Electronic Supporting Information

Efficient NIR light blockage with matrix embedded silver nanoprism thin films for energy saving window coating

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Experimental

Chemicals and Materials

Silver nitrate, trisodium citrate dihydrate (TSCD), tetraethyl orthosilicate (TEOS), allyltriethoxysilane (APTES), methyl methacrylate (MMA, with <30ppm monomethyl ether of hydroquinone (MEHQ) as inhibitor), dimethylamine 40 wt.% in H_2O (DMA) and potassium chloride were purchased from Sigma-Aldrich (UK). Sodium borohydride was purchased from Acros Organic (Belgium). Hydrogen peroxide was purchased from Fisher Scientific (UK).

Azobisisobutyronitrile (AIBN) was purchase from Molekula (UK). Poly(acrylic acid) (PAA), MW 50000, was purchased by Polyscience Europe (Germany). Polydimethylsiloxane (PDMS) monomer and curing agent were purchased from Dow Corning (USA).

All the chemicals were used as received, with the exception of MMA which was purified for removing the inhibitor prior to the polymerization.

TEM images were collected using a FEI Technai12 transmission electron microscope, with an electron acceleration of 120 kV and a tungsten filament source. TEM grids (Carbon on Cu, 400 mesh) were purchased from Agar Scientific (UK).

UV-vis-NIR spectra (300-900 nm) were collected using a Cary Varian 300 Bio using a quartz cell (10 mm optical path). UV-vis-NIR spectra (300-2500 nm) were collected using a Jasco V-570 Spectrophotometer. The glass slides with the deposited polymer film were attached directly to the cell holder with tape, with the polymer film facing the incoming beam.

IR spectroscopy was performed on a Nicolet 380 FT-IR equipped with a diamond crystal Smart Orbit for ATR experiments.

[1]H Nuclear Magnetic Resonance (NMR) spectra were acquired with a 400 MHz Bruker DPX-400 spectrometer while for ^{13}C Solid State NMR spectra were acquired with a 400MHz Bruker spectrometer. Solid State ^{13}C NMR sample preparation is reported further below.

Size exclusion chromatography was performed with a Viscotek GPCmax cromatography coupled with a Water 410 differential refractive index detector, using a flow rate of 1mL/min.

Thermogravimetric analysis was performed using a Mettler Toledo TGA/SDTA 851e thermogravimetric analyser. The sample were analysed under flowing Ar (65 ml/min), using a heating rate of 10 °C/min.

Synthesis of SNPs

In order to synthesise SNPs, the protocol proposed by Métraux et al. [1] was used. In a typical reaction, to a freshly prepared solution of $AgNO_3$ (20 mL, 0.1 mM, 2μmol) a 30 mM solution of TSCD (1.2 mL, 36 μmol) was added. H_2O_2 (48 μL, 30% w/v, 422.2 mol) was added and the solution was left to stir for 5 minutes. Finally, a 0.1 M aqueous solution of $NaBH_4$ (0.2 mL, 20 μmol) was rapidly injected. The solution colour started to change from an intense yellow (typically shown by spherical particles) to a dark blue colour (characteristic of triangular silver nanoprisms). The reaction batch was stirred until no further change in colour could be observed. The solution was then centrifuged at 13,200 rpm for 5 minutes and the surfactant replaced with MilliQ water or ethanol. The solution stored in the fridge was stable for months. The size of SNPs can be increased by ~20 nm by adding KCl to the nanoparticles precursor before the addition of $NaBH_4$ according to the work of Cathcart et al.[2] In particular, to a standard batch

prepared as above, 44 µL of a 0.05 M solution of KCl were added before the addition of the reducing agent. The reaction was then carried out as for the usual standard preparation of SNPs.

Synthesis of SiO$_2$@SNPs nanoparticles
To 1 mL of Ag nanoprisms, 20 µL of a 1mM ethanolic solution of MHA (20 nmol, final concentration in solution 19.6 µM) was added. After vigorously shaking for few second, the sample was left to rest for 3 minutes. The SNP solution was then centrifuged at 13,200 rpm for 15 minutes and re-dispersed in a 0.5 mM ethanolic solution of TEOS, under gentle sonication. To the solution, 155 µL of a 20% v/v solution of dimethylamine (DMA) was added and then the sample was left to stir for 1 hour. The sample was then centrifuged at 13,200 rpm for 15 minutes and re-dispersed in EtOH under gentle sonication (2 times). Functionalization of SNPs@SiO$_2$ surface with allyl groups can be achieved by co-condensation of different ratio of TEOS and ATES (from 100% TEOS/0% ATES, to 0% TEOS/100% ATES) in the same experimental condition used for the coating with just TEOS.

Spectral shift of SNPs absorbance during the coating with silica
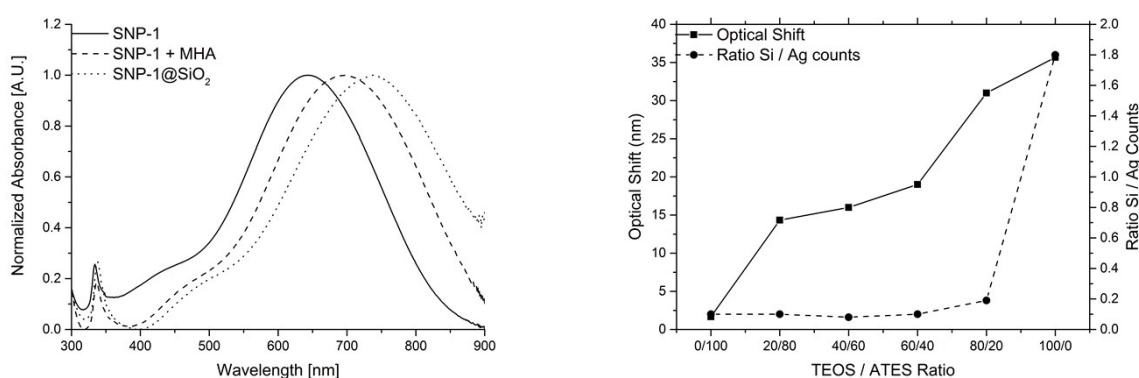

Figure S1: Left: typical red-shift of bare silver nanoprisms SPR (solid line), after the addition of MHA (dashed line), and after the formation of the silica shell (dotted line). Right: Optical shift of SNPs *vs* amount of ATES used in silica coating, combined with EDAX data showing ratio of Si to Ag.

Synthesis of SNPs@SiO$_2$/PMMA composites
MMA was washed ~5-6 times with a 0.5 M solution of NaOH. The MMA was then dried with Na$_2$SO$_4$, filtered and stored at +4 °C. To 0.75 mL of purified MMA the same amount of toluene was added, along with different percentage of AIBN (1, 2, 4 and 6% w/w). To this solution, different percentages of silver nanoprisms (0, 0.1, 0.2 and 0.5% w/w) dispersed in 200 mL of EtOH were mixed with the monomer solution. The flask was wrapped in aluminium foil and degassed with Ar in order to remove O$_2$ from the solution. After 30 minutes the aluminium foil was removed and the solution irradiated with a UV lamp (100 W, λ=365 nm). After two hours, the solution was added dropwise into ice cold methanol for the polymer to precipitate. The polymer was then filtered off and washed several times with cold methanol to remove unreacted monomer and toluene.
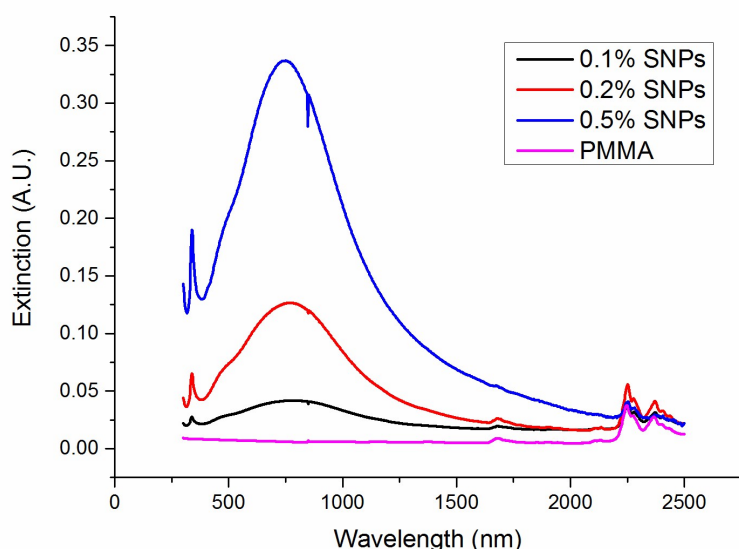
Figure S2: Extinction spectra of SNPs@SiO2/PMMA composites with different loading of SNPs in the polymer matrix.

Preparation of SNPs@SiO$_2$/PMMA Films

To prepare films for optical tests, polymer solutions were cast into a glass/PDMS mold. The mold was prepared by strongly pressing thin PDMS films (2 mm thick) with a square section cut in it on a clean glass slide for few minutes. The solutions were prepared by dispersing the composite solution into chloroform. Attempts to use toluene as solvent resulted in very thick films (approximately 1.5 mm) with a fragile honeycomb structure. To make the film more homogeneous, the mold holes were covered with a watchglass to slow down the evaporation of chloroform; polymer solutions evaporated without the watchglass show a cracked and corrugated surface. After leaving the polymer solution to rest overnight the PDMS film can be peeled off and the higher edges on the side of the film can be removed by cutting them with a scalpel. The polymer films were prepared using a 20% solution of SNPs@SiO$_2$/PMMA loaded with different amounts of silver nanoparticles (0.1, 0.2 and 0.5%); use of more dilute solutions resulted in peeling of the PDMS film due to infiltration between the glass slide and the PDMS interface. Using polymer concentration >20%, instead, results in film with a very intense colouration (almost pitch black).

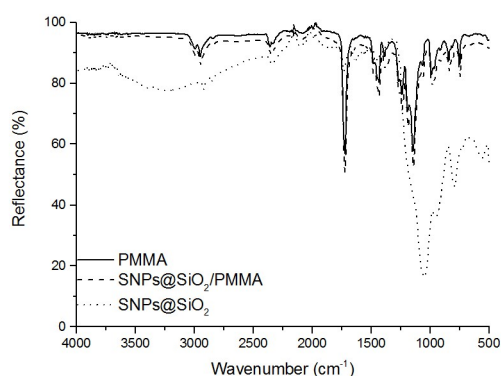**IR spectra of SNPs with silica coating and embedded in PMMA**

Figure S2: IR spectra of PMMA (solid line), silica coated SNPs with alkene functionalization (dotted line), and covalent conjugation of SNPs with PMMA (dashed line).

Table S1a: M_n of samples prepared with different amounts of AIBN and SNPs@SiO$_2$

M_n (Daltons)

	SNPs@SiO$_2$ % (w/w)			
AIBN %	0%	0.1%	0.2%	0.5%
1	20432.3	27453	17968	24236
2	11877.6	12138	15554	11753
4	8802	12201	9345	8255
6	7501	12511	8177	7324

Table S1b: Mw of samples prepared with different amounts of AIBN and SNPs@SiO2

M_w (Daltons)

	SNPs@SiO$_2$ % (w/w)			
AIBN %	0%	0.1%	0.2%	0.5%
1	35437.6	51413	32217	43495
2	21080.3	21493	21203	22797
4	13998.6	20690	15025	16394
6	14339.3	19479	12070	13099

Solid state sample preparation

A solution of SNPs@SiO$_2$/PMMA composite was centrifuged and the surfactant was then removed. The precipitate was redispersed in chloroform and spun down again. This process was repeated until no more PMMA signals were observed in ^{1}H NMR. The precipitate was then redispersed in chloroform and a few drops of the solution were added inside the NMR rotor, and the solution removed *in vacuo*.

Magic-angle spinning solid state NMR measurements

All experiments were performed on a 4 mm double resonance APEX probe at 9.4 T on a Bruker Ascend 400WB magnet and a Chemagnetics Infinity console, at a spinning frequency of 8 kHz. The spectra displayed in Figure 2 are the result of 24600 scans on (SNP-1)@SiO$_2$, 480 scans on PMMA and 15200 scans on (SNP-1)@SiO$_2$/PMMA, with a 3 s pulse delay and SPINAL64 ^{1}H decoupling[3] during acquisition.
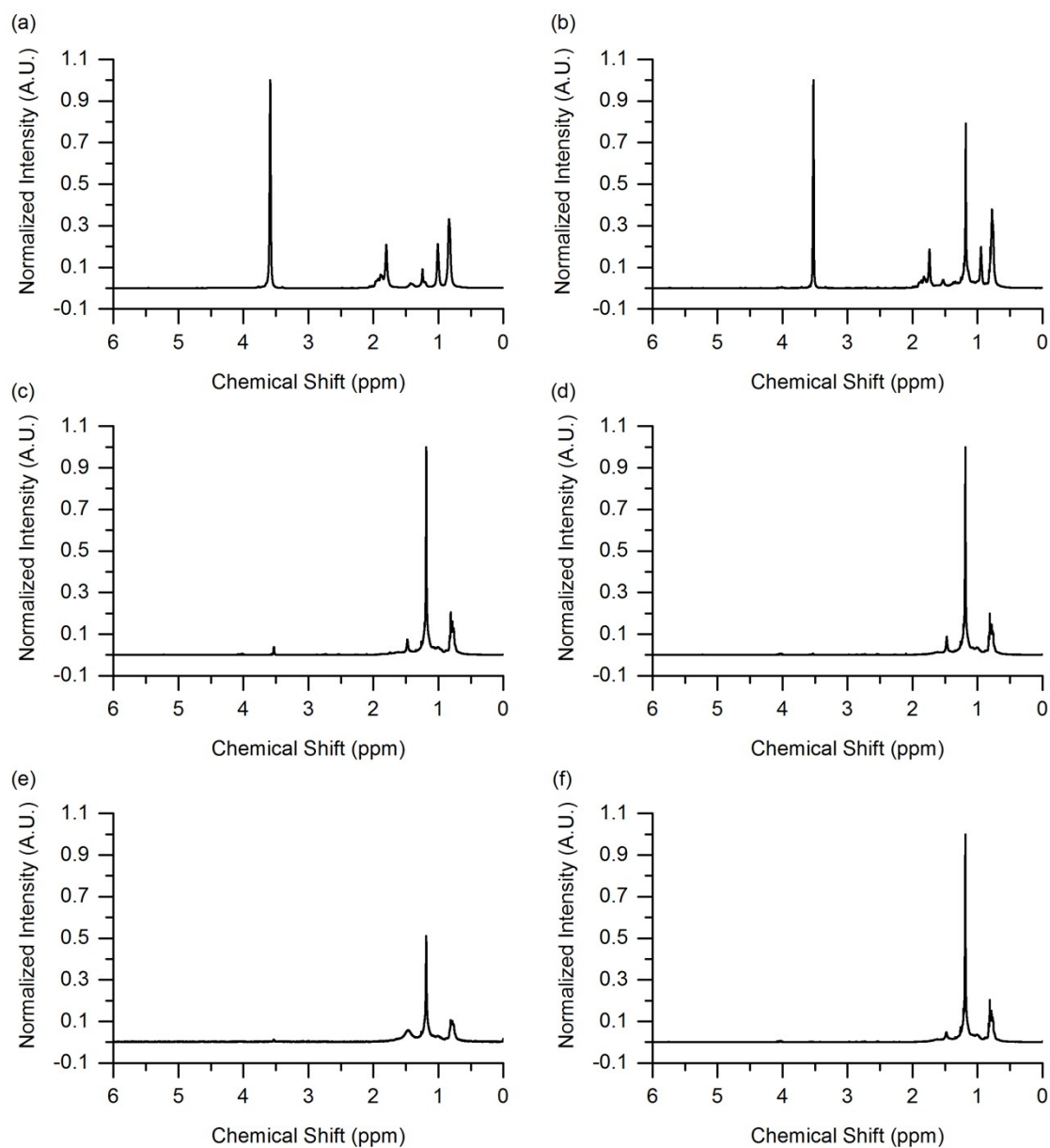
NMR spectra of different surfactant fractions

Figure S3: ^{1}H NMR spectra of different fractions of surfactant. Peaks at lower ppm values are due to plasticisers leached from the Eppendorf vials.

Table S2: Weight of polymer in the surfactant	
Fraction	**Polymer Weight (g)**
1	6.4600
2	0.0250
3	0.0090
4	0.0017
5	0.0012
6	0.0000

FOM analysis of composites
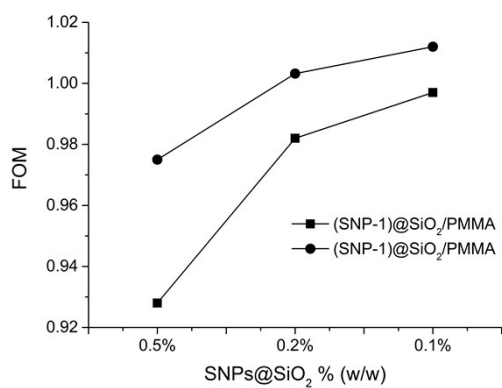
Figure S4: FOM of 0.1 mm films in response to SNP loading.
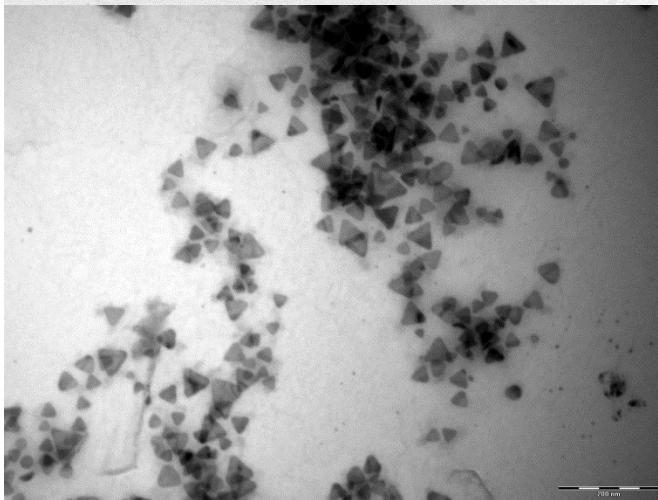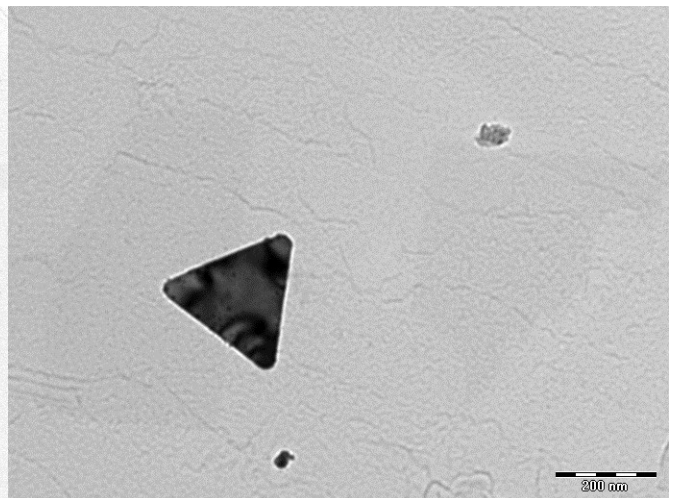
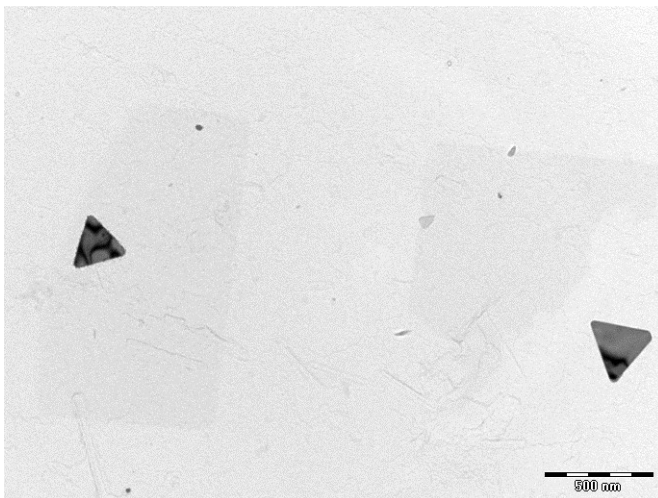**TEM images of SNPs and SNPs@SiO₂**
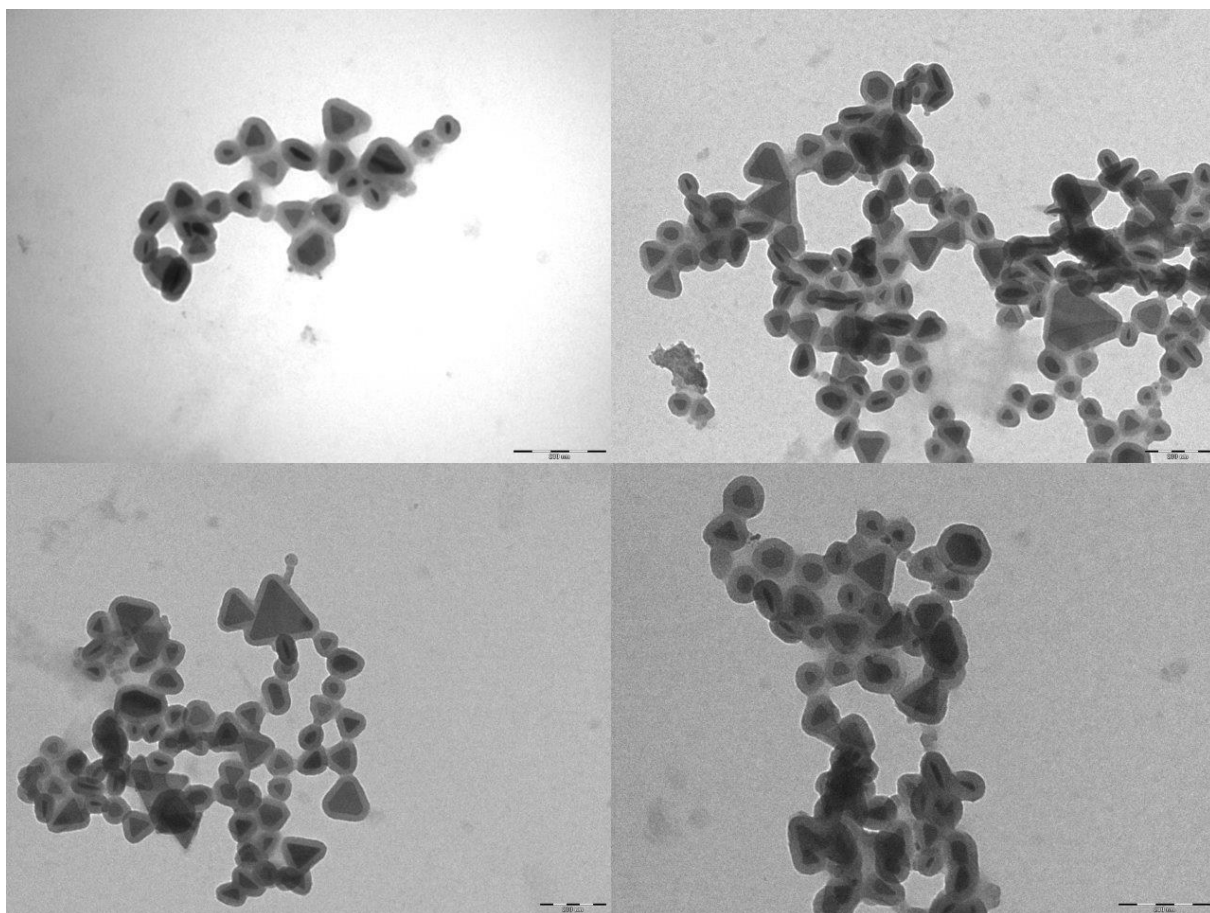
SNP-1
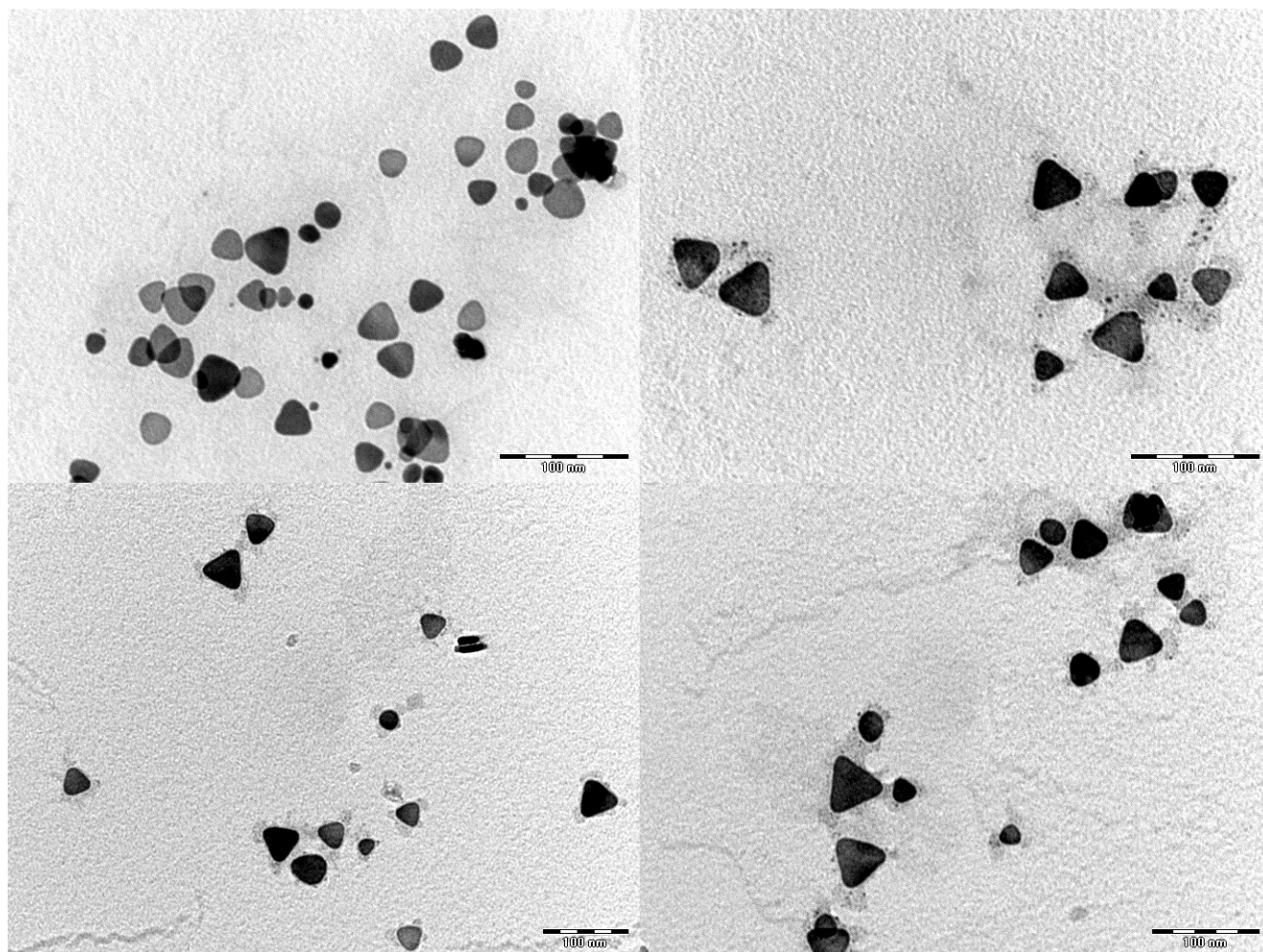
(SNP-1)@SiO₂
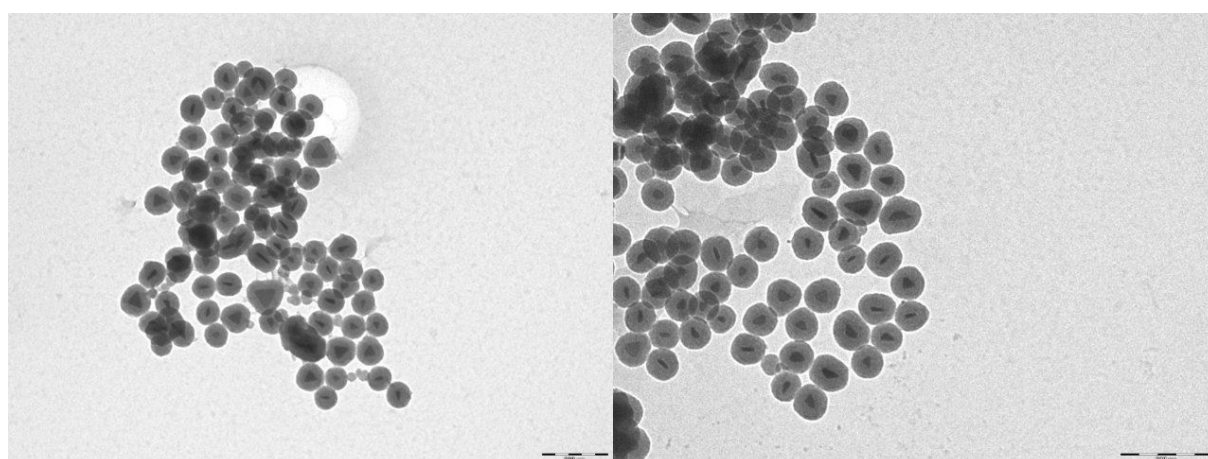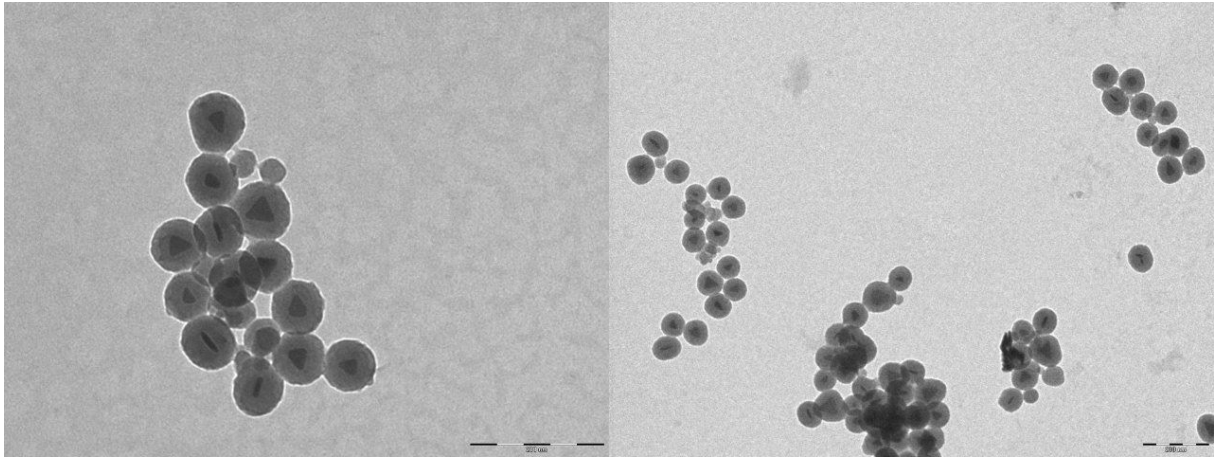
SNP-2
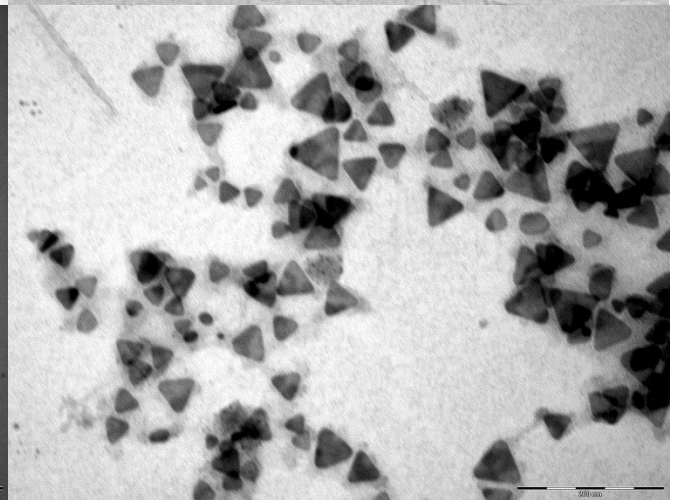
(SNP-2)@SiO$_2$

References
[1]   G. S. Métraux, C. A. Mirkin, *Adv. Mater.* **2005**, *17*, 412-415.
[2]   N. Cathcart, A. J. Frank, V. Kitaev, *Chem. Commun.* **2009**, 7170-7172.
[3]   B.M. Fung, A.K. Khitrin, K. Ermolaev, *J. Magn. Reson. A* **2000**, *142*, 97-101.