

# Exercises NMN 2223

## Metal Nanoparticles

1. Why are noble metals preferable to other transition metals in the exploitation of localized surface plasmon resonance effect in nanoparticles?

2. Describe the size effect on the extinction coefficient ( $\sigma_{\text{ext}}$ ) in the visible part of the electromagnetic spectrum of small gold particles (radii 10- 50 nm) making a reference to the scattering and absorption relative intensities.

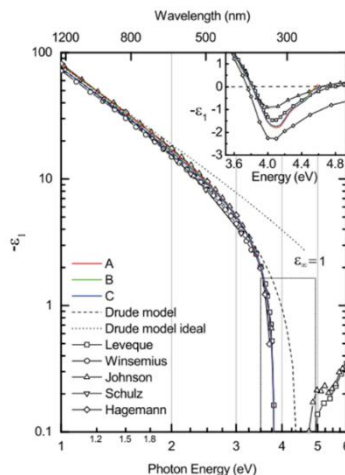


FIG. 1. (Color online) Negative real part of the dielectric function of silver  $-\epsilon_1$  in the visible/ultraviolet spectral range for three different samples A (red), B (green), and C (blue). Data from Leveque *et al.* [47] (squares), Winsemius *et al.* [42] (circles), Johnson and Christy [28] (triangle), Schultz [44,45] (inverted triangle), and Hagemann *et al.* [46] (diamond) are shown for comparison. Drude fit for sample C with  $\hbar\omega_p = 8.9$  eV,  $\tau = 18$  fs, and  $\epsilon_\infty = 5$  (dashed) or  $\epsilon_\infty = 1$  (dotted line). Inset: Data near 3.8 eV shown in linear scale, where  $-\epsilon_1(\omega)$  transitions from positive to negative values due to the interband transition.

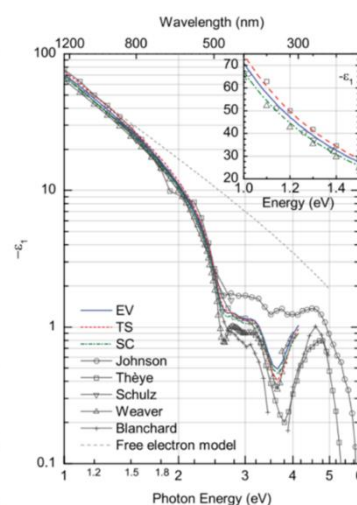


FIG. 2. (Color online) Dielectric function of Au (negative real part  $-\epsilon_1$ ) in the visible spectral region for our evaporated (EV), template-stripped (TS), and single-crystal (SC) gold samples. For comparison, data from Johnson and Christy (Johnson), Thye,<sup>4</sup> Schultz,<sup>20,21</sup> Weaver *et al.*,<sup>16</sup> and Blanchard *et al.*<sup>8</sup> are shown, as well as the dielectric function calculated for a Drude free-electron metal with  $\hbar\omega_p = 8.5$  eV and  $\tau_D = 14$  fs. Solid lines are guides for the eye. Inset: Linear scale plot of  $-\epsilon_1$  for 1.0-1.6 eV photon energy.

3. Explain how can we detect single-molecules using metal nanoparticles?

4. Considering the real part of the permittivity function of gold and silver ( $\epsilon_1$ ) shown in figure 1, at which wavelength can we expect to find the maximum extinction coefficient (resonance conditions) for 10 nm silver and 20 nm gold nanoparticles in water? Assume that the permittivity function of water is constant in the 200-1200 nm range and equal to 1.77.

**ANSWER:** The maximum extinction coefficient is expected at 3 eV (413 nm) and 2.3 eV (539 nm) for silver and gold, respectively.

5. Gold nanorods (AuNR) with larger aspect ratios are more efficient in converting absorbed radiation into heat (J. Phys. Chem. B 2014, 118, 1319). Represent the extinction coefficient of two AuNRs with different aspect ratios and explain the main features of the spectra and the differences between them. Why do high aspect ratio AuNRs generally show better performance in photodynamic therapy applications?

## Semiconductor Nanocrystals

1. If we prepare nanoparticles of GaAs, ZnS and CdSe with radius varying between 1-5 nm, which of the materials would exhibit stronger quantum confinement effect in such diameter range? Use the data in table 2 in your calculations.

**ANSWER:** The quantum confinement is determined by the radius of the Bohr exciton. The Bohr exciton radius is 12.2 nm (GaAs), 3.43 nm (ZnS) and 5.35 nm (CdSe). The material that exhibits a stronger confinement effect will be GaAs because it has a larger Bohr exciton radius.

2. Which one of the materials above would you choose to prepare 5 nm particle for imaging in thick biological tissue, assuming they will all have similar emission efficiencies?

**ANSWER:** For imaging in thick biological tissue quantum dots with emission in the red or NIR are recommended due to a deeper penetration depth in the tissue. The calculated energy gaps are  $E_g^{GaAs} = 750 \text{ nm}$ ,  $E_g^{ZnS} = 332 \text{ nm}$  and  $E_g^{CdSe} = 690 \text{ nm}$ . Based on the wavelength alone, I would recommend GaAs that absorb at longer wavelength.

3. Estimate the radius of CdSe quantum dots emitting at 600 nm.

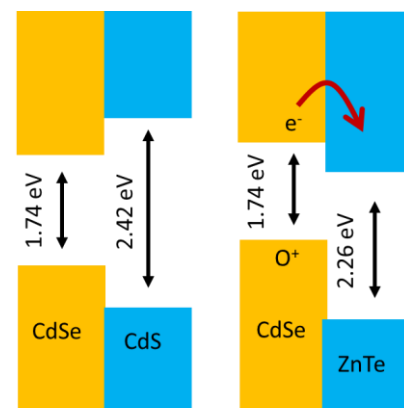
**ANSWER:** From 
$$E_g^{QD} = E_g^B + \frac{\hbar^2 \pi^2}{2R^2} \left( \frac{1}{m_e^*} + \frac{1}{m_h^*} \right) - \frac{1.8e^2}{\epsilon R} \quad \epsilon = 4\pi\epsilon_0\epsilon_r$$
  
 $R = 3.21 \text{ nm}$

4. What is the main difference between type I and type II core-shell semiconductor nanocrystals represented in figure 3? Which one of the core-shell systems has the lowest energy gap?

5. Describe two distinct processes for the preparation of semiconductor nanoparticles, one top down and one bottom up process.

6. How can semiconductor quantum dots be used to increase the efficiency of photovoltaic cells?

7. What are the strong points driving the application of quantum dots in nanomedicine and the main limitations hindering their translation from lab to market?



**Type I** **Type II**  
 FIG. 3. Illustration of the band gap structure of prototypical core-shell semiconductor quantum dots of Type I and Type II .

8. The figure below show the emission wavelength of CdTe QDs as a function of reaction time and size of the alkyl chain of the ligand.

How do these two reaction parameters affect the size of the QDs?

**ANSWER:** Reaction time increases fluorescence emission wavelength that corresponds to a decrease of the energy gap  $E_g = hc/\lambda$  which in turn is associated with an increase in size based on equation:

$$E_g^{QD} = E_g^B + \frac{\hbar^2 \pi^2}{2R^2} \left( \frac{1}{m_e^*} + \frac{1}{m_h^*} \right) - \frac{1.8e^2}{\epsilon R} \quad \epsilon = 4\pi\epsilon_0\epsilon_r$$

An increase in the alkyl chain length has the opposite effect, it reduces the emission wavelength, thus the energy gap increases, and the size is reduced. Bulky ligands and ligands with a long alkyl chain slow down particle growth.

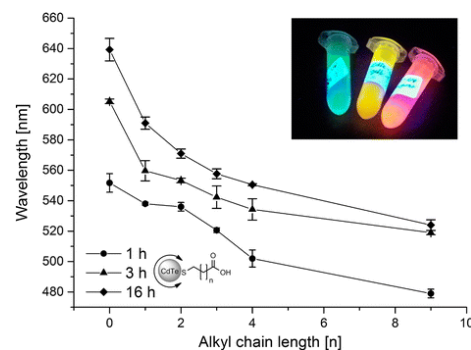


FIG 4 . Comparison of the fluorescence emission maxima of the synthesized mercaptocarboxylic acid-coordinated QDs after a reaction time of 1, 3, and 16 h. Photography of a section of QDs synthesized in this project under the UV lamp (*inset*;  $\lambda_{ex} = 366$  nm) [ligands: MUDA (n=9, green), MHA (n=4, yellow), MPA (n=1, orange)] (color figure online)

<https://link.springer.com/article/10.1007/s11051-017-3757-2>

**Table 2:** Hole and electron effective mass ( $m^*$ ), bulk energy gap ( $E_{bulk}$ ) and relative dielectric constant.

	materials		
	CdSe	ZnS	GaAs
$m_e^*/m_0$	0.13	0.34	0.063
$m_h^*/m_0$	0.45	0.23	0.51
$E_{bulk}$ at 300 K (eV)	1.7	3.68	1.424
$\epsilon_r$ (dielectric const)	10.2	8.9	12.9

$$\begin{aligned}
 m_0 &= 9.11 \times 10^{-31} \text{ kg} \\
 \epsilon_0 &= 8.85 \times 10^{-12} \text{ C}^2/\text{Nm}^2 \\
 c &= 3 \times 10^8 \text{ m/s} \\
 h &= 6.63 \times 10^{-34} \text{ Js} \\
 e &= 1.60 \times 10^{-19} \text{ C} \\
 a_0 &= 0.529 \text{ Å}
 \end{aligned}$$

## Carbon Nanomaterials

1. How would you describe fullerenes in terms of their main structural features and properties. Give a couple of examples of possible applications of fullerenes.
2. Which of the carbon nanomaterials is more suitable for application as dye in fluorescence imaging: graphene, graphene quantum dots and graphene nanoribbons?
3. Fig 5 shows the G band of three isolated carbon nanotubes with indication of the frequency of the radial breathing mode ( $\omega_{\text{RBM}}$ ). What can you tell about the semiconducting or metallic properties of the carbon nanotubes featured in A, B and C traces, classify them according to the number of walls (SWCNT or MWCNTs) and their relative diameters?

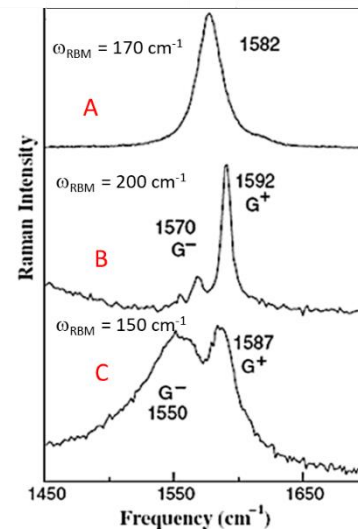


FIG. 5 Raman spectra of three isolated carbon nanotubes in the 1450-1650  $\text{cm}^{-1}$  range showing details of the G band.

**ANSWER:** Tube A is MWCNT because the G mode do not have two well defined bands corresponding to the G<sup>+</sup> and G<sup>-</sup> tangential modes as it would be expected in SWCNTs. The C tube is a metallic SWCNT because the G<sup>-</sup> mode is broadened by phonon-plasmon interaction. The B tube is a semiconductor SWNT with two well defined G bands.

The Radial Breathing Mode frequency decreases with the tube diameter in SWNTs. Tube C has a larger diameter than tube B.

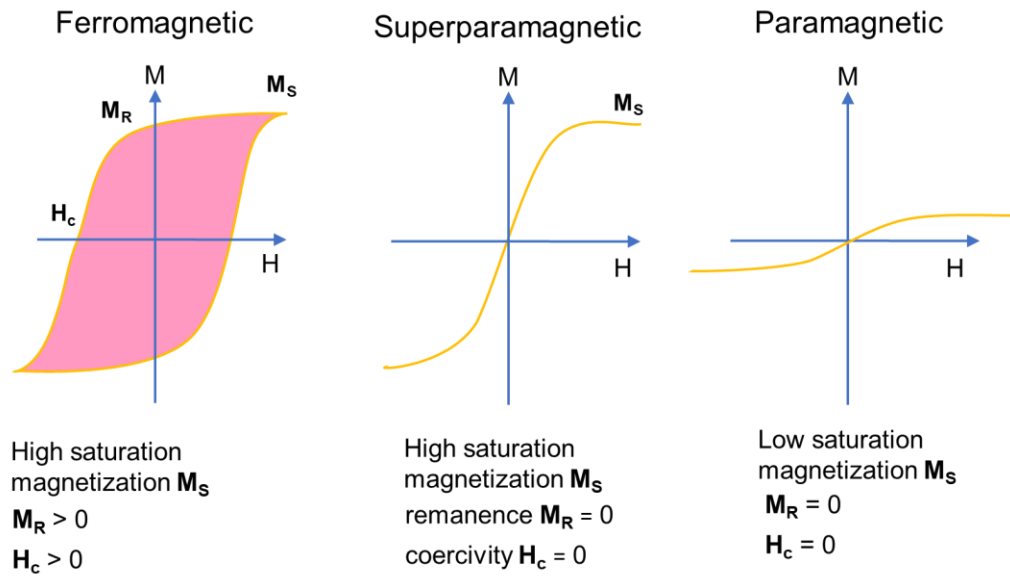
4. Describe a method for preparation of vertically aligned carbon nanotubes.
5. Describe two strategies to obtain graphene from graphite. Compare them in terms of quality of the material obtained.
6. Carbon nanotubes (CNTs) are used in a wide range of applications. For sensing and electronic applications, single wall CNTs are preferably used. In this case, the CNT structure is very important in determining their electric properties. Describe the armchair and zigzag structures. Which of these structures always yields metallic properties?

**ANSWER:** Armchair always gives metallic tubes, zig-zag always give semiconduction, chiral will be metallic when  $n-m$  is a multiple of 3

## Magnetic Nanoparticles

1. Draw the hysteresis curve (magnetization  $M$  as a function of the applied field  $H$ ) for paramagnetic, hard ferromagnetic and superparamagnetic materials. Identify the relevant points: coercive field, remanence and the saturation magnetization.

**ANSWER:**



2. What is the energy barrier (in eV) for a superparamagnetic material with a characteristic time of  $5 \times 10^{-10}$  seconds and a relaxation time of 1 second at 300 K? What is the blocking temperature of the material if the magnetization is measured by DC magnetization and Mössbauer spectroscopy with measurement times of 100 and  $10^{-8}$  seconds, respectively?

**ANSWER:** The energy barrier is  $K_{eff}V = 53.42 \text{ kJ/mol}$  and

$$T_B = \frac{K_{eff}V}{k_B \ln(\tau/\tau_0)} = 2144 \text{ K for Mössbauer}$$

$$T_B = \frac{K_{eff}V}{k_B \ln(\tau/\tau_0)} = 247 \text{ K for DC magnetization}$$

In DC magnetization the particles are in a blocked state because the temperature (300K) is well below  $T_B$  the blocking temperature. In Mössbauer measurements the particles behave like a superparamagnet because  $T_B$  is below 300 K

3. Explain why the size of the magnetic nanoparticles can be used to control the heat dissipated by magnetic particles in an alternating magnetic field.
4. Discuss the applications of superparamagnetic and ferromagnetic particles in magnetic hyperthermia treatment of cancer considering the advantages and disadvantages of the two types of particles.