Birla Institute of Technology and Science, Pilani, Rajasthan 333031
Mid Term Examination 2nd Semester, 2017-2018

CHEM F336: NANOCHEMISTRY **(Closed Book)** **Max. Marks: 50**
Time: 90 mins. **Date: 08.03.2018**

Instructions to the students:
1. There are **four 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. $E^0_{Au3+/Au}$ = 1.5 V, $E^0_{Ag+/Ag}$ = 0.78 V, $E^0_{Pd2+/Pd}$ = 0.83 V, $E^0_{Pt2+/Pt}$ = 0.91 V, $E^0_{Co2+/Co}$ = -0.28 V, $E^0_{BH4-/H3BO3}$ = -0.481 V, $E^0_{N2H4/N2}$ = -0.23 V vs. NHE

Read the following paragraph for bimetallic nanoparticle synthesis carefully.

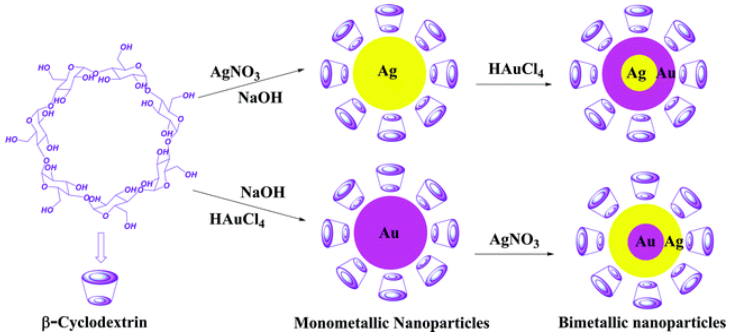
Preparation: Water was used as the solvent in all reactions. For a typical preparation, the silver nanoparticles were prepared by adding 14 g of polyvinylpyrrolidone (PVP) to 500 mL of silver metal salt ($AgNO_3$, 5.6 mM) solution. The solution was then heated at 60 °C in an oil bath for 10 min, and then 37 mmol of $NaBH_4$ was added. The mixture was then allowed to react for another 20 min in an oil bath. The reaction mixture was stirred for 30 min to remove the excess reducing agent ($NaBH_4$). The solution was then allowed to cool before the 2nd and 3rd steps were performed.

In the 2nd step, an aliquot of 0.26 mM H_2PtCl_6 (10 mL) solution was added drop wise to the silver colloidal solution at room temperature. The mixture continued to undergo the reaction for another 20 min to yield nanoparticles with Ag-Pt bimetallic nanoparticle (NP). In the 3rd step, an aliquot of 0.005 M H_2PtCl_6 (500 mL) solution were added to the silver nanoparticle solution and continue the reaction for another 30 min. All the products were cleaned via centrifugation. This centrifugation procedure needed to be repeated several times. The overall replacement reaction is stoichiometric. Vigorous magnetic stirring was maintained throughout the synthesis.

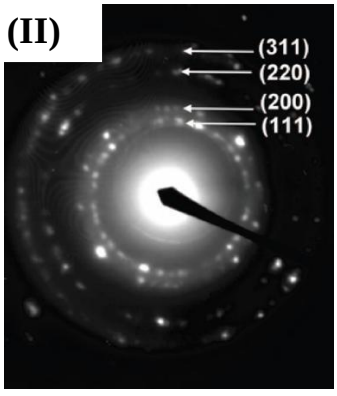
Q. 1. Based on the above synthetic procedure answer the following questions: **[4+4+4+2]**
(a) What type of bimetallic nanoparticle formation would you expect from this synthesis? Justify your answer with appropriate mechanism. **(b)** What would be your expectation if you selectively oxidize Ag(0) in Ag-Pt bimetallic nanoparticle and then re-reduce with $NaBH_4$? Justify your answer. **(c)** What happens if you add 0.26 mM H_2PtCl_6 (10 mL) solution first followed by addition of PVP, $NaBH_4$ and finally in 2nd step 500 mL of silver metal salt ($AgNO_3$, 5.6 mM) solution? Justify your answer with proper chemical reaction. **(d)** What would be the product(s) after 3rd step of reaction?

Q. 2. Schematic representation for the formation of mono- and bimetallic nanoparticles using beta-cyclodextrin is given below (I). SAED pattern of Ag@Au is also given below (II).

(I)



(II)



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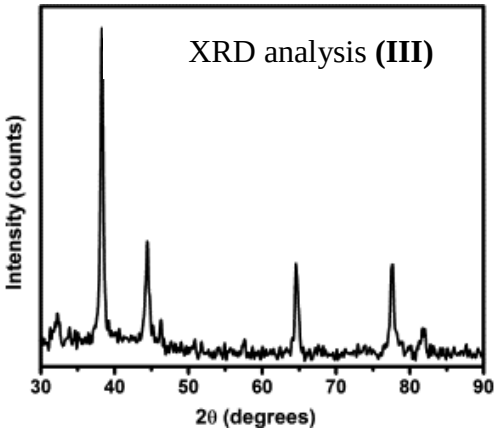
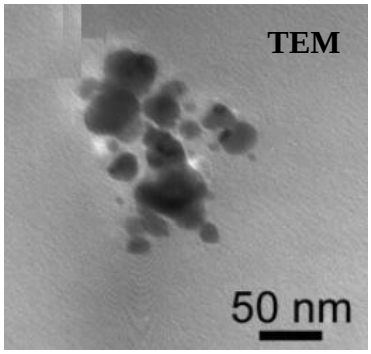
(a) What characterization technique you will prefer to quantify the presence of Au@Ag and Ag@Au bimetallic nanoparticle? Justify your answer. **(b)** Identify the crystal structure of Ag@Au bimetallic NP from SAED analysis with proper justification. **(c)** From XRD analysis ($2\theta = 38.5^0$, 44.7^0, 64.9^0, and 78.1^0), identify the approx 2θ value for (200) plane. Show your calculation properly. **(d)** What is the approx cluster size of Ag@Au bimetallic NP using the same 2θ value for (200) plane? XRD was performed using a Rigaku Mini Flex II diffractometer with Cu-Kα radiation ($\lambda = 1.54$ Å) and n = 1 at 25 °C. Given that, $K = 0.9$ and FWHM = 0.06 for (200) plane. **[4+3+4+3]**

Q. 3. Synthetic procedure of Au nanoparticle is given below:



To an aqueous solution of $HAuCl_4$ (100 mL, 0.5 mM), 20 mg of tetraethylammonium chloride (TEAC) was added and toluene (100 mL) was introduced above the aqueous layer. Upon shaking, $AuCl_4^-$ ions were transferred. The organic phase was separated and divided into five equal portions. Five different surfactants bearing C_nTAC (n) 10, 12, 14, 16, or 18) moieties were added and mixed well so that the final concentration of C_nTAC in all of the sets was maintained at 5 mM. Finally, 2.0 mg of sodium borohydride was introduced into each solution and all the reaction mixtures were shaken vigorously. During shaking, at first, the yellow color due to $AuCl_4^-$ disappeared and the solution became colorless within a few minutes. The solution turned into the characteristic color of gold colloids upon further shaking. Answer the following questions.



(a) Is there any phase transfer catalyst in this procedure? **(b)** In which phase (i.e., solvent) you will be able to synthesize Au NP? **(c)** Write the involved chemical steps for Au NP synthesis in desired phase. **(d)** Corresponding TEM image for Au NP is given below, where the particles are not uniform in size and distribution. Will you be able to convert all the particles into an uniform smaller size distribution and how? Write your answer with proper justification. **(e)** How do you identify the way of electron tunneling between tip and substrate in scanning tunneling microscope? **[1+1+3+4+3]**

Q. 4. (a) During formation of nanoparticle the process initiates with nucleation followed by growth. What is nucleation? **(b)** What is anisotropic nanomaterials? Why anisotropic nanostructures are required? **(c)** How electrostatic stabilization is maintained within the nanocluster system during stabilization of nanoparticles? **(d)** Sodium borohydride ($NaBH_4$) and hydrazine hydrate (N_2H_4) are two available reducing agents in your laboratory. Which one you will prefer to use for the synthesis of Co nanoparticle and why? **[2+3+3+2]**

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