Electronic Supporting Information for:

Directed organization of gold nanoparticles in polymer coatings through infrared-assisted evaporative lithography

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1. Synthesis of 10 nm gold nanospheres (AuNSs)

1.1. Materials

In all synthetic protocols, ultrapure deionized water (Milli-Q) was used. All glassware was cleaned with aqua regia (3 HCl : 1 HNO_3) and rinsed thoroughly with milli-Q water before being used. Sodium tetrachloroaurate dehydrate and trisodium citrate dehydrate were purchased from Sigma-Aldrich. Bis(*p*-sulfonatophenyl) phenyl-phosphine dihydrate dipotassium salt (BSPP) was purchased from Strem Chemicals. All chemicals were used without further purification.

1.2 Synthesis of AuNSs by the Turkevich-method

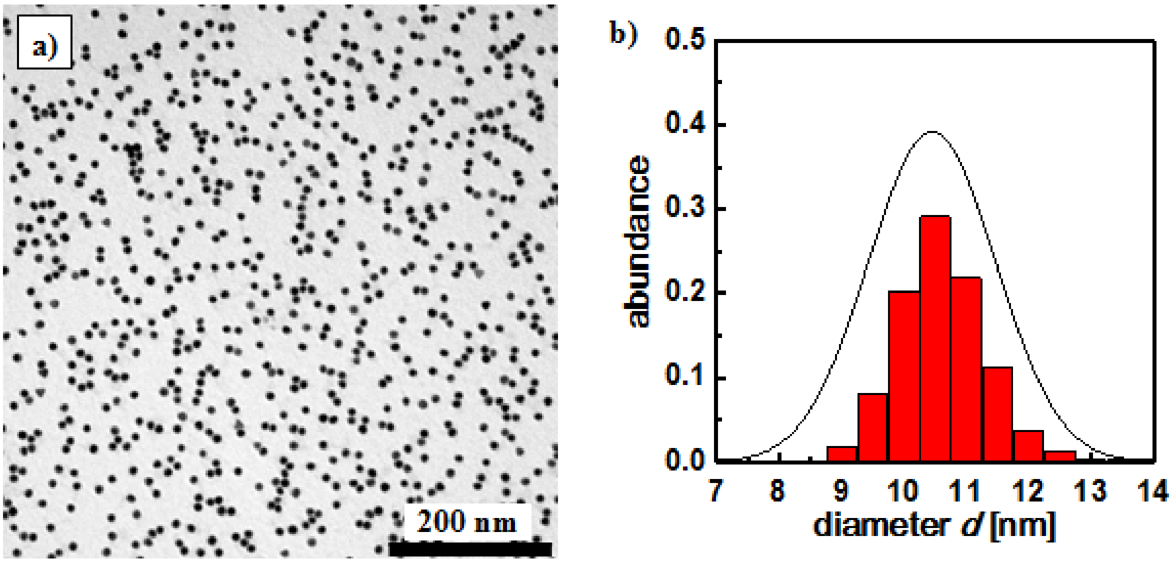
AuNSs were prepared by the well-established Turkevich-method: In detail, to a boiling $NaAuCl_4$ aqueous solution (100 ml,1 mM), preheated trisodium citrate aqueous solution (5 ml, 2 wt %) was added under vigorous stirring. After addition of the trisodium citrate to the yellowish $NaAuCl_4$ solution, the mixture immediately became colorless. Within 5 minutes, the color of the reaction solution changed to dark blue, purple and finally red, indicating the formation of the AuNSs. The mixture was boiled and stirred for a further 15 minutes and cooled down to room temperature.

1.3 Coating of citrate-capped AuNSs with BSPP

For the purification of the AuNSs by centrifugation and to increase the stability of the dispersion against aggregation, the particles were coated with BSPP by a ligand exchange reaction. This step is necessary because citrate capped AuNSs cannot be re-dispersed in water when they are aggregated. To 100 mL of a dispersion of the as-prepared citrate-coated AuNSs, 50 mg of BSPP was added. The reaction mixture was stirred overnight and, afterwards, filtrated through a 0.45 µm filter (Millipore). A saturated sodium chloride solution was added to the AuNSs dispersion until the colour changed from red to blue, indicating the formation of aggregates. The suspension was centrifuged for 10 minutes at 5000 rpm. The supernatant, containing the excess BSPP, citrate and sodium chloride was discarded, and the black precipitate was re-dispersed in 1 mL purified water and sonicated. The reddish solution of gold nanoparticles was kept at 4 ^{o}C until further use.

TEM of AuNSs

1.4 TEM of AuNSs



A TEM image of AuNSs is shown in a). For TEM a FEI Technai12 microscope operated at 80 kV was used. For the histogram in b) ImageJ was used and at least 1000 particles were counted. The average diameter of the AuNSs is 10.4 ± 0.5 nm. The line in b) represents a Gaussian fit.

2. Experimental procedure for polymer-nanoparticle coatings

2.1 Materials and preparation of samples

The acrylic particles were synthesised by semicontinuous emulsion polymerization. The particles were composed of a copolymer of methyl methacrylate, butyl acrylate and methacrylic acid (in a weight ratio of 18.3 : 13.3 : 1). Ammonium persulfate was used as the initiator and an anionic, ethoxylated alcohol surfactant (Rhodafac RK500A, Rhodia) as the surfactant in the synthesis. The size of the particles was measured by photon correlation spectroscopy (Coulter N4 plus, Beckman-Coulter) and the T_g of the dry latices was 37.9 °C, measured by differential scanning calorimetry (Q1000, TA instruments). The ζ-potential for each type of particles was measured with a Malvern ME11 Zetasizer Nano ZS. All results of these measurements are summarized in Table S1.

Table S1 Diameters d_{Poly}, ζ-potentials of the polymer particle

Code name	Diameter d_{poly} [nm]	ζ-potential [mV]
Latex A	160	-66.9 ± 1.0
Latex B	280	-68.2 ± 0.9
Latex C	400	-69.3 ± 0.5

For the preparation of the desired blends, acrylic particles and AuNSs were mixed in an aqueous solution. The vials were shaken for at least 30 minutes to ensure that the blend was mixed thoroughly. From this mixture a volume of $V = 1.2$ mL was casted on a degreased glass substrate (A = 26 mm x 76 mm) to obtain an initial thickness of the wet film of h_i = 0.6 mm (calculated by $h_i = V/A$). For the IRAEL experiment, an infrared light emitting lamp (250 W) was placed at a distance of d_l = 18.5 cm above an aluminum mask. The mask contained circular holes with a diameter d_h = 2 mm and a centre-to-centre distance or pitch P = 4 mm arranged in a square array. The mask was placed at a distance of 0.4 mm above the wet film, and the sample was irradiated by the IR lamp for 25 minutes.

3. Optical properties of samples using spatial resolved transmission spectroscopy

The optical properties of the patterned films, containing the AuNPs, were investigated with a specially created UV-Vis-NIR setup, which is schematically illustrated in Figure S1: A broadband supercontinuum laser (Fianium) with an output power of 2 W was used as a light source. To select a narrow wavelength range of a few nanometers, the light beam was spectrally filtered by a subtractive-mode double prism monochromator and focused by a moveable lens on the sample surface. The transmitted beam was collected by an integrating sphere equipped with detectors for the visible (Si) and near-infrared (InGaAs) range. A chopper and lock-in amplifier were used for recovery of intensities (not shown). For focusing the beam on the sample surface, the reflected beam was directed by a thin glass slide to a CCD camera after passing through a ND-filter and a lens. This setup is equivalent to an optical microscope in reflection mode. The focus was adjusted by placing the moveable lens into the right position, which could be found when a clear shape of the reflected beam was visible in the picture transmitted by the CCD camera.

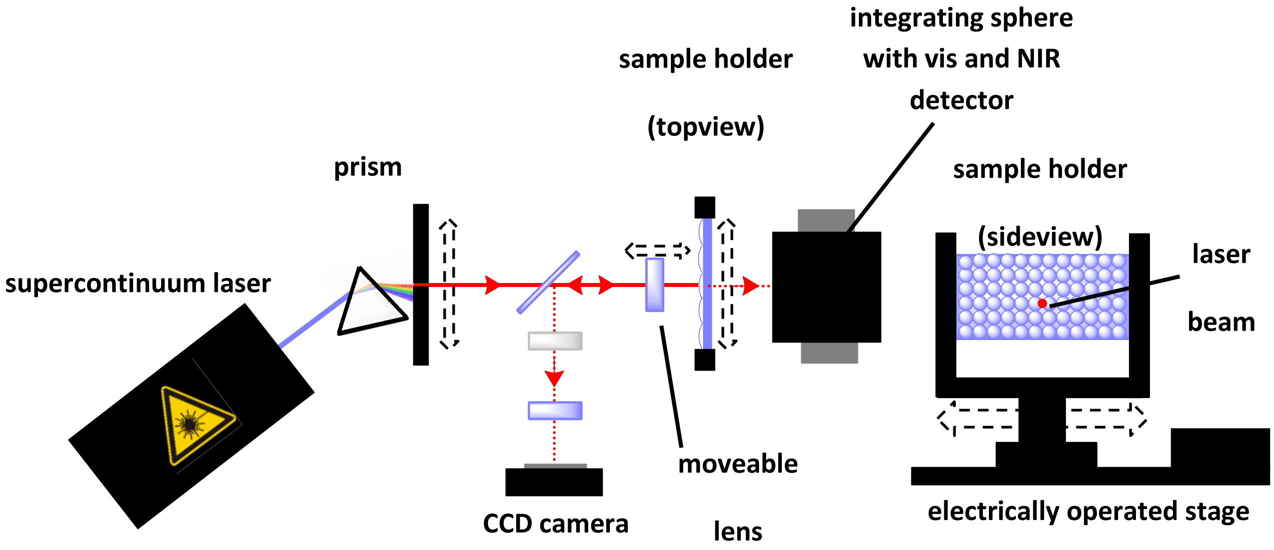


Figure S1. Schematic illustration of the technical setup for spatially resolved transmission measurements. The moveable elements are marked by the dashed arrows. The sample holder is placed on a lateral moveable stage, which enables spatially resolved measurements with a 50 µm resolution.

4. Optical transmission spectra for nanomaterials as a function of the volume fraction of AuNSs

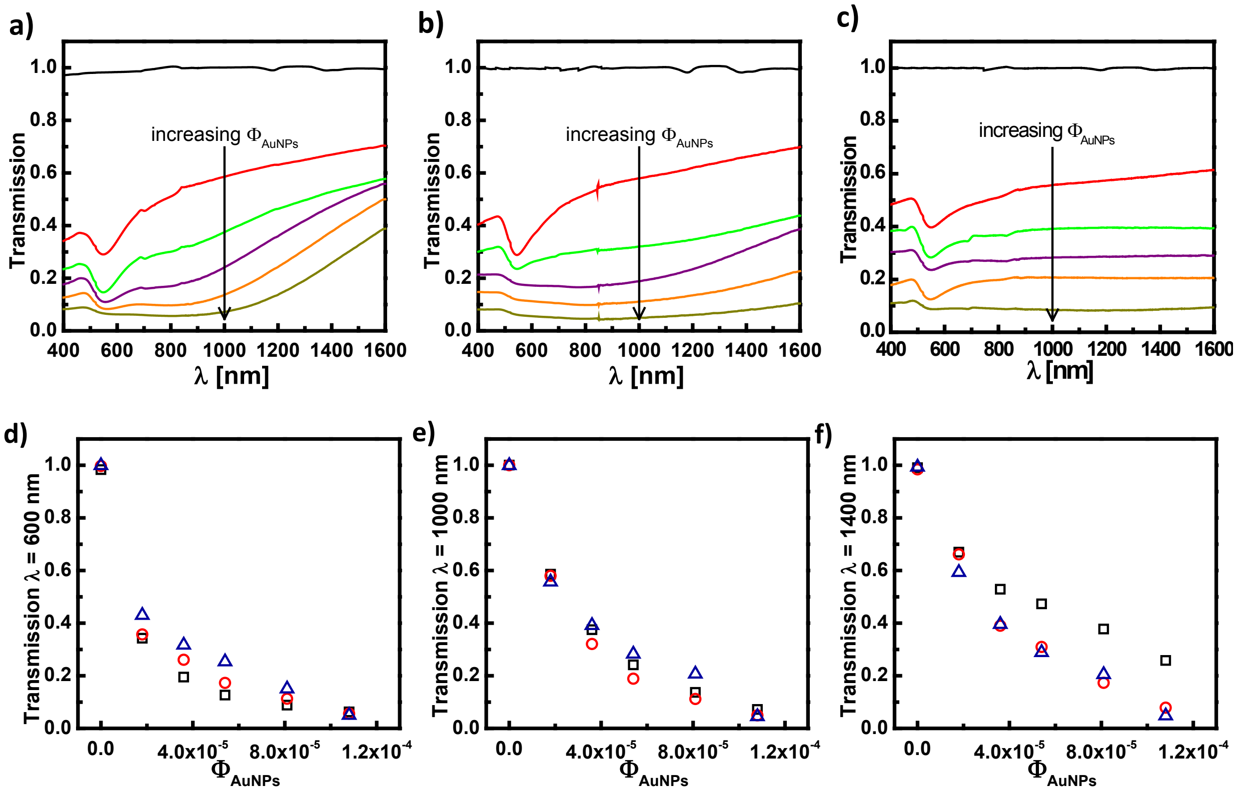


Figure S2. UV-Vis-NIR spectra of patterned films with AuNPs prepared from (a) latex A, (b) B or (c) C. The volume fractions of the AuNPs in the films were: $\Phi_{AuNPs} = 0$, $1.8 \cdot 10^{-5}$, $3.6 \cdot 10^{-5}$, $5.4 \cdot 10^{-5}$, $8.1 \cdot 10^{-5}$ and $1.08 \cdot 10^{-4}$ (in (a) – (c) from the top to the bottom). The transmission obtained at (d) λ = 600 nm, (e) 1000 nm and (f) 1400 nm as a function of Φ_{AuNPs} for latex A (black squares), B (red circles) and, C (blue triangles) are plotted in (d) – (f).

5. Optical images over a larger area of the gold-polymer nanocomposites.

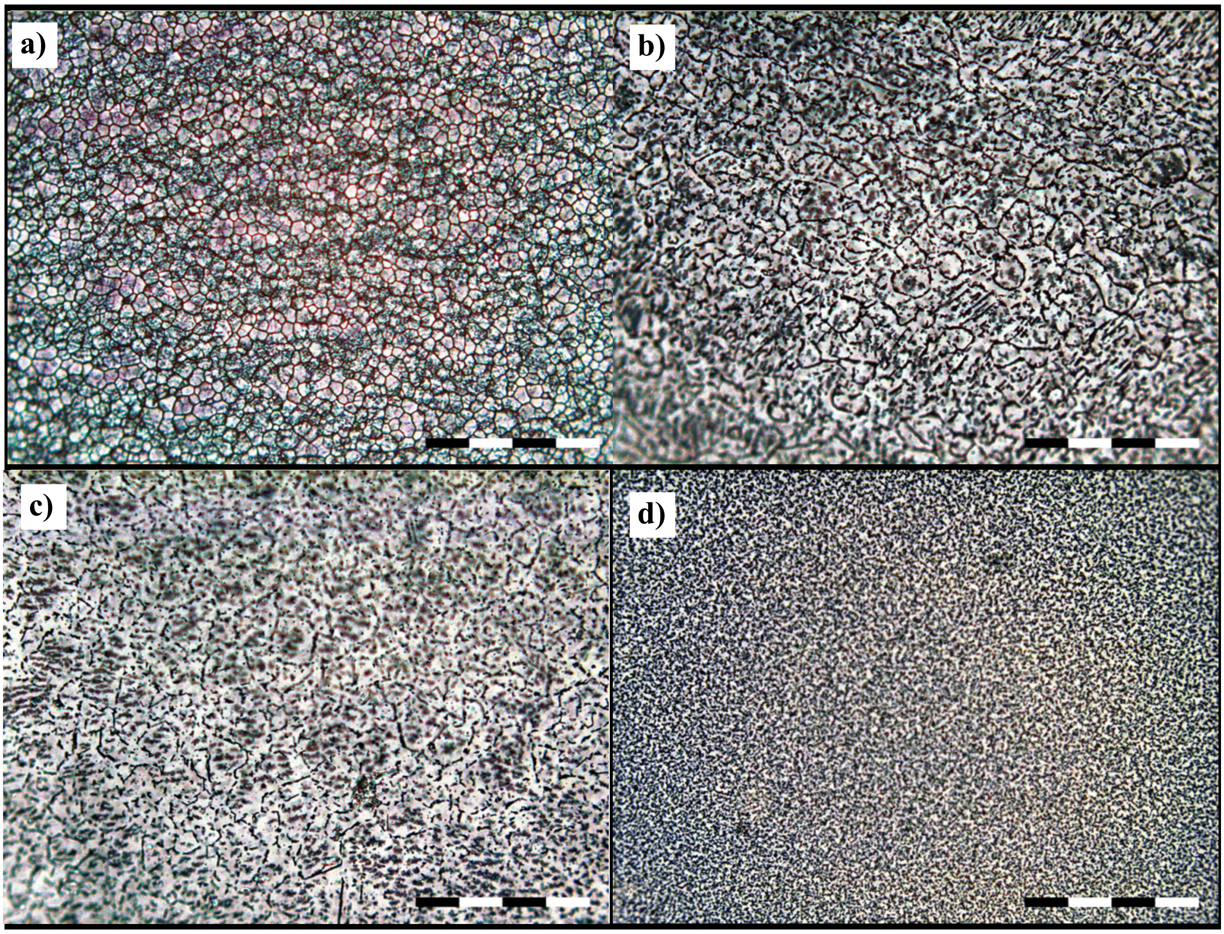


Figure S3. Optical microscopy images of the patterned films prepared of blends of 10 nm AuNSs with three different sizes of polymer particles (a) 160 nm, (b) 280 nm, (c) 400 nm and (d) all three sizes of polymer particles. The images were taken from the surface of the dome-like features with an optical microscope and 20x magnification. The volume fraction of the AuNSs is in all cases is $1.08 \cdot 10^{-4}$. The scale bars in all images are 100 µm.

6. Scanning Electron Microscopy Characterization

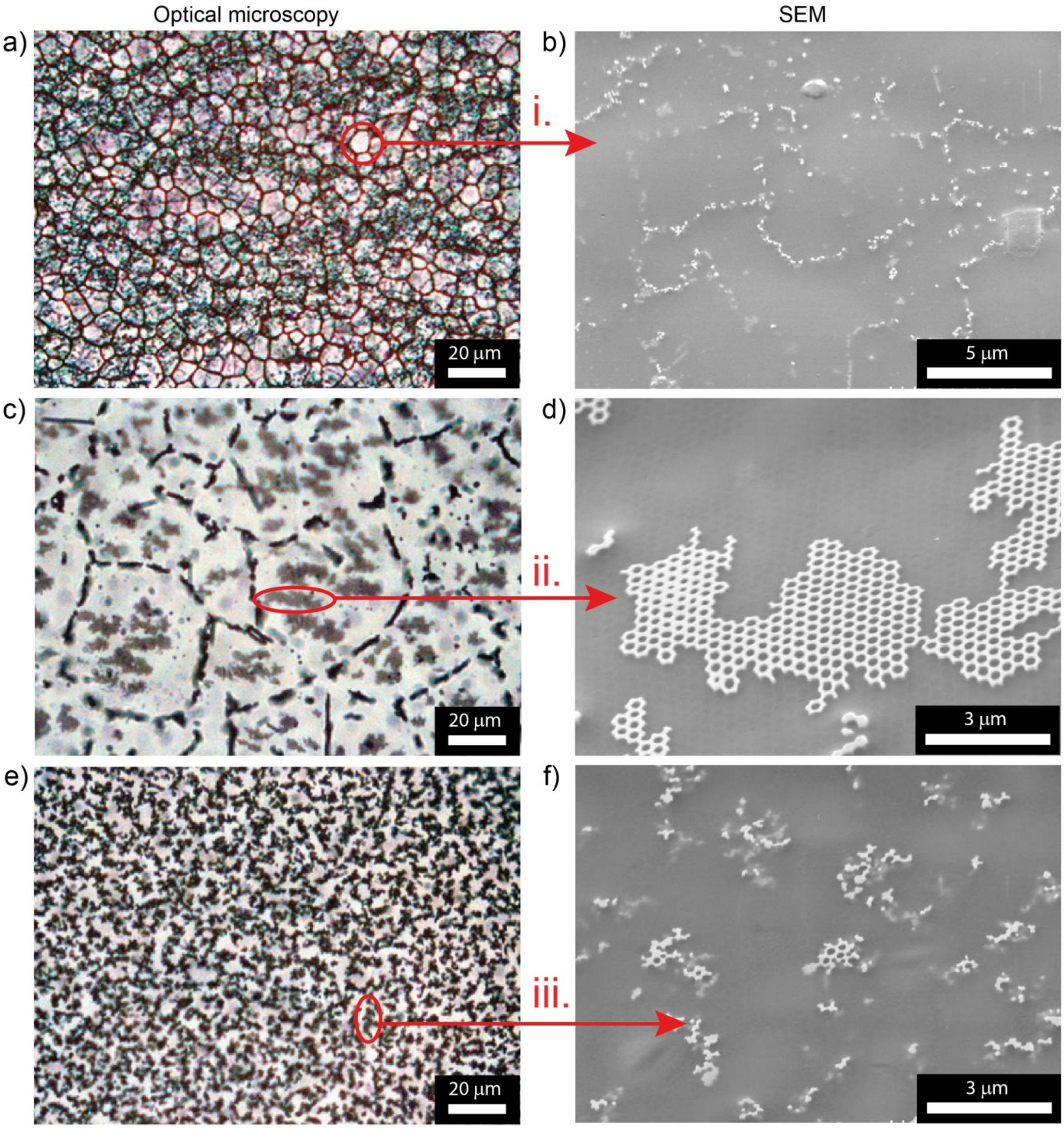


Figure S4. Comparison between mesoscale structures in optical images (left) with SEM micrographs (right) of gold nanoparticles in the polymer matrix. Red circles and arrows represent the typical feature types observed in both optical and SEM images. SEM images (on the right) show the various ways of AuNSs organization on micrometer length scales (bright arrangements): SEM images correspond to various surface domains (i.e. lines, islands) derived from blends of AuNSs with: 160 nm polymer particles (a,b), 400 nm polymer particles (c,d), and a mixture of the three different polymer particle sizes (e,f). **i)**. Linear chains of AuNSs at crystal boundaries, **ii)**. Large scale assemblies of AuNSs with a periodic hole pattern moulded by polymer particle crystal, **iii)**. Small flakes with irregular hole pattern moulded by randomly packed polymer particle mixture.

Experimental protocol: Electron scanning microscopy was conducted with a Hitachi S4000 SEM, operated at an acceleration voltage of 5 kV. Secondary electrons were used for imaging. The stage on which the samples were placed was tilted by 45°. In order to increase the conductivity of the samples the surface was coated with a thin layer (12 – 20 nm) of carbon using an Edwards Auto 306 coater.

7. Transmission Electron Microscopy of a cross-section of the polymer-nanoparticle matrix.

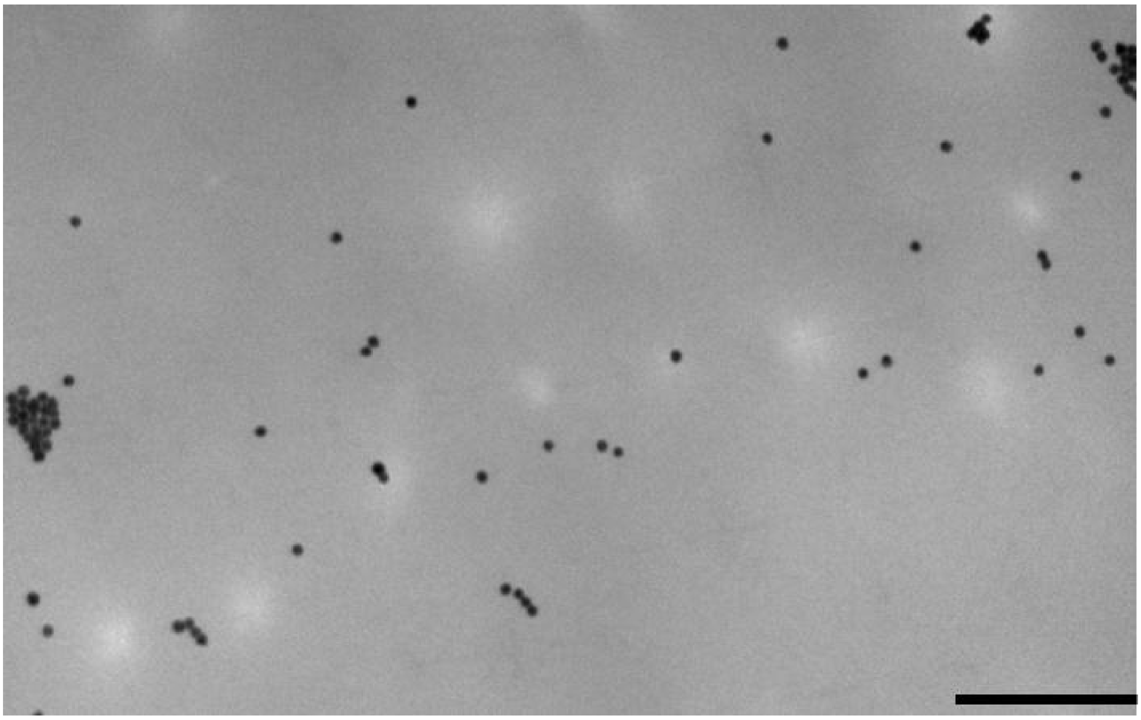


Figure S5. TEM cross sectional images of the polymer matrix containing AuNSs. The image shows that the AuNSs are not organised on short (nm) scale. Organization is possible only in longer scales as shown in Figure S3 and S4. Bright dots in the polymer matrix (background) correspond to thinner regions that are remnants of the voids between polymer particles. Scale bar is 200 nm.

Experimental protocol: To prepare the TEM cross section, a dome-like feature was cut out of the film. Approximately 100 nm thick sections were cut using a Reichert-Jung Ultracut E ultramicrotome. The sections were cut perpendicular to the substrate and embedded in epoxy resin. The epoxy was cured at room temperature under UV irradiation overnight. Specimens were imaged with a FEI Tecnai microscope operated with an acceleration voltage of 80 kV.