Model Answers

Question 1 - solution

*a* = lattice constant

*r* = radius of gold atom = 0.1442 nm

\[
(4r)^2 = a^2 + a^2 \iff 16r^2 = 2a^2 \iff 8r^2 = a^2 \iff a = \sqrt{8}r
\]

\[
r \approx 0.1442 \text{ nm}
\]

\[
a = \sqrt{8}r = \sqrt{8} \times 0.1442 \approx 0.4079 \text{ nm}
\]

Question 2 – solution

The shell thickness is half of the lattice parameter, and 0.2039 nm.

The total volume of the nanoparticle of radius *R* is:

\[
V_{\text{total}} = \frac{4}{3} \pi R^3
\]
The volume of the core after accounting for the finite shell thickness is:

\[ V_{\text{core}} = \frac{4}{3} \pi (R - 0.2039)^3 \]

The volume of the shell is the difference between the total volume and the volume of the core, \textit{i.e.:}

\[ V_{\text{shell}} = V_{\text{total}} - V_{\text{core}} = \frac{4}{3} \pi R^3 - \frac{4}{3} \pi (R - 0.2039)^3 \]

Now since the lattice constant of the Au unit cell is 0.4079 nm the volume of a single unit cell is:

\[ V_{\text{unit}} = 0.4079R^3 \]

The number of unit cells making up the shell can be calculated from:

\[ \text{Unit cells}_{\text{shell}} = \frac{V_{\text{shell}}}{V_{\text{unit}}} \]

Since the number of atoms per unit cell is 4, the total number of surface atoms is:

\[ \text{Atoms}_{\text{surface}} = 4 \times \text{Unit cells}_{\text{shell}} \]

To calculate the total number of atoms in the entire particle, first it is necessary to find the total number of unit cells.

\[ \text{Unit cells}_{\text{total}} = \frac{V_{\text{total}}}{V_{\text{unit}}} \]

The number of atoms per unit cell is 4 giving the total number of atoms in the particle:

\[ \text{Atoms}_{\text{total}} = 4 \times \text{Unit cells}_{\text{total}} \]

Thus, the fraction of surface atoms is:

\[ f = \frac{\text{Atoms}_{\text{surface}}}{\text{Atoms}_{\text{total}}} \]

For a 10 nm gold nanoparticle:

\[ V_{\text{total}} = \frac{4}{3} \pi R^3 = \frac{4}{3} \pi (5)^3 \approx 523.6 \text{ nm}^3 \]
\[ V_{\text{core}} = \frac{4}{3} \pi (5 - 0.2039)^3 \approx 462.1 \text{ nm}^3 \]

\[ V_{\text{shell}} = V_{\text{total}} - V_{\text{core}} = 523.6 - 462.1 = 61.5 \text{ nm}^3 \]

\[ V_{\text{unit}} = 0.4079^3 \approx 0.068 \text{ nm}^3 \]

\[ \text{Unit cells}_{\text{shell}} = \frac{V_{\text{shell}}}{V_{\text{unit}}} = \frac{61.5}{0.068} \approx 904 \]

\[ \text{Atoms}_{\text{surface}} = 4 \times \text{Unit cells}_{\text{shell}} = 4 \times 904 = 3616 \]

\[ \text{Unit cells}_{\text{total}} = \frac{V_{\text{total}}}{V_{\text{unit}}} = \frac{523.6}{0.068} = 7700 \]

\[ \text{Atoms}_{\text{total}} = 4 \times \text{Unit cells}_{\text{total}} = 4 \times 7700 = 30800 \]

\[ f = \frac{\text{Atoms}_{\text{surface}}}{\text{Atoms}_{\text{total}}} = \frac{3616}{30800} \approx 0.12 \]

For a 2 nm gold nanoparticle:

\[ V_{\text{total}} = \frac{4}{3} \pi R^3 = \frac{4}{3} \pi (1)^3 \approx 4.2 \text{ nm}^3 \]

\[ V_{\text{core}} = \frac{4}{3} \pi (1 - 0.2039)^3 \approx 2.1 \text{ nm}^3 \]

\[ V_{\text{shell}} = V_{\text{total}} - V_{\text{core}} = 4.2 - 2.1 = 2.1 \text{ nm}^3 \]
\[ V_{\text{unit}} = 0.4079^3 \approx 0.068 \text{ nm}^3 \]

\[ \text{Unit cells}_{\text{sheet}} = \frac{V_{\text{sheet}}}{V_{\text{unit}}} = \frac{2.1}{0.068} \approx 31 \]

\[ \text{Atoms}_{\text{surface}} = 4 \times \text{Unit cells}_{\text{sheet}} = 4 \times 31 = 124 \]

\[ \text{Unit cells}_{\text{total}} = \frac{V_{\text{total}}}{V_{\text{unit}}} = \frac{4.2}{0.068} = 62 \]

\[ \text{Atoms}_{\text{total}} = 4 \times \text{Unit cells}_{\text{total}} = 4 \times 62 = 248 \]

\[ f = \frac{\text{Atoms}_{\text{surface}}}{\text{Atoms}_{\text{total}}} = \frac{124}{248} \approx 0.50 \]

**Question 3 – solution**

The surface area of a 15 nm gold nanoparticle is:

\[ S_{\text{sphere}} = S_{15 \text{ nm nanosphere}} = 4\pi R^2 = 4\pi(7.5)^2 \approx 706.9 \text{ nm}^2 \]

Thus, the number of PEG-SH molecules necessary to create a monolayer in a 15 nm gold nanosphere, \( N_{\text{SH 15 nm nanosphere}} \), is given by:

\[ N_{\text{SH 15 nm nanosphere}} = \frac{S_{15 \text{ nm nanosphere}}}{\text{Footprint}_{\text{PEG-SH}}} = \frac{706.9}{0.35} = 2020 \]

The surface area of a 45×15 nm gold nanorod is:
\[ S_{45 \times 15 \text{ nm gold nanorod}} = S_{\text{lateral of cylinder}} + S_{\text{sphere}} = 2\pi R h + 4\pi R^2 \]
\[ = 2\pi \times 7.5 \times (45 - 15) + 4\pi (7.5)^2 \approx 2120.6 \text{ nm}^2 \]

Thus, the number of PEG-SH molecules necessary to create a monolayer in a 45×15 nm gold nanorod, \( N_{\text{SH 45×15 nm nanorod}} \), is given by:

\[ N_{\text{SH 45×15 nm gold nanorod}} = \frac{S_{45 \times 15 \text{ nm gold nanorod}}}{\text{Footprint}_{\text{PEG-SH}}} = \frac{2120.6}{0.35} = 6059 \]