Electronic Supplementary Material (ESI) for ChemComm.

Nanoparticle-sulphur “inverse vulcanisation” polymer composites-Supporting information

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S1: Materials

Cobalt(II) chloride hexahydrate (reagent grade), 1,2-dichlorobenzene (ReagentPlus, 99 %), 1-dodecanethiol (≤ 98 %), gold(III) chloride trihydrate (49.96 %, Au assay), hexadecylamine (98 %), indium(III) chloride (98 %), iron(III) chloride hexahydrate (98 %), lead(II) oxide (≥99.0 %), nickel(II) chloride tetrahydrate (≥ 98 %), 1-octadecene (technical grade, 90%), oleic acid (technical grade, 90%), bis(trimethylsilyl)sulphide (synthesis grade), sodium oleate (≤ 82 % fatty acid content), sodium borohydride (≥ 96 %), stearic acid (reagent grade, 95 %), sulphur (≥ 99.5 %) tetraoctylammonium bromide (98 %), trioctylphosphine (technical grade, 90%), tris(trimethylsilyl)phosphine (95 %), zinc diethyldithiocarbamate (97 %), zinc undecylenate (98 %) were purchased from Sigma Aldrich and used as received. 1,3-diisopropenylbenzene (> 97 %) was purchased from TCI and used as received. Olive oil was purchased from Tesco Ltd.

Laboratory solvents of the highest possible grade were purchased from Sigma Aldrich Limited.

S2: Nanocrystal synthesis

S2.1: Gold (Au) nanoparticles

Au nanoparticles were synthesised according to Palgrave and Parkin with modifications.[1–3] Briefly, a solution of gold(III) chloride trihydrate (0.146 g, 0.43 mmol) in deionised water (15 ml) was mixed with a solution of tetraoctylammonium bromide (1.04 g, 1.90 mmol) in toluene (40 ml) under vigorous stirring. To reduce Au^{3+}, a solution of sodium borohydride (0.190 g, 5.02 mmol) in deionised water (25 ml) was added dropwise over 30 minutes. During this time, the solution turned from orange to colourless to purple, indicating the formation of gold nanoparticles. The toluene layer was separated and washed with 2 × 50 mL portions of 1 M sulphuric acid solution and deionised water (100 mL). The toluene layer was dried over sodium sulphate (5 g) and diluted to 100 mL with toluene.

Further functionalisation with 1-dodecanethiol was used to increase the longevity of colloidal stability. Briefly, the Au nanoparticles in toluene (100 mL) were heated with 1-dodecanethiol (20 ml, 83.5 mmol) to 70 °C for 24 hours. The gold nanoparticles were then precipitated with ethanol (~ 200 mL), centrifuged at 1000 × g and re-dispersed in fresh toluene (100 mL) prior to use.

S2.2: Iron oxide (Fe_3O_4) nanoparticles

Fe_3O_4 nanoparticles were synthesised by thermal decomposition of iron oleate, according to Park *et al.*[4] Briefly, the iron oleate complex was prepared by heating a suspension of iron(III) chloride hexahydrate (10.8 g, 40 mmol) and sodium oleate (36.5 g, 120 mmol) in a solvent mixture of *n*-hexane (140 mL), deionised water (60 mL) and ethanol (80 mL) to 70 °C for 4 hours. The dark brown organic layer was separated and washed with 3 × 30 ml portions of distilled water to remove sodium chloride. The organic layer was dried *in vacuo* to remove hexane, yielding the iron oleate complex as a waxy solid.

Iron oleate (18.0 g, 20 mmol) and oleic acid (2.35 mL, 10 mmol) were dissolved in 1-octadecene (100 g, 396.1 mmol) and stirred thoroughly at room temperature. The reaction mixture was heated to 320 °C at a rate of 3.3 °C min^{-1} and held at 320 °C for 1 hour. The resulting black dispersion was allowed to cool to room temperature before addition of ethanol (250 mL) to precipitate the particles. The dispersion was centrifuged at 504 × *g* for 10 minutes, giving a solid precipitate. If the precipitate was not fully solid, excess oleate-type species were removed by washing with ethanol (2 × 80 mL). The supernatant was discarded and the solid particle precipitates dispersed in chloroform (30 mL total).

S2.3: Cobalt oxide (CoO) nanoparticles

CoO nanoparticles were synthesised according to Crick *et al.*[3] Cobalt oleate was prepared according to the procedure for iron oleate (section S2.2), but cobalt(II) chloride hexahydrate (9.51 g, 40 mmol) and two equivalents of sodium oleate were used (24.3 g, 80 mmol). On decomposition, the cobalt oleate gave a green suspension of nanocrystals, using identical conditions and reagents described for Fe_3O_4.

S2.4: Lead sulphide (PbS) quantum dots

PbS quantum dots were synthesised according to Akhtar *et al.*[5]

Briefly, lead(II) oxide (0.92 g, 4.12 mmol) was added to olive oil (12.5 ml), oleic acid (1 ml, 3.14 mmol) and 1-octadecene (1 ml). The mixture was degassed at room temperature for 45 minutes and then degeassed at 100 °C for 1 hour. The mixture was heated to 150 °C for one hour under nitrogen. Bis(trimethylsilyl)sulphide (520 μl, 2.47 mmol) in degassed 1-octadecene (1 ml) was rapidly injected and heated for one minute. The particles were collected by aggregation of the nanocrystals by addition of excess acetone, centrifugation at 3000 × *g* for 20 minutes and re-dispersion in hexane. The washing procedure was repeated three times.

S2.5: Indium phosphide/zinc sulphide (InP/ZnS) core/shell quantum dots

InP quantum dots were synthesised according to Xu *et. al.*[6,7] Briefly, a nitrogen-purged Schlenk flask was charged with stearic acid (28.5 mg, 0.1 mmol), zinc undecylenate (86 mg, 0.2 mmol), indium(III) chloride (22 mg, 0.1 mmol) and hexadecylamine (48 g, 0.2 mmol). To this, 1-octadecene (2 ml) was added, and the mixture vacuum/back filled with nitrogen three times before heating to 270 °C. On reaching 270 °C, a solution of tris(trimethylsilyl)phosphine (1 ml, 0.1 M) in 1-octadecene was rapidly injected, and the solution heated at 240 ºC for 20 minutes to allow the quantum dots to grow. The flask was then placed in water to cool to room temperature.

InP quantum dots were shelled through the addition of zinc(II) diethyldithiocarbamate (72 mg, 0.2 mmol) and zinc undecylenate (44 mg, 0.102 mmol) to the flask, which was vacuum/back filled with nitrogen three times. The solution was heated at 180 ºC for 10 minutes and then increased to 240 °C for 20 minutes, before rapidly cooling the flask in water. Once cooled, toluene (4 ml) was added, and the solution added to ethanol (~100 mL) to precipitate the quantum dots. The dispersion was then centrifuged at 2000 × *g* for 20 minutes, and the solid precipitate dispersed in *n*-hexane (~10 mL) prior to use.

S3: Sulphur polymer synthesis (50 wt.%)

The native sulphur polymer was synthesised according to the protocol developed by Chung *et al.* [8] Briefly, elemental sulphur (S_8, 2 g, 7.81 mmol) was added to a vial and heated to 185 °C in an oil bath under vigorous stirring. Once 185 °C was reached, 1,3-diisopropenylbenzene (2.16 mL, 12.6 mmol) was injected, the whole mixture agitated with a glass rod and stirred for 4-5 minutes.

At this point, the solution can be poured into a mould and cured for 30 minutes at 200 °C or stirred at 185 °C for a further 5-10 minutes until fully cured.

Transmission electron microscope samples were prepared by grinding the hardened composite in a pestle and mortar before dispersion in 1,2-dichlorobenzene to dissolve much of the polymer matrix. The dispersion was then drop-cast onto a 400 mesh gold grid with holey carbon film (Agar Scientific Ltd). The Au nanoparticle- sulphur polymer composite was analysed on a copper TEM grid. Partial dissolution of the composites in 1,2-dichlorobenzene allowed thinner sections to be analysed within the TEM and facilitated analysis and spectroscopy due to the reduced amount of background polymer.

Thin films were synthesised by drop-casting a small amount (~ 1 mL) of the molten sulphur polymer mixture onto a cold microscope slide, adding a second slide as a cover-slip before curing at 200 °C for 30 minutes.

S4: Sulphur polymer/nanoparticle composite synthesis

Sulphur polymer-nanoparticle composites were synthesised according to the method outlined in section S3, except that chosen nanoparticles (~ 0.1 g) were precipitated with ethanol, centrifuged and re-dispersed in the desired amount of 1,3-diisopropenylbenzene (2.16 mL, 12.6 mmol for a 50 wt. % product). The nanoparticle dispersion in 1,3-diisopropenylbenzene was then injected at 185 °C and processed in the same way as the native sulphur polymer in section S3.

S5: Additional characterisation

S5.1: Instrumentation details

Transmission electron microscopy (TEM) and High resolution transmission electron microscopy (HRTEM) measurements were collected using a Philips CM200 FEG TEM operating at an acceleration voltage of 200 kv with an ISIS EDS system running Aztec software and Gatan Imaging filter for EELS. Samples were prepared by drop-casting a suspension of the sulphur polymer [composite] in 1,2-dichlorobenzene (~0.05 g in 2 mL) Scanning electron microscopy (SEM) micrographs were collected on a field emission Jeol 6700F FEG SEM operating at 10 kV. UV-vis absorption spectra were recorded using a Perkin Elmer Lambda 1050 UV/VIS spectrometer single beam instrument over a range of 350–1000 nm, with IR measurements recorded over 350-2000 nm. X-Ray photoelectron spectroscopy was undertaken using a Thermo Scientific K-alpha spectrometer with monochromated Al Kα radiation, a dual beam charge compensation system and constant pass energy of 50 eV (spot size 400 μm). Survey scans were collected in the range 0–1200 eV. High-resolution peaks were used for the principal peaks of S (2p), O (1s), and C (1s). Elemental analysis was performed by the University of Manchester Microanalytical Laboratory.

S5.2: Scanning electron microscopy

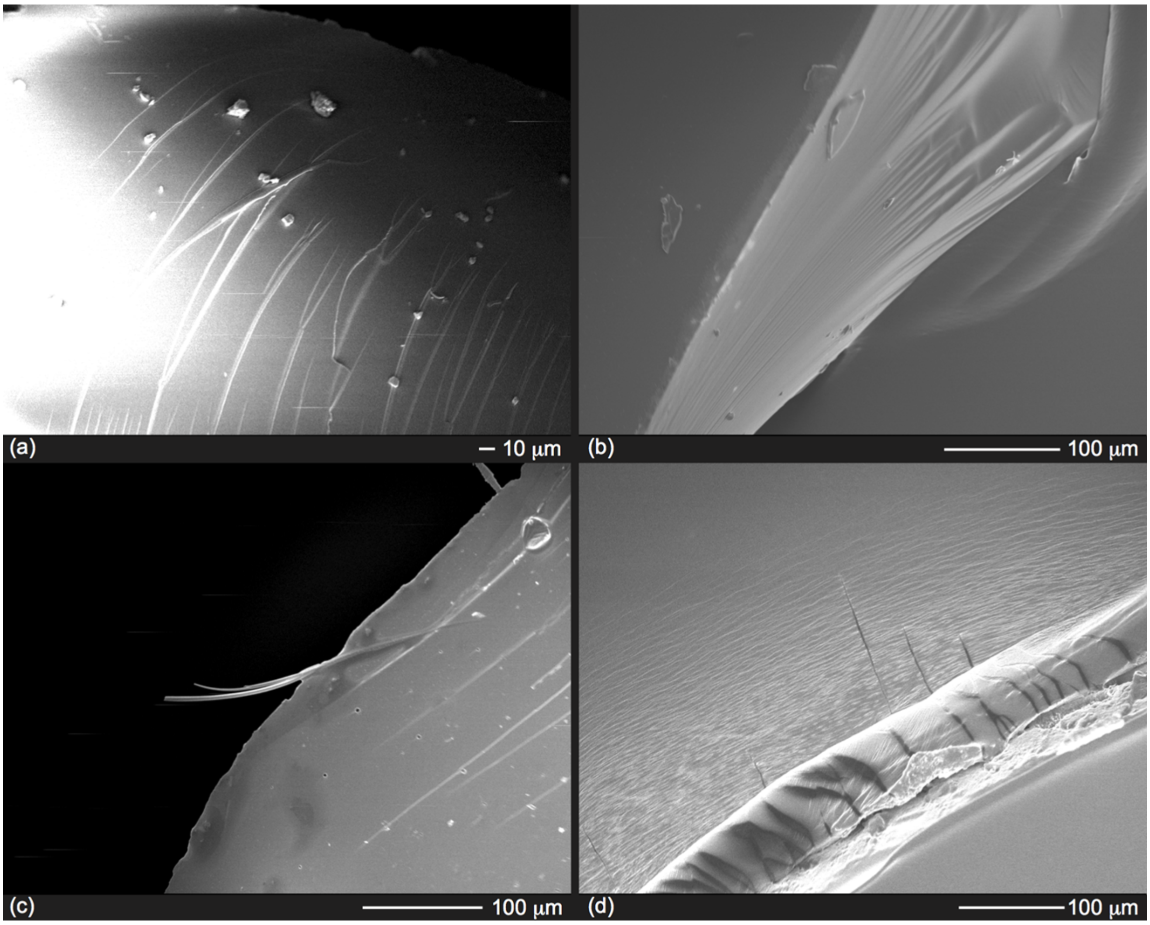

Figure S5.2.1: SEM micrographs of: a) Plain S-polymer, b) Au-nanoparticle-S-polymer composite, c) InP/ZnS-nanoparticle-S-polymer composite and d) CoO-nanoparticle-S-polymer composite. All show a glass-like morphology, with the incorporated nanoparticles leaving the overall structure of the S-polymer unaffected.

S5.3: Transmission electron microscopy

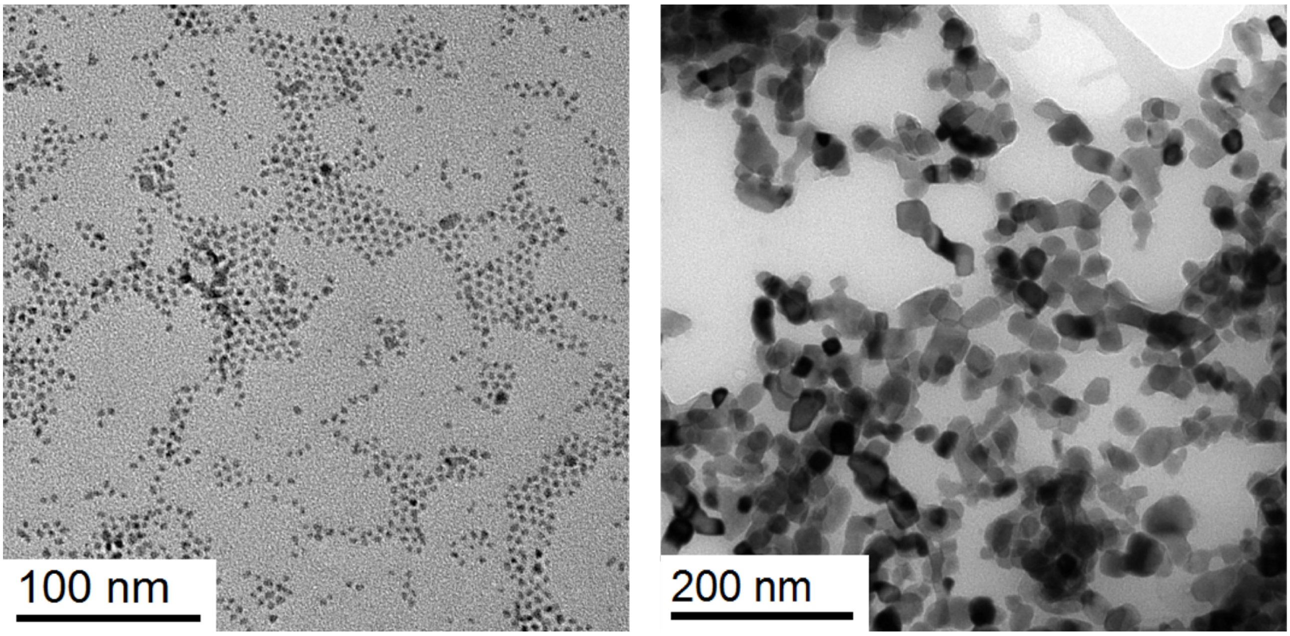

Figure S5.3.1: TEM micrographs of: (left) as synthesised PbS nanocrystals in toluene and (right) PbS nanocrystal-sulphur polymer composite. The sulphur polymer is visible as a darker “coat” around the majority of the nanoparticles. The ripening effects due to the high temperatures used in the synthesis of the composite are obvious when comparing the sizes of the as-synthesised nanoparticles (left) and the more defined, cubic PbS in the composite (right).

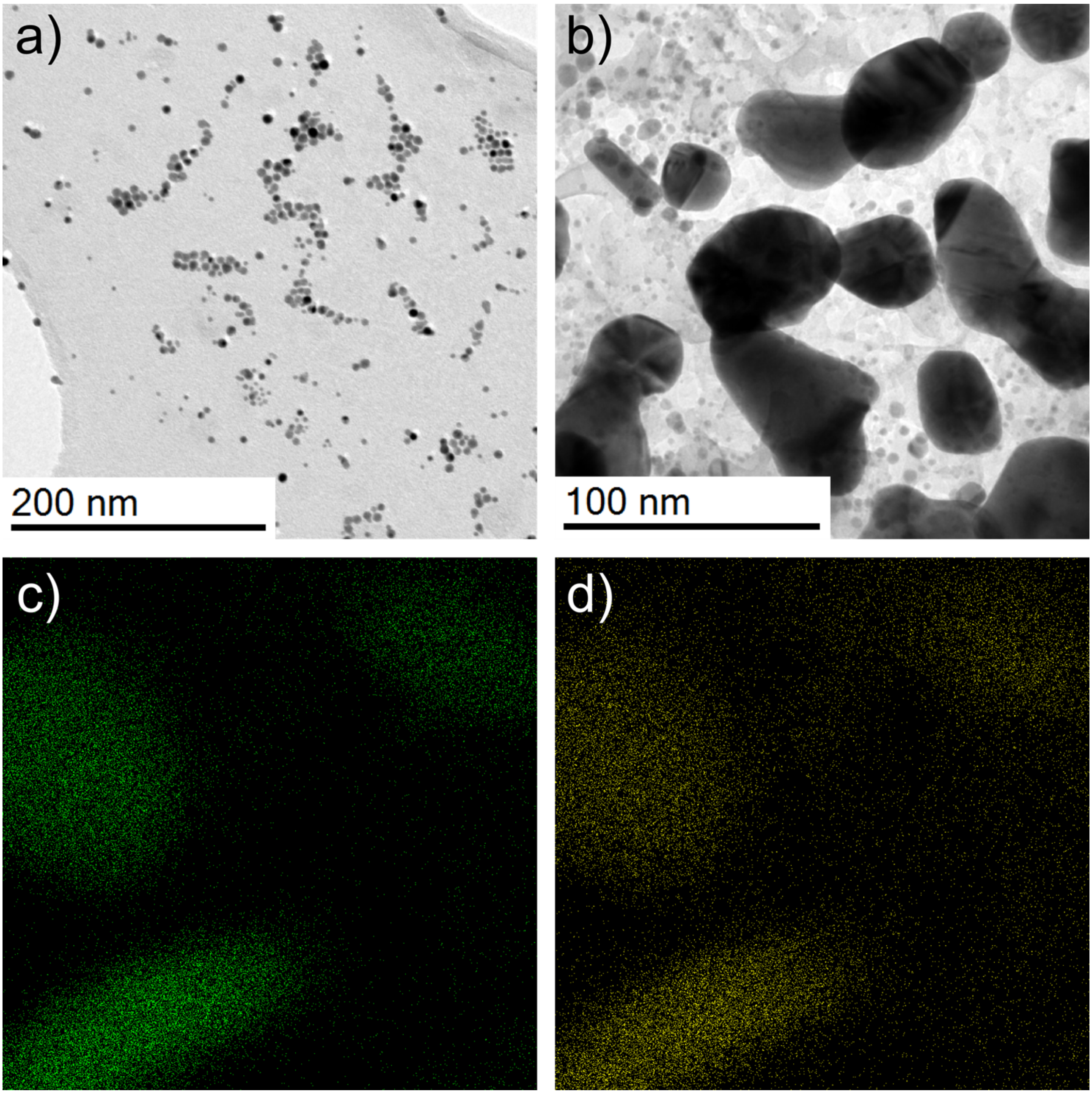

Figure S5.3.2: TEM micrographs of: a) as synthesised Au nanoparticles in toluene, b) ripening observed in the Au nanoparticle sulphur polymer composite, c) EDS Au map and d) EDS S map showing a broader distribution of sulphur throughout the composite compared to Au.

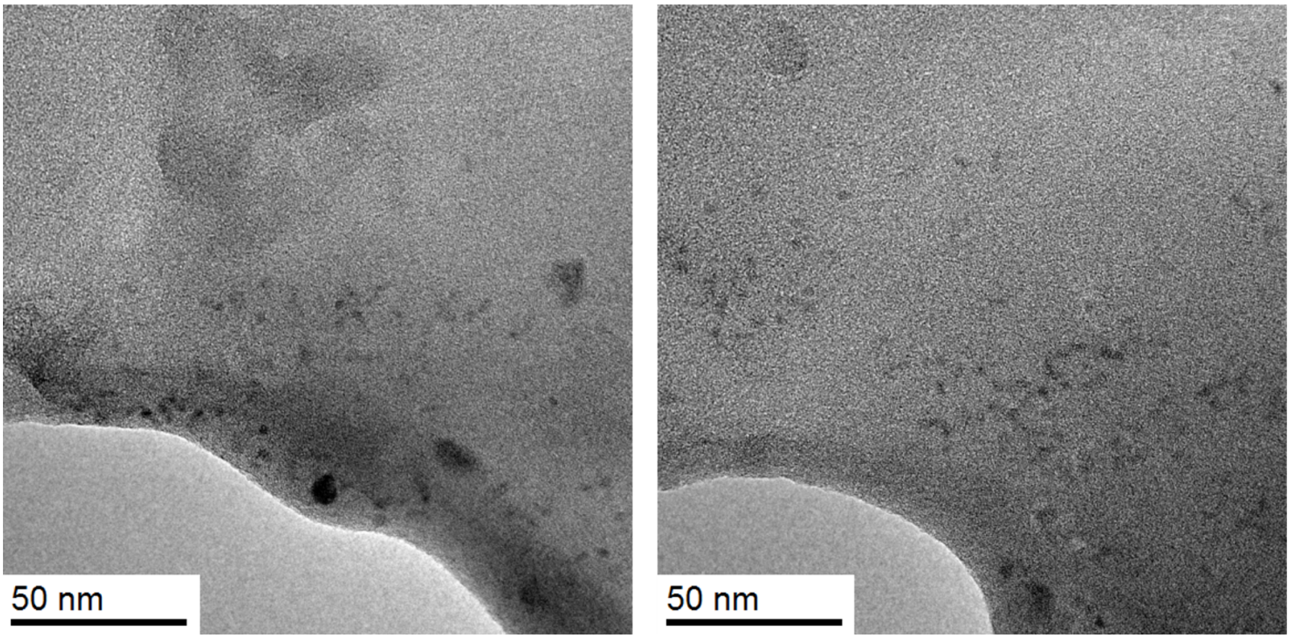

Figure S5.3.3: TEM micrographs of InP/ZnS quantum dots embedded in the sulphur polymer.

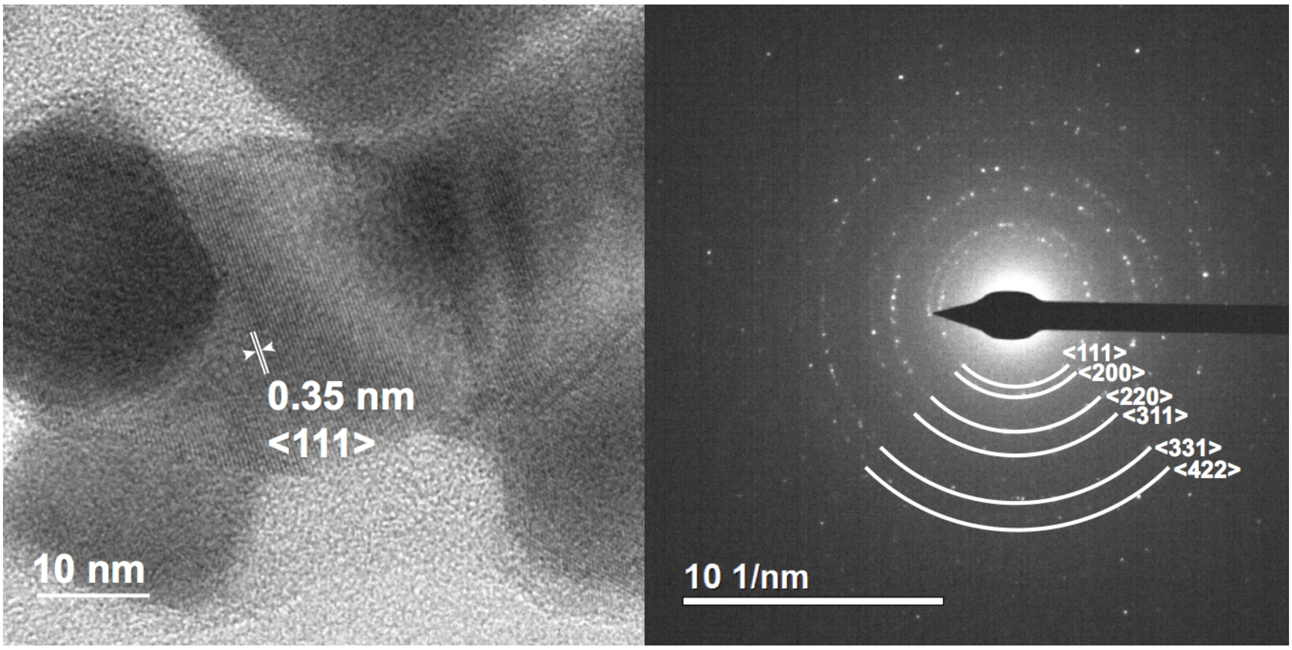

Figure S5.3.4: (Left): HRTEM micrograph of PbS nanocrystals in the PbS-S polymer composite highlighting the <111> plane of PbS (galena) and (right): A selected area electron diffraction pattern of PbS nanocrystals in the PbS-S polymer composite.

S5.4: Energy dispersive X-Ray spectroscopy

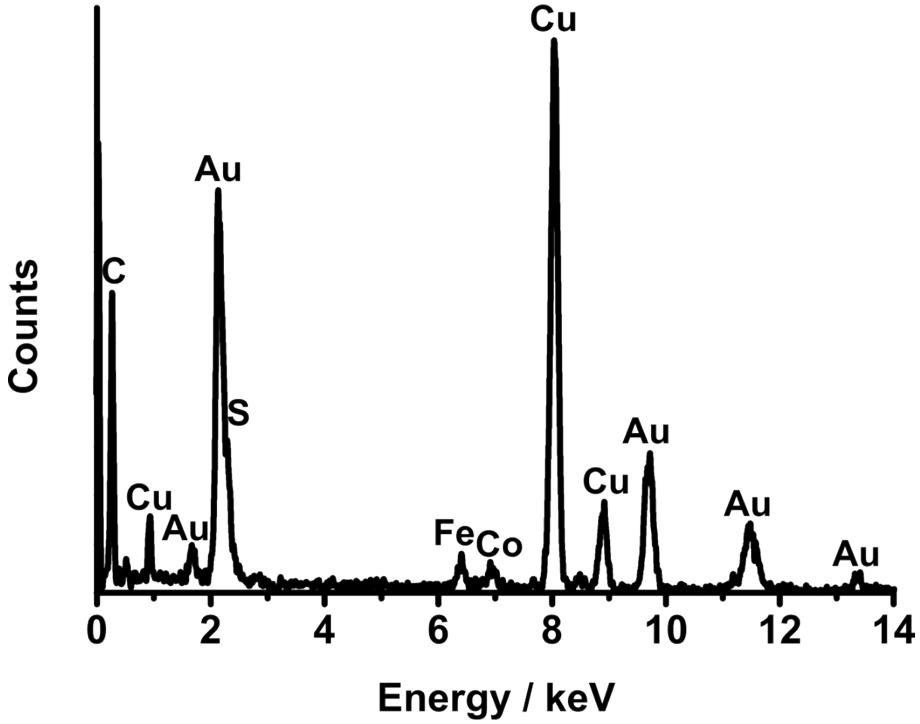

Figure S5.4.1: EDS spectrum of Au nanoparticle-sulphur polymer composite. The copper emanates from the Cu mesh TEM grids used, whilst Fe and Co emanate from the steel goniometer (sample stage) in the TEM.

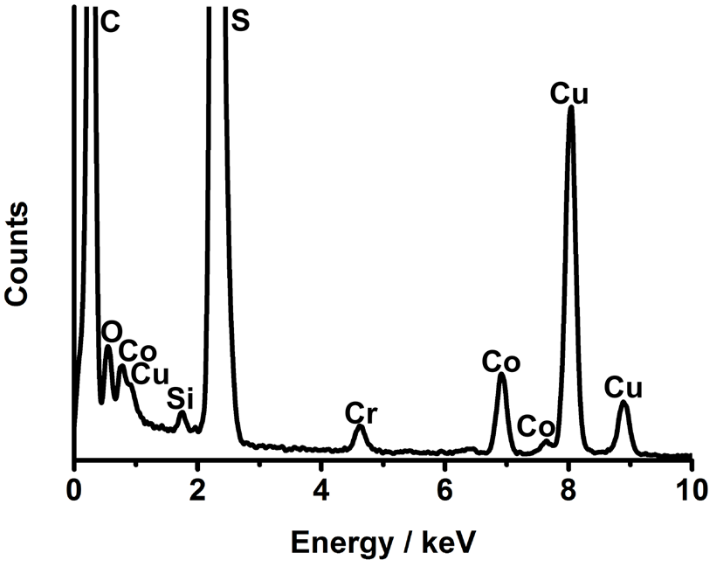

Figure S5.4.2: EDS spectrum of CoO nanoparticle-sulphur polymer composite. The copper emanates from the Cu mesh TEM grids used, whilst Cr emanates from the steel goniometer (sample stage) in the TEM.

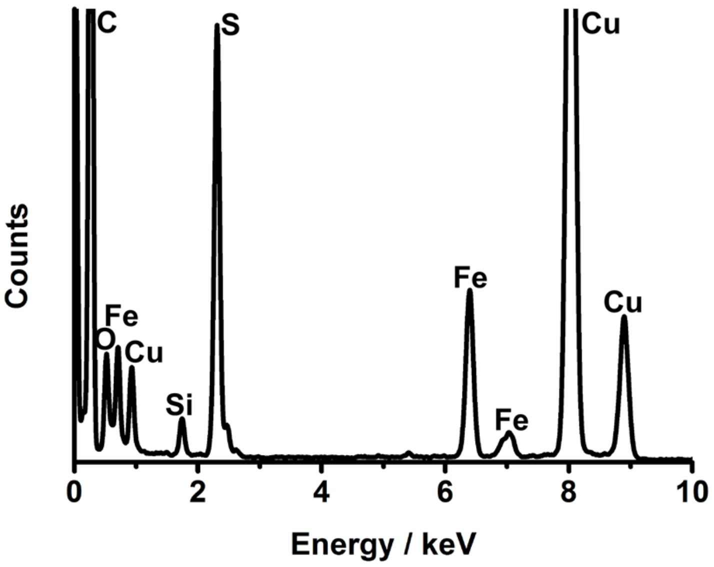

Figure S5.4.3: EDS spectrum of CoO nanoparticle-sulphur polymer composite. The copper emanates from the Cu mesh TEM grids used.

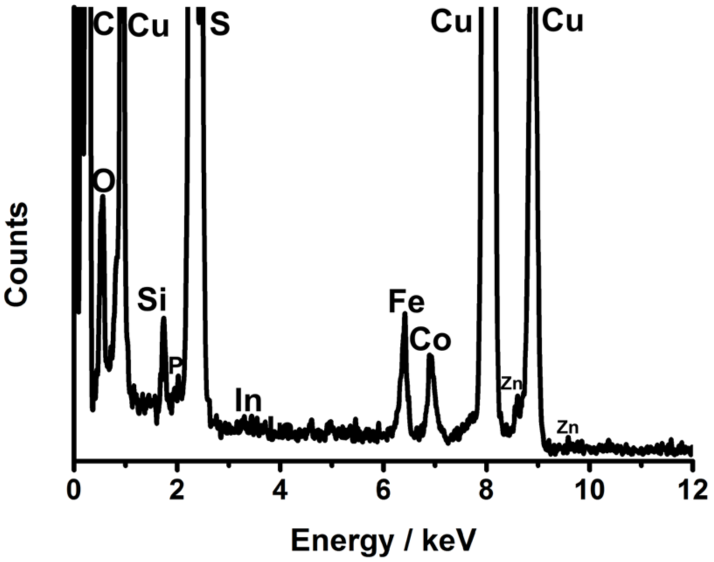

Figure S5.4.4: EDS spectrum of InP/ZnS nanoparticle-sulphur polymer composite. The copper emanates from the Cu mesh TEM grids used, whilst Cr emanates from the steel goniometer (sample stage) in the TEM. Although sample loading was low, there was evidence of In, P and Zn from the quantum dots themselves.

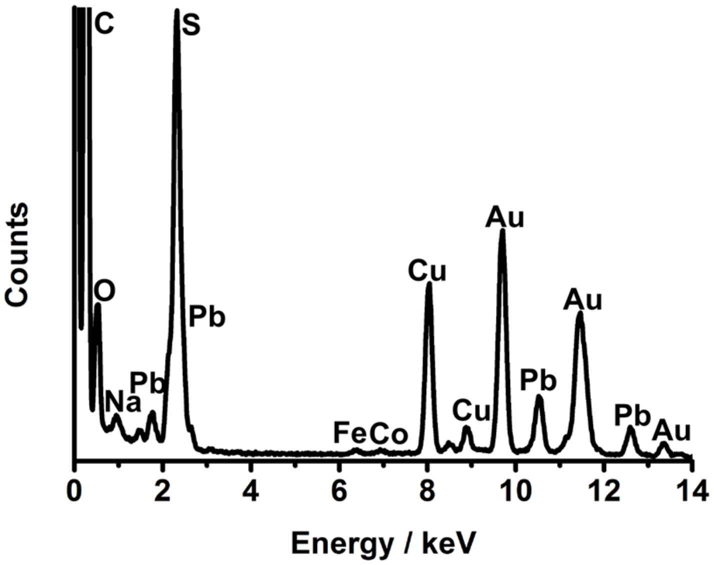

Figure S5.4.5: EDS spectrum of PbS nanoparticle-sulphur polymer composite. The gold emanates from the Au mesh TEM grids used.

S5.5: X-Ray photoelectron spectroscopy

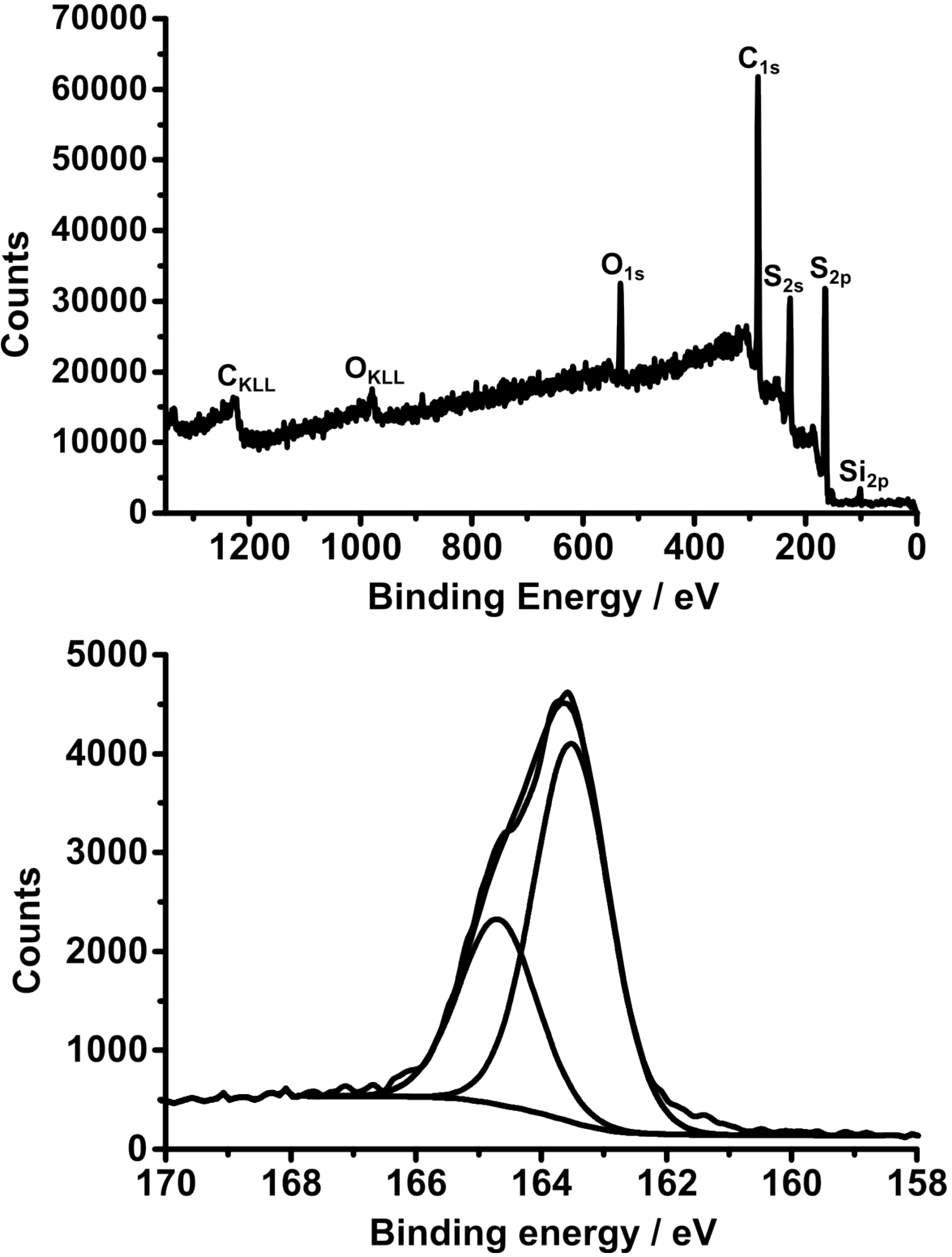

Figure S5.5.1: Top): XPS survey scan for the native sulphur polymer and bottom): Fitted S2p XPS spectrum of the native sulphur polymer, indicating a single sulphur oxidation state, commensurate with elemental sulphur.[9]

S5.6: Thermogravimetric analysis

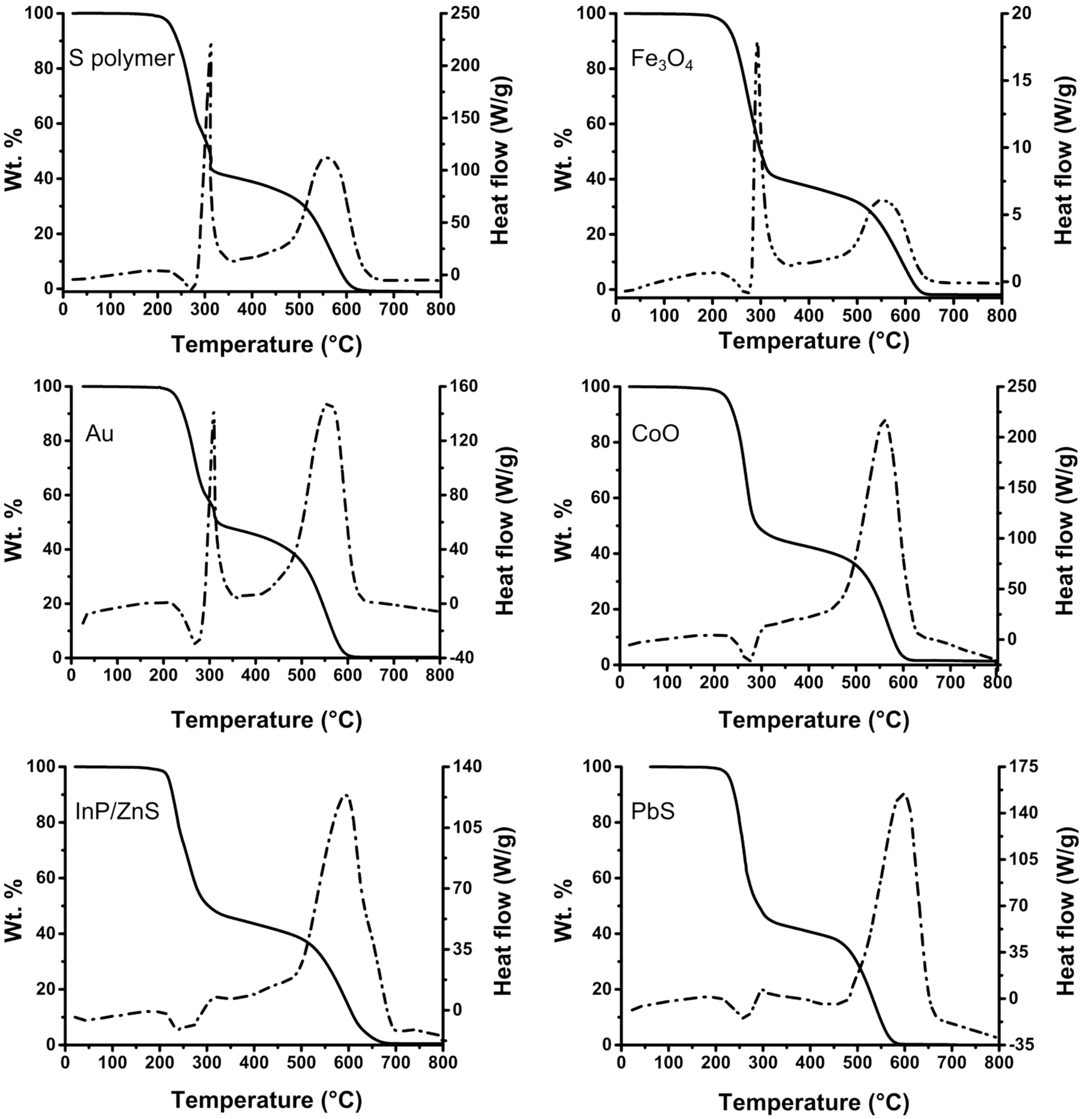

Figure S5.6.1: TGA (solid line) and DSC (dot-dashed line) traces of sulphur polymer-nanoparticle composites. Although polymer glass transition temperatures (T_g) were not observable due to their occurrence near 0 °C.[8] The DSC traces show an exothermic peak followed by an endothermic peak (more pronounced in the native sulphur polymer, Fe$_3$O$_4$ and Au composites) at around 270 °C associated with the melting of the composite and combustion of organic material. A second transition at around 480 °C is associated with the oxidation and combustion of sulphur.

S5.7: UV/vis absorption spectra

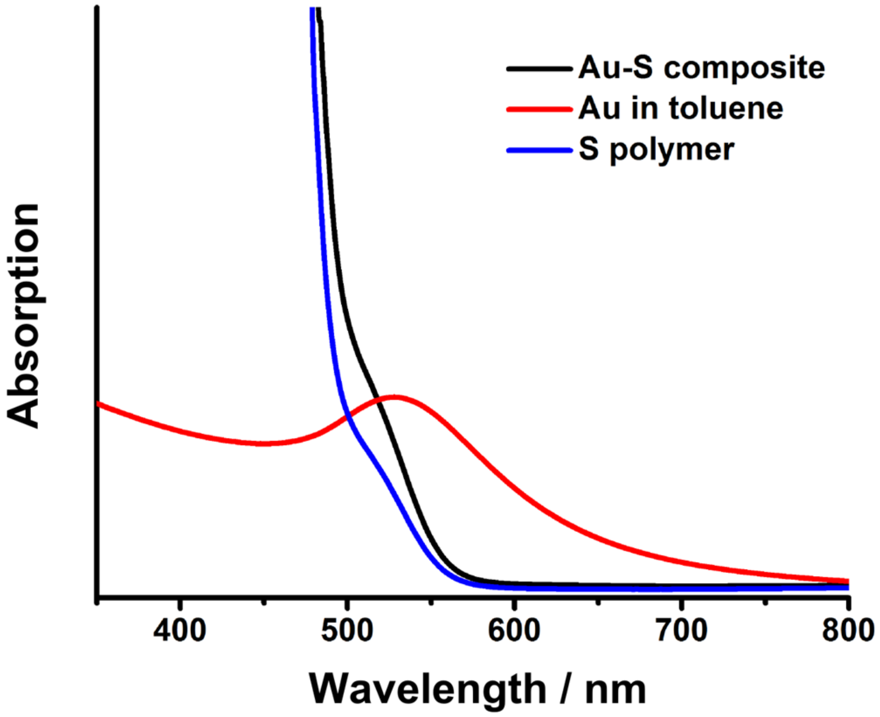

Figure S5.7.1: UV-vis spectra of: Au nanoparticle sulphur polymer composite (black), 1-dodecanethiol functionalised Au nanoparticles in toluene (red) and the native sulphur polymer (blue). The absorption spectrum of the Au nanoparticle sulphur polymer composite differs from the native polymer by virtue of the surface plasmon resonance of the incorporated gold nanoparticles.

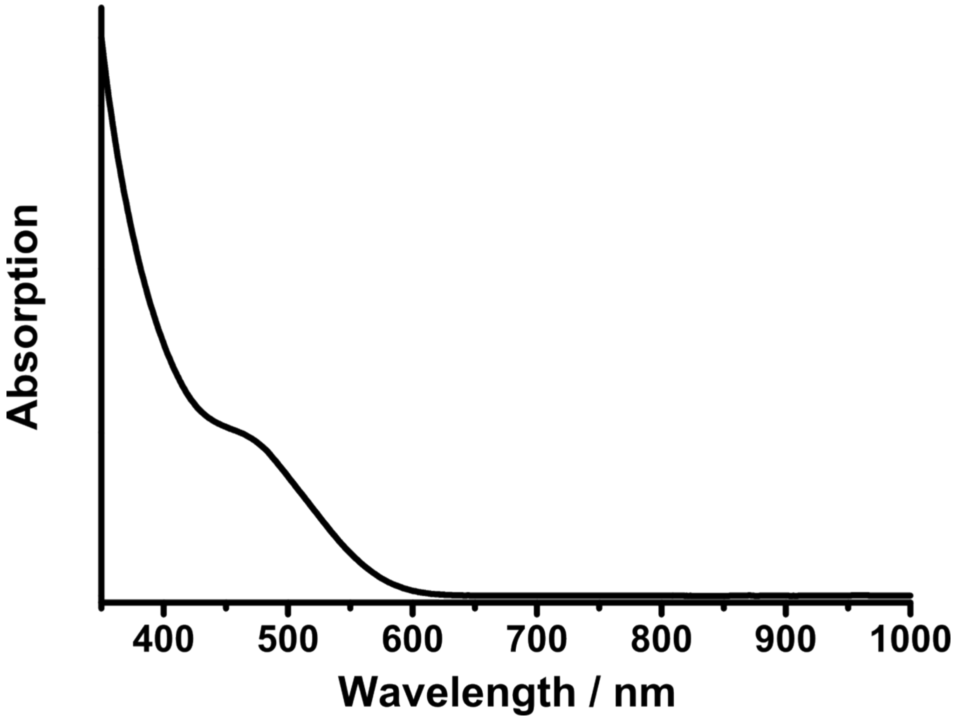

Figure S5.7.2: UV-vis spectrum of a dispersion of InP/ZnS core/shell quantum dots in *n*-hexane showing the band-edge at 455 nm.

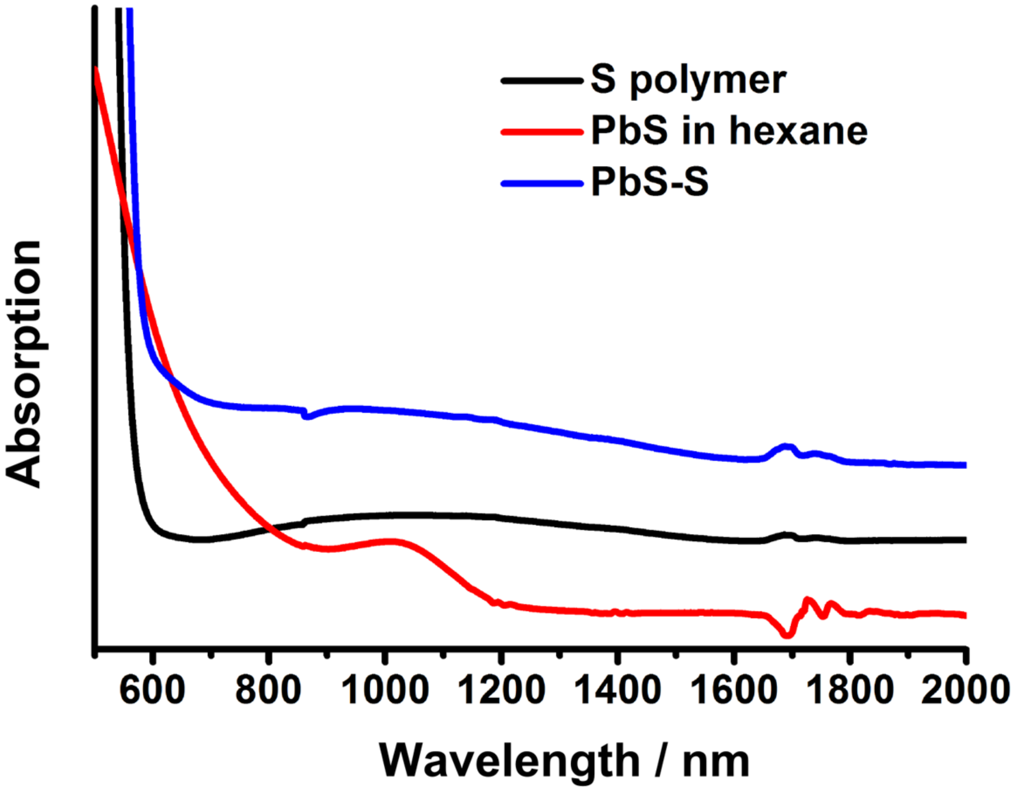

Figure S5.7.3: UV-vis spectrum of: the native sulphur polymer (black), PbS nanocrystals in *n*-hexane (red) and the PbS-sulphur polymer composite (blue). Note missing features in the composite around 1700 nm.

6. References

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9 *NIST X-Ray Photoelectron Spectrosc. XPS Database Version 35*.