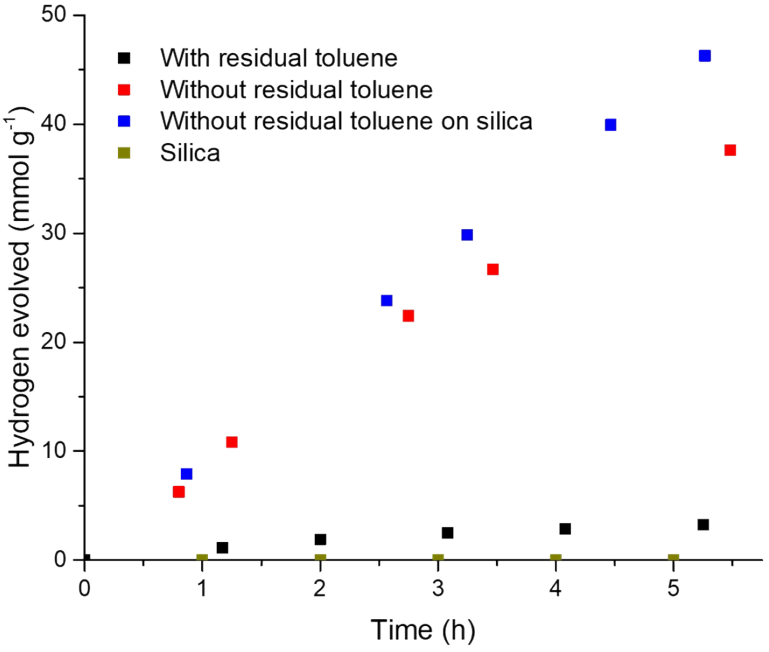


**Figure S50:** Hydrogen evolution of P10-e as synthesised (2.5 mg) in 2.5 mL TeOA, 14.2 mL water and 8.3 mL water: toluene (9:1), SDS surfactant 10 mg $mL^{-1}$ and $Na_2CO_3$ 3.5 mg $mL^{-1}$ (black), P10-e without residual toluene (2.5 mg) (red), P10-e without residual toluene deposited onto silica (3.27mg P10-e on 6.73 silica by microanalysis, mass of silica is ignored in hydrogen evolved per gram calculation) (blue) and just silica (yellow) in 25 mL containing 2.5 mL TeOA, 22.5 mL water. All irradiated by a 300 W Xe lamp fitted with a $\lambda > 420$ nm cut off filter.

## 10.2.5 Different sacrificial donors summary

**Table S2: Particle size in different sacrificial systems**

| Polymer | Size as synthesized (nm) | Size in 10% TeOA (nm) | Size in 0.1 M ascorbic acid[a] (nm) |
|---|---|---|---|
| MeCMP-e | 247.6 | 94.3[a] | 208.6 |
| SCMP-e | 179.6 | 87.6[a] | 226.3 |
| P10-e | 180.2 | 59.0[a] | 159.9 |
| P10-e salt added | - | ~ 4000[a] | - |
| P10-e toluene removed | - | 65.6 [a] | - |
| P10-e on silica | - | 7910[b] | - |

[a]Particle size by DLS at photolysis concentration; 0.1 mg $mL^{-1}$ P10-e, 0.07 mg $mL^{-1}$ S-CMP1-e, 0.06 mg $mL^{-1}$ ME-CMP-e. [b] Particle size by SLS, value is $D_x(50)$.

**Table S3: Hydrogen evolution rates when irradiated by a 300 W Xe lamp fitted with a λ > 295 nm cut off filter unless stated otherwise.**

| Polymer | HER 10% TeOA[a] (µmol $h^{-1}$ $g^{-1}$) | HER 0.1 M ascorbic acid[b] (µmol $h^{-1}$ $g^{-1}$) |
|---|---|---|
| MeCMP | 82 ± 3 | 218 ± 7 |
| MeCMP-e | 34 ± 3 | 148 ± 9 |
| SCMP | 3583 ± 616 | 1818 ± 42 |
| SCMP-e | 102 ± 23 | 2662 ± 53 |
| P10 | 6832 ± 256[c] | 4534 ± 67[c] |
| P10-e | 501± 63[c] | 2089 ± 18[c] |
| P10-e salt added | 1222 ± 27 [c] | - |
| P10-e toluene removed | 6938 ± 377 [c,d] | - |
| P10-e on silica | 9008 ± 132[c,d] | - |

[a] 25 mL, containing 2.5 mL TeOA, 14.2 mL water and 8.3 mL water: toluene (9:1), SDS surfactant 10 mg $mL^{-1}$ and $Na_2CO_3$ 3.5 mg $mL^{-1}$ and polymer concentrations as described in Table 1. [b] 25 mL 0.1 M Ascorbic Acid including 8.3 mL water: toluene (9:1), SDS surfactant 10 mg $mL^{-1}$ and $Na_2CO_3$ 3.5 mg $mL^{-1}$ and polymer concentrations as described in Table 1. [c] Using a λ > 420 nm cut-off filter. [d] No toluene or $Na_2CO_3$.

## 11. Palladium Content via ICP – OES

**Table S4: Palladium content of the different polymers.**

| Polymer | Pd[a] used for synthesis (wt. %) | Pd content by ICP(wt. %) | |
|---|---|---|---|
| | | Average | Standard Deviation |
| ME-CMP | 1.30 | 0.363[b] | 0.006 |
| ME-CMP-e | 1.63 | 0.542[c] | 0.002 |
| S-CMP1 | 1.73 | 0.332[b] | 0.007 |
| S-CMP1-e | 1.32 | 0.420[c] | 0.003 |
| P10 | 1.73 | 0.650[b] | 0.020 |
| P10-e | 0.98 | 0.403[c] | 0.001 |

[a] In the form of $[Pd(PPh_3)_4]$. [b] Pd content measured by ICP-OES, average and standard deviation of 5 repeats.
[c] Pd content measured by ICP-MS, average and standard deviation of 3 repeats.

## 12. References


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