

Calculation:

1. Concentrations of CNPs:

The molarity of pure phase cerium oxide (CeO_2 ; molecular weight 172.11 g/mol) in 1 g/L was calculated as,

$$1 \frac{\text{g}}{\text{L}} \div 172.11 \frac{\text{g}}{\text{mol}} = 5.8 \times 10^{-3} \frac{\text{moles}}{\text{L}} = 5.8 \text{ mM}$$

From this concentration, dilutions were made for larval and adult experiments.

Larval experiment:

0.01 mM CNPs was used in larval experiments; the volume of stock CNP solution required to produce 40 mL (experimental volume):

$$(0.01 \text{ mM} \times 40 \text{ mL}) \div 5.8 \text{ mM} = 0.069 \text{ mL}$$

Adult experiment:

1 mM, 0.5 mM and 0.1 mM CNPs was used for adult experiments. Dilutions from stock concentration for these experiments were prepared as such:

a. 1mM CNPs

$$(1 \text{ mM} \times 1 \text{ mL}) \div 5.8 \text{ mM} = 0.172 \text{ mL}$$

Thus 0.172 mL of 5.8 mM CNPs was added to 0.828 mL water to make 1 mM solution

b. 0.5 mM CNPs

$$(0.5 \text{ mM} \times 1 \text{ mL}) \div 5.8 \text{ mM} = 0.086 \text{ mL}$$

Thus 0.086 mL of 5.8 mM CNPs was added to 0.914 mL water to make 0.5 mM solution

c. 0.1 mM CNPs

$$(0.1 \text{ mM} \times 1 \text{ mL}) \div 5.8 \text{ mM} = 0.0172 \text{ mL}$$

Thus 0.0172 mL of 5.8 mM CNPs was added to 0.9828 mL water to make 0.1 mM solution

2. Concentrations of AgNO_3 :

Larval experiment:

Firstly, a stock solution of 1 mM AgNO_3 was produced as:

$$169.87 \frac{\text{g}}{\text{mol}} \times 0.001 \frac{\text{mol}}{\text{L}} \times 1 \text{ mL} = 0.170 \text{ g (AgNO}_3\text{) |}$$

0.025 mM AgNO_3 was used in larval experiments and produced by dilution from stock:

$$(0.025 \text{ mM} \times 40 \text{ mL}) \div 1 \text{ mM} = 1 \text{ mL}$$

1 mL of 1 mM AgNO_3 was added to 39 mL water to make 0.025 mM AgNO_3 ,

Calculating mg/L (ppm) of silver in 0.025 mM AgNO₃:

Molecular weight of AgNO₃ is 169.87 g/mol; so 1 mM AgNO₃ has 169.87 μg/mL of AgNO₃

$$0.025 \times 10^{-3} \frac{\text{mol AgNO}_3}{\text{L}} \times \frac{1 \text{ mol Ag}}{1 \text{ mol AgNO}_3} \times 169.87 \frac{\text{g Ag}}{\text{mol Ag}} = 4.24 \frac{\text{mg}}{\text{L}} \text{ or ppm}$$

The atomic weight of Ag is 107.87 g/mol; so 1 mM has 107.87 μg/mL

$$0.025 \times 10^{-3} \frac{\text{mol AgNO}_3}{\text{L}} \times \frac{1 \text{ mol Ag}}{1 \text{ mol AgNO}_3} \times 107.87 \frac{\text{g Ag}}{\text{mol Ag}} = 2.697 \frac{\text{mg}}{\text{L}} \text{ or ppm}$$

Adult experiment:

a. 0.025 mM AgNO₃

$$(0.025 \text{ mM} \times 1 \text{ mL}) \div 1 \text{ mM} = 0.025 \text{ mL}$$

0.025 mL of 1 mM AgNO₃ was added to 0.975 mL blood or sugar solution to make 0.025 mM AgNO₃,

Per the above calculation, 0.025 mM equates to 4.24 ppm of AgNO₃ or 2.697 ppm Ag

b. 0.050 mM AgNO₃

$$(0.050 \text{ mM} \times 1 \text{ mL}) \div 1 \text{ mM} = 0.050 \text{ mL}$$

0.050 mL of 1 mM AgNO₃ was added to 0.950 mL blood or sugar solution to make 0.050 mM AgNO₃,

Calculating mg/L (ppm) of silver in 0.050 mM AgNO₃ leads to twice the concentration calculated for 0.025 mM (8.48 ppm AgNO₃ or 5.394 ppm Ag).

3. Calculation of amount of Ag in doped nanoparticles:

XPS showed that 0.72 atomic percent (at%) of Ag is incorporated in AgCNPs (per Avantage software). The ratio of Ce³⁺ to Ce⁴⁺ redox states in each formulation was determined analytically. First, a baseline correction was fit to the data using a *smart* baseline function (Avantage). Next, peaks were fit using curves constrained by state-specific properties (e.g. separation between multiplet spin states, relative peak heights for associated peaks split due to spin-orbit coupling). Fitting was optimized by least squares regression (Avantage) and the peaks associated with Ce³⁺ and Ce⁴⁺ were integrated numerically. Sum peak contributions for each state were then normalized as,

$$[Ce^{3+}] = \frac{\sum Ce^{3+}}{\sum Ce^{3+} + \sum Ce^{4+}} = \frac{\sum(v_0 + v' + u_0 + u')}{\sum[(v_0 + v' + u_0 + u') + (v + v'' + v''' + u + u'' + u''')]}]$$

Where ‘v’ peaks are related to emissions from the Ce3d5/2 and ‘u’ peaks to Ce3d3/2 multiplets respectively, per literature convention, along with associated satellite peaks (arising from complex, final state emissions). The average Ce³⁺/Ce⁴⁺ ratio for the silver-modified ceria formulation was determined as 37.4%. Atomic percent silver (produced using Avantage analysis software, with respect to spectral contributions from O, Ag, and Ce) and relative Ce³⁺ content were subsequently used in describing the silver content per mass of nanomaterial.

We consider cerium and oxygen percentages as arising from proportions of the oxide in each redox state in fixed molar ratios, weighted by the fraction of each cerium redox state. Mass percents of silver were thereby calculated from the molarities of total atom proportions:

$$0.72 \text{ at\% Ag} \rightarrow 99.28\% \sum (Ce\% + O\%)$$

Given the percent of cerium and oxygen represents contributions from (37.4%) Ce₂O₃ and (62.6%) CeO₂ stoichiometries,

$$\frac{0.72}{0.626(33.09 + 66.18) + 0.374(39.712 + 59.568) + 0.72} = \frac{0.72 \text{ atoms of Ag}}{100 \text{ atoms of 'NP'}}$$

Converting atomic masses of Ag {107.87}, Ce {140.0}, and O {16.0 g/mol} allows conversion of atomic to mass ratio as:

$$\frac{0.72\{107.87\}}{0.626(33.09\{140.0\} + 66.18\{16.0\}) + 0.374(39.712\{140.0\} + 59.568\{16\}) + 0.72\{107.87\}} = \frac{0.0128 \text{ g Ag}}{100 \text{ g 'NP'}}$$

Lastly, using the stock concentration of nanoparticles and the experimental dilution factor (5.8 mM → 0.01 mM: 1.72x10⁻³) noted in section 1:

$$\frac{1 \text{ g 'NP'}}{1 \text{ L}} \times 1.72 \times 10^{-3} \times \frac{0.0128 \text{ g Ag}}{100 \text{ g 'NP'}} = \frac{2.2 \times 10^{-7} \text{ g}}{\text{L}} = \frac{0.22 \mu\text{g}}{\text{L}} = 0.22 \text{ ppb Ag}$$