Supporting Information

Tailoring core size, shell thickness, and aluminium doping of Au@ZnO core@shell nanoparticles

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1. Synthesis of Au@ZnO core@shell NPs

1.1. X-Ray Diffraction Measurement

The XRD analysis was carried out using a Brucker D8, equipped with a Cu K α radiation source (λ = 1.5406 Å). The samples were prepared by depositing a layer of the Au@ZnO NPs (43 nm core and 47 nm shell thickness) onto silicon wafers. The wafers were then mounted on a standard flat sample holder. Data were collected over a 20 range from 30° to 70° at a scan rate of 0.02° per second. Figure SI.1 shows a background corrected X-ray diffractogram from a Au@ZnO core@shell sample. ZnO has a hexagonal wurtzite crystal structure. The primary diffraction peaks for ZnO are found at 31.77°, 34.42°, 36.25°, 47.54°, 56.60°, 62.86° and 68.0°. Gold has a facecentred cubic crystal structure with primary diffraction peaks at 38.18° and 44.39°.^{1,2} The peak widths corrected by the instrumental broadening indicate an average crystallite size for ZnO of ~50 nm, which is comparable to the shell thickness.



Figure SI.1 Background corrected X-Ray Diffractogram of Au@ZnO powder on Si-wafer.

1.2. Calculations of Nanoparticle concentration

We calculate the nanoparticle density using the Beer Lambert relation:

$$NP \ density\left[\frac{NP}{m^3}\right] = \frac{\ln (10) \times OD}{\sigma_{ext} \left[m^2/NP\right] \times l \left[m\right]}$$

where OD is the optical density of the NP suspension at the LSPR wavelength, I is the optical path length, and $^{\sigma}_{ext}$ is the extinction cross section of the nanoparticle at the LSPR wavelength, calculated with Mie theory using literature values of the gold dielectric function.³

1.3. Calculation of maximum theoretical yield of ZnO shell

Volume of a single AuNP core

$$V = \frac{4}{3}\pi r^3$$

 $r_{Au} = 21.5 \ nm = 2.13 \times 10^{-8} \ m$

 $r_{Au@ZnO} = r$

Volume of the ZnO Shell of a single core@shell NP

 $V_{Zn0} = \frac{4}{3}\pi(r^3 - r_{Au}^3)$

Total ZnO Volume per synthesis:

$$N_{Au\,NPs} \times \frac{4}{3}\pi (r^3 - r_{Au}^3)$$

Mass of ZnO Shell

$$[Zn^{2+}] = 2.75 \text{ mmol} / l = 2.75 \times 10^{-3} \text{ mol} / l$$
$$n_{Zn^{2+}} = 2.75 \times 10^{-6} \text{ mol}$$

The stoichiometry is suggesting that each mole of Zn²⁺ yields one mole of ZnO

$$Zn(NO_3)_2 \rightarrow ZnO + 2NO_2 + 1/2O_2$$

$$n_{Zn0} = 1 \times 2.75 \times 10^{-6} mol$$

ZnO has a molar mass of 81.38 g/mol and a density of 5.6 g/cm³. Therefore the molar density M/ρ is

$$^{M}/_{\rho} = 14.5^{cm^{3}}/_{mol} = 1.45 \times 10^{-5} \, m^{3}/_{mol} = 1.45 \times 10^{-22} \, nm^{3}/_{mol}$$

Total Mass of ZnO shell per synthesis

$$2.75 \times 10^{-6} \frac{mol}{ml} \times 1.45 \times 10^{-22} \frac{nm^3}{mol} = 3.99 \times 10^{16} \frac{nm^3}{mol}$$

Furthermore, we calculate the maximum theoretical yield of product of our Au@ZnO NP synthesis.

Calculation of number of moles of zinc nitrate

The number of moles n is calculated using the formula

 $n = c \times V$

in which he concentration of Zinc Nitrate $(Zn(NO_3)_2)^c$ is 0.275 mM in a volume of 20 ml.

 $n = 2.75 \times 10^{-3} \text{ mol}/l \times 2 \times 10^{-2} l = 5.5 \times 10^{-5} \text{ mol}$

Conversion to mass of zinc nitrate

The molar mass M of Zinc Nitrate (Zn(NO₃)₂) is 189.36 g/mol. The mass m of the zinc nitrate used can be calculated as:

 $m = n \times M = 5.5 \times 10^{-5} mol \times 189.36 \frac{g}{mol} = 0.00104 g$

Calculation of ZnO yield from zinc nitrate:

Assuming complete conversion of zinc nitrate to zinc oxide, the stoichiometry suggests that each mole of zinc nitrate yields one mole of ZnO. Thus, the theoretical yield of ZnO based on the moles of zinc nitrate used is:

 $n \times M_{Zn0} = 5.5 \times 10^{-5} mol \times 81.38 \frac{g}{mol} = 0.0048 g$

Calculation of volume and mass of gold nanoparticles:

The concentration of gold nanoparticles is given as 3.155×10¹⁰ NPs/ml with each nanoparticle having a radius of 21.5 nm. The volume of the solution containing Au NPs is 1 ml. Therefore, the total number of Au NPs in the solution is:

 $Total \, Au \, NPs = 3.155 \times 10^{10} \, \frac{NPs}{ml} \times 1 \, ml = 3.155 \times 10^{10} \, NPs$

To calculate the volume of each nanoparticle, use the volume formula for a sphere $V = \frac{4}{3}\pi r^3$ where *r* is the radius of a nanoparticle. Thus, the volume of 3.155×10^{10} nanoparticles is:

$$V = \frac{4}{3}\pi (21.5 \times 10^7 \, cm)^3 \times 3.115 \times 10^{10} \approx 1.313 \times 10^{-7} \, cm^3$$

The density of gold is 19.32 g/cm³, so the mass of gold in the nanoparticles is:

 $m_{Au} = V_{total} \times \rho_{Au} = 1.313 \times 10^{-7} cm^3 \times 19.32 \frac{g}{cm^3} = 0.00253 g$

The total theoretical yield of the Au@ZnO synthesis

The total theoretical yield of the Au@ZnO synthesis would therefore be:

 $m_{Au@ZnO} = 0.00253 \; g + \; 0.0048 \; g = 0.00773 \; g = 7.33 \; mg$

2. Extinction spectra of Au@ZnO with different core sizes

We synthesised Au@ZnO core@shell nanostructures using Au nanospheres with different diameters. The LSPR of AuNPs shifts towards higher wavelengths with increasing size^{4,5}, which can be seen in the extinction spectra of the reaction solutions prior to hydrothermal synthesis in Figure SI.2a, corresponding to the nanoparticles in Figure 4 in the main text. This Figure also shows extinction of a reaction solution of AuNR@ZnO, which has two peaks attributed to the transversal and longitudinal LSPR of the nanorods prior to hydrothermal synthesis. Both peaks shift towards higher wavelengths when covered with a Zn(OH)₂ shell post hydrothermal synthesis (Figure SI.2b).



Figure SI.2 a) Normalised extinction spectra of reaction solutions prior to hydrothermal synthesis with 25 nm Au nanospheres (black), 43 nm Au nanospheres (red), 69 nm Au nanospheres (blue) and 54 × 118 nm Au nanorods (orange). b) Normalized extinction spectra of the reaction solution of AuNR@ZnO before5 (orange) and after hydrothermal synthesis (blue).

3. Aluminium doping of Au@ZnO core@shell nanoparticles

3.1. In situ addition of acidic Aluminium nitrate

In several attempts to synthesize Au@AZO core@shell nanoparticles, aluminium nitrate was added as a dopant directly to the reactant mixture prior to hydrothermal processing. However, this approach resulted in unsuccessful synthesis outcomes. The acidic nature of the aluminium nitrate solution significantly lowered the pH affecting the formation of the core@shell structures. As shown in Figure SI.3, the core@shell structure progressively deteriorates with increasing concentrations of the dopant.



Figure SI.3 Secondary electron SEM images of Au@AZO from 0-4 at.% Al. All scalebars are 500 nm.

3.2. In situ addition of pH-neutralized Aluminium nitrate

Upon recognizing the critical impact of the pH level of the dopant solution on the overall hydrothermal synthesis, a modified approach was developed in which the dopant solution was neutralized to a pH of 6.5 using ammonium hydroxide solution and added in situ among with the other reactants prior to hydrothermal heating. Despite the formation of Au@AZO core@shell nanoparticles, a notable decrease in particle size

was observed with increasing concentrations of the dopant. This trend is illustrated in Supplementary Figure SI.4.



Figure SI.4 Secondary electron SEM images of Au@AZO 0-4 at.% Al. Dopant concentration had been neutralised prior to in situ addition to the hydrothermal synthesis reaction. All scalebars are 500 nm.

3.3. Comparison of redispersion in acidic and pH neutralized Aluminium nitrate

Initial attempts were made by synthesising the spherical Au@Zn(OH)₂ nanoparticles via hydrothermal synthesis without any addition of dopant in the first step. Subsequently these particles had been exposed to the dopant solution in a post-synthesis redispersion step. It was observed that the acidic nature of the dopant solution adversely affected the Zn(OH)₂ shell, which is known to be stable under neutral to alkaline conditions.^{6,7}

Although core@shell structures were still obtained, the post-redispersion step involving an acidic dopant solution resulted in compromised particle morphology and uniformity as seen in Figure SI.5a. These characteristics are significantly degraded compared to those observed when using a pH-neutral dopant solution during the redispersion step (Figure SI.5b).



Figure SI.5 Secondary electron (top) and backscattered electron (bottom) SEM images of Au@AZO NPs with 2 at.% Al doping, synthesized through a redispersion step with a) a non-neutralized and b) pH-neutral aluminium nitrate solution. All scalebars are 500 nm.

3.4. Effect of remaining surfactant in washing step

We studied the effects of residual CTAB concentration that remains after removing the supernatant in the centrifugation and washing step. All samples were initially synthesized under the identical reaction conditions and reactant concentrations. After hydrothermal synthesis, each product was redispersed in a CTAB solution with concentration ranging from 0 - 0.825 mM and annealed. The samples were characterized using SEM imaging. Our results demonstrate that the presence of residual surfactant significantly influences and disrupts the formation of core@shell structures with increased residual CTAB levels.



Figure SI.6 Secondary electron SEM images of Au@ZnO NPs obtained from syntheses in which, after the hydrothermal treatment, the Au@Zn(OH)₂ NPs were redispersed in CTAB solutions with concentrations ranging from 0 to 0.825 mM. All scalebars are 500 nm.

4. References

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