CHEM F336: NANOCHEMISTRY   (Open Book)   **Max. Marks: 70**
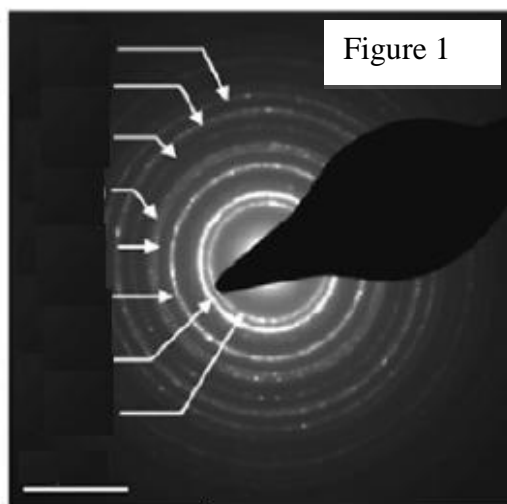**Time: 180 mins.**   **Date: 09.05.2018**
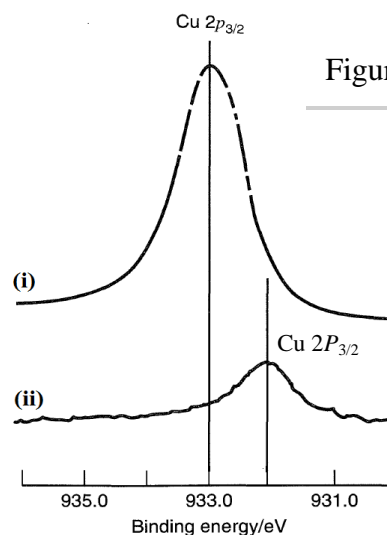
Instructions to the students:
1. There are **five questions** in all. Attempt all the questions.
2. Start answering each question on a fresh page. **Answer all parts of a question together.**
3. **Write brief answers to the point with proper justifications.**
4. Exchange of book and calculator is not allowed
5. Useful information: molar mass of Cu = 63.5×10^{-3} kg/mol, N = 6.023×10^{23} mol^{-1}, E$_g$ of ZnO = 3.3 eV, C$_3$N$_4$ = 2.64 eV, and p-Si = 1.11 eV at 300 K.

Q. 1. Nanocluster of copper crystallizes in a face-centered cubic (FCC) structure with unit cells of side 361 pm. **(a)** Predict the appearance (identify corresponding 2θ value) of the powder diffraction pattern using 154 pm radiation at n = 1 order of the reflection for (111), (200), and (311), and (222) planes. Write all the calculation step properly. **(b)** Calculate the density of copper on the basis of this information. For a FCC crystal there are 4 atoms in each unit cell. (**Hint:** density = mass/volume). **(c)** SAED pattern of copper cluster, which consisted of eight diffraction rings is shown in Figure 1. Identify the presence of any two planes in the SAED pattern. Considering FCC structure, unit cells of side 361 pm, 154 pm radiation, at n = 1. Show all the calculation steps. **(d)** XPS responses for (i) bulk and (ii) copper deposited at underpotential on platinum is shown in Figure 2. Suppose the XPS bands are excited by the Al K$_\alpha$ line at 1486.6 eV. What are the kinetic energies of the photoelectrons (both for i and ii) by ignoring the spectrometer work function? **(e)** Assume that you have synthesized bulk Cu$_2$O nanosheet, which contain many layers in a cluster. Based on which characterization technique and how (mention briefly) you will be able to identify the presence of many layers if the height of a single layer is 0.32 nm.

[4+2+3+3+3]

Figure 1

12 1/nm

Figure 2

Cu 2$p_{3/2}$

(i)

Cu 2$P_{3/2}$

(ii)

935.0   933.0   931.0
Binding energy/eV

Q. 2. Stepwise synthetic procedure for the development of Ag nanoparticle (NP) on semiconductor ZnO nanorod (NR) is given below. Here, ITO was used as a substrate only and it has no role for ZnO NR and Ag NP formation and on dye degradation.

Step A: Preparation of semiconductor ZnO NRs on ITO substrate:

The general reaction conditions were followed based on _two steps_. Briefly, in the _first step_, ITO was immersed in 0.5 mM zinc acetate aqueous solution for 3 minutes and heated at 60 °C for 30 minutes. This procedure was repeated for two times. In the _second step_, ITO containing material developed in the first step was soaked into 25 mM zinc nitrate and 25 mM hexamethylenetetramine (HMTA, $C_6H_{12}N_4$) aqueous solution (pH > 8) and was kept at 92 °C in an oil bath for four hours. Then, the sample (ZnO NR/ITO) was washed with DI water and ethanol.

Step B: Preparation of Ag NPs on ZnO NRs/ITO:

In this process, ZnO NRs/ITO was immersed in 0.125 mM silver nitrate aqueous solution with N_2 purging for 45 minutes to adsorb Ag^+ on the ZnO NR surface. Then, for the reduction of Ag^+ to Ag(0), the solution containing ZnO/ITO was irradiated by 8 W, LED visible lamp for 10 minutes. The prepared sample (Ag NPs/ZnO NRs/ITO) was washed with DI water to remove the remaining Ag^+ ions.

Step C: Photocatalytic activity test using Ag NPs/ZnO NRs/ITO semiconductor nanomaterial:

The photocatalytic performance of the prepared samples was measured by degradation of methylene blue (MB) solution (10 ppm) under UV and visible light irradiation. To conduct this experiment, 0.3 mg of as-prepared photocatalyst was added into the prepared 10 mL MB solution (10 ppm). Then, the samples were exposed to the UV irradiation (15 W UV-C, linear tube lamp) and visible irradiation (8 W, LED lamp) for photocatalytic activity under UV and visible light, respectively. At a given time interval, 2.5 mL of MB solution was drawn to analyze by recording the variation of the maximum absorption peak of MB at 664 nm.

Read the above synthetic procedure carefully and answer the following questions.
(a) What is the purpose in the first step of step A? **(b)** Write all the involved chemical reaction for the formation of ZnO NR on ITO surface in the second step of step A? **(c)** What is the mechanism of Ag(0) NP formation on ZnO NR/ITO surface in step B. **(d)** In step C, Ag NP/ZnO NR/ITO semiconductor nanomaterial is used for MB dye degradation using UV and visible light. Show the mechanism of MB dye degradation on Ag NP/ZnO NR/ITO catalyst surface under visible light. **(e)** Will you be able to differentiate the band energies for the material developed in the first and second step of step A? Justify your answer. **[1+3+3+4+3]**

Q. 3. Schematic representation for the preparation of WO_3/graphene nanocomposites is given in Figure 3, which includes step I to IV. **(a)** _(i)_ What is the importance of step I and II while forming WO_3/graphene nanocomposite? _(ii)_ What would be the difference in final product if you reduce ultrasonic time in step I and ignore stirring in step II? _(iii)_ In the final product identify the matrix and reinforcing material. **[2+1+1]**
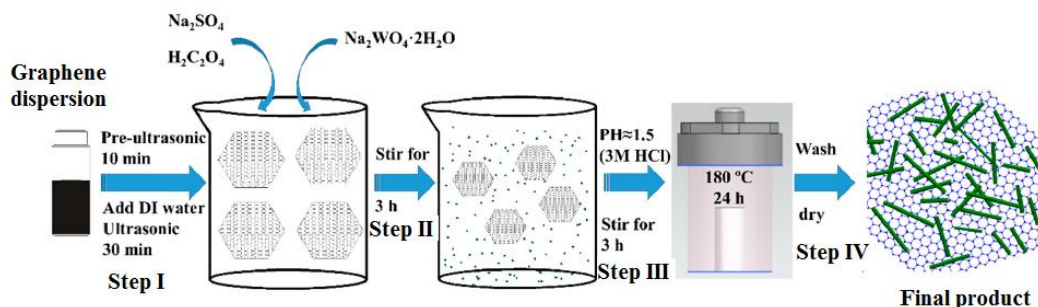

Figure 3

(b) There are two approaches to make a self assemble monolayer of a molecule on a metal surface. Discuss how fluoroalkylsilane form a self assemble monolayer on silicon substrate via Langmuir-Blodgett and self-assembly technique and show all the steps. **[3]**

(c) Which class of material is the most promising for hydrogen storage in transport applications? What are the different requirements of a static system that might be used to store hydrogen produced from renewable energy? **[1+2]**

(d) The structure of a cylindrical tube is best described in terms of a tubule diameter (d) and a chiral angle (Θ). Image of a graphene sheet is given in Figure 4 with d = 10 nm. *(i)* Draw the rolling up direction to get a semiconducting nanotube. *(ii)* What is the difference in the electronic property before and after rolling up of graphene sheet? Justify your answer in 3-4 sentences. **[1+3]**
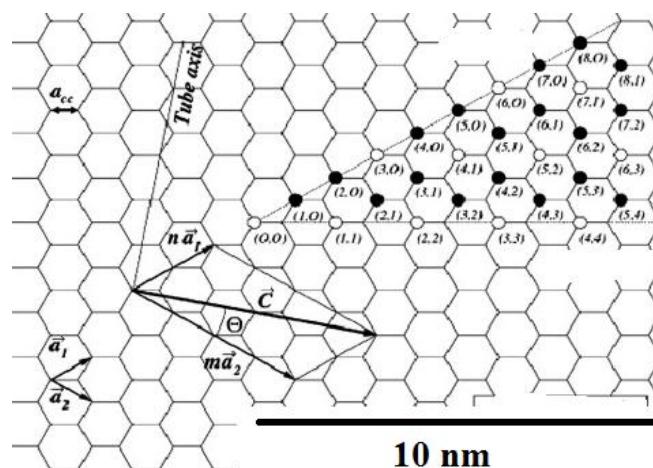

10 nm

Figure 4

Q. 4. (a) Decoration of Au nanoparticle as co-catalyst on ultrathin 2D sheets of carbonnitride (C_3N_4) is shown in Figure 5, which can be used for the generation of hydrogen and oxygen gas photoelectrochemically, an example of fuel cell reaction. *(i)* Show all the reaction steps how hydrogen and oxygen are generated on Au/C_3N_4 nanocatalyst surface photoelectrochemically. **[4]**
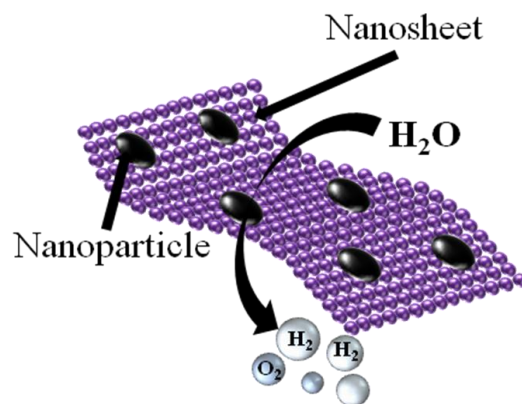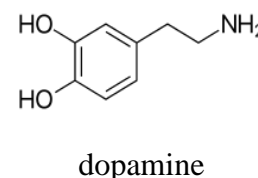

Figure 5

(b) Assume that you have synthesized dendrimer-encapsulated nanoparticles (DENs) of Au using generation 6th and 8th of hydroxyl terminated polyamidoamine dendrimer (G6-OH and G8-OH). Now, you want to extract Au NPs from both the dendrimer using dodecane thiol as a stabilizing agent.

(i) What would be your observation regarding extraction of NPs and why?
(ii) What is the essential condition to prepare dendrimer-stabilized NPs of Au using G6-OH. The interior diameter of G6-OH is 42 Å. **[2+2]**

(c) Assume that you have synthesized 20 mL Ag nanoparticle in aqueous medium using sodium borohydride as a reducing and stabilizing agent. After that, 20 mL Ag NP was divided into two test tubes (1 and 2) with 10 mL each. Now, 0.5 M KCl and 0.5 M dopamine, a neurotransmitter were added in test tube 1 and 2, respectively. After addition of KCl and dopamine, *(i)* what would be your observation in test tube 1 and 2? *(ii)* will you be able to quantify the test tube 1 and 2 via surface enhanced Raman scattering study? Justify your answer in 4-5 sentences. **[2+3]**

dopamine

3

PTO

Q. 5. Schematic representation for the fabrication of Pt(0) decorated Au nanofilm on p-silicon is given in Figure 6, which consists of three steps. All the different color spherical balls are represented for different meaning. Product a, b, and c are Au nanofilm on p-silicon, Cu(0) decorated Au nanofilm on p-silicon, and Pt(0) decorated Au nanofilm on p-silicon, respectively.

Answer the following questions:
(a) What is/are the involved chemical reaction in step I to get product a? **(b)** What is the best suited method in step II to synthesize product b and why? **(c)** What is the advantage of step III and mention the reducing agent used in this step? **(d)** If you compare this fabrication method over co-reduction of Au^{3+} and Pt^{2+} ions on p-silicon, which method would be more useful and why? **(e)** Will you be able to quantify the product a, b and c using surface plasmon resonance spectroscopy? **(f)** The as-synthesized final catalyst, product c, exhibit enhanced photoactive sensor property as glucose sensor. Show all the photoactive steps for the catalyst to be a glucose sensor. **[2+2+2+3+2+3]**
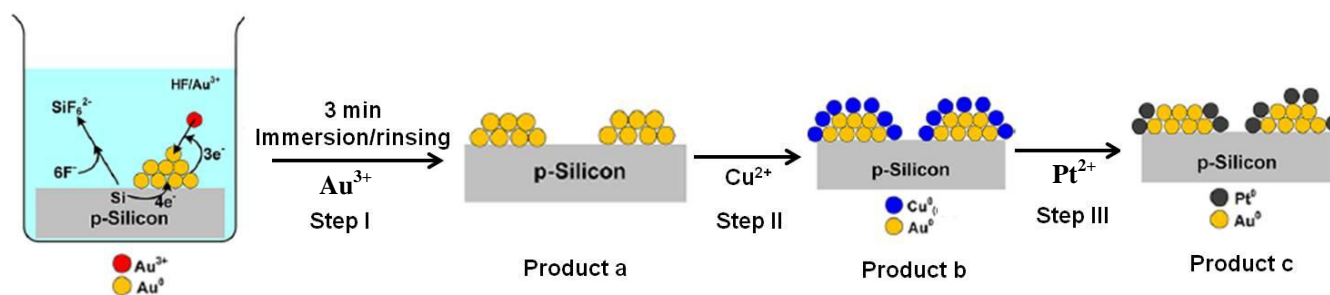

Figure 6

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