Supporting Information

Facile Fabrication of Gold Nanorods@Polystyrenesulphonate Yolk–Shell Nanoparticles for Spaser Applications

Roman G. Parkhomenko¹*, Mato Knez¹,²

1. CIC NanoGUNE, Tolosa Hiriidea 76, E-20018 San Sebastian, Spain.
2. IKERBASQUE, Basque Foundation for Science, Plaza Euskadi 5, E-48009 Bilbao, Spain.

*Corresponding author’s email: r.parkhomenko@nanogune.eu

Experimental Measurements.

UV-Vis spectra were registered by Jasco V-630bio spectrophotometer. Emission spectra were measured using a Jasco FP-6600 spectrofluorometer. FTIR spectra were recorded by a Perkin Elmer Frontier FT-IR spectrometer using a universal sampling for simple IR spectroscopic analysis accessory. X-ray diffraction XRD measurements were performed using a Panalytical X’PertPRO diffractometer with Cu Kα radiation (40 kV, 40 mA). Transmission electron microscopy, EDX mapping images were registered by a Helios NanoLab 450S microscope (FEI, The Netherlands) with a STEM detector at an accelerating voltage of 20 kV and a beam current of 0.2 nA.

Materials.

Cetyltrimethylammonium bromide (CTAB, 98%), 3-aminophenol (98%), hydrogen tetrachloroaurate trihydrate (HAuCl₄·3H₂O, 99.9%), silver nitrate (AgNO₃, 99%), sodium borohydride (NaBH₄, 98%), ammonia solution (35%), tetraethoxy silane (TEOS, 98%), O-[2-(3-Mercaptopropionylamino)ethyl]-O’-methylpolyethylene glycol (PEG-SH, Mw 5000) polystyrene sulphonate sodium salt (PSS, Mw 70000), uranine (98%) were purchased from Sigma-Aldrich. ICG (98%) were purchased from Abrc GmbH. All chemicals were used as received without purification. Deionized water was obtained from a Milli-Q reference system and was used in all experiments.

Synthesis of gold nanorods.

Synthesis of gold seeds. 12.5 μL of 0.05 M HAuCl₄·3H₂O was mixed with 2.35 mL of 0.1 M CTAB solution, at 30 °C. After stirring for 15 min, 0.15 mL of 0.01M NaBH₄ solution (in ice cold water), was quickly added under vigorous stirring. The mixture immediately turned brown. After stirring for 2 min, the solution was kept undisturbed for 30 min before use.

Typical synthesis of gold nanorods. 0.33 mL of 0.015 M HAuCl₄·3H₂O and 0.2 mL of 0.01 M AgNO₃ were mixed with 9 mL of 0.1 M CTAB solution at 30 °C. After stirring for 20 min, 0.8 mL of 0.1 M 3-aminophenol solution was added and stirred for 2 min. The solution turned from yellow to colorless. Subsequently, 62.5 μL of gold seed solution was injected and stirred for 2 min. The mixture was left undisturbed for 12 hours.
Synthesis of gold nanorods@mSiO₂.

10 ml of the synthesized nanorods were centrifuged (4400 rpm 30 min) to a CTAB concentration of 0.8 mM. Afterwards, 60 μL of 0.1M NaOH and 50 μL of TEOS solution (20% in methanol) were added to the gold nanorods suspension and mixed for 24 hours at room temperature.

Synthesis of gold nanorods@PSS.

Stage 1. To 10 ml of the suspension of gold nanorods@SiO₂ 35 μL of PSS (5 mg/ml, water solution) was added. The suspension was mixed for 8 hours at room temperature and then was centrifuged once (4400 rpm 30 min) discarding all the supernatant. The tube was filled with 10 ml of water and left undisturbed at room temperature for 48 hours.

Stage 2. Subsequently 120 μL of PSS (5 mg/ml, water solution) was added, and the suspension was very gently mixed for 8 hours. The final product was purified by centrifugation (4400 rpm 30 min) and washed three times with water.

Uranine and ICG loading.

After stage 1 (see above), water solutions of uranine and ICG (0.1 mL, 10⁻⁴ M) were added to the suspension of the gold nanorods@PSS particles and very gently mixed overnight. Then 120 μL of PSS (5 mg/ml, water solution) was added, and the suspension was very gently mixed for another 8 hours. The dye-loaded particles were purified by centrifugation and washed three times with water. The loading capacity of uranine and ICG in the gold nanorods@PSS particles was measured by a UV-Vis spectrophotometer and calculated using the following formula:

$$LC = \frac{(Abs_{\text{initial dye}} - Abs_{\text{residual dye}})}{Abs_{\text{initial dye}}} \times 100\%$$

Synthesis of gold nanorods@dense SiO₂.

To 10 ml of the suspension of gold nanorods (CTAB concentration 0.8 mM) 1 mL of PEG-SH solution in water (10 mg/mL) was added. The mixture was stirred for 12 hours followed by centrifugation (4400 rpm 30 min) and addition of 3.75 mL of ethanol and 1.25 mL of water. To this suspension 65 μL of ammonia solution (35%) and 3 μL of TEOS were added. The mixture was stirred for 12 hours with subsequent centrifugation (4400 rpm 30 min) and washing three times with water. The procedure of the mesoporous silica shell growth and the following steps are identical to those described above.
Fig. S1. TEM images of GNR@mSiO2@PSS particles after 48 hours of hydrolysis
Fig. S2. Low-magnification TEM image of GNR@PSS yolk-shell particles.
Fig. S3. EDX data of GNR@PSS yolk-shell particles. The relative element ratio is difficult to estimate due to a large amount of copper and carbon from the TEM grid.

Fig. S4. Zeta potential of GNR@PSS yolk-shell particles.
Fig. S5. XRD pattern of GNR@PSS yolk-shell particles.

Fig. S6. TEM image of GNR@SiO₂ particles.