Some reflections on the surface Plasmon resonance of nanomaterials

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Introduction

The study of nanomaterials is basically centred around the size of the particles which is by convention materials to be classified as no materials must satisfy that at least in one of the dimensions, it should satisfy nano meter scale. However it is interesting and intriguing to see what size and shape will be reflected in any of the observable characteristics and how these observable characteristics can be used to predict or estimate the size and shape of the nano materials that have been synthesized. This aspect has been occupying the minds of many scientist in the past five years and this presentation is the first part in this direction. We do hope to come up many more reflections on this aspect in the near future. In this presentation we restrict our discussion to gold nano particles.

- The color of bulk gold is yellow whereas the colloidal solution of gold nanoparticles is wine red. This property is related to the variation in optical property of the material with its size.
- The optical properties arise due to the interaction of electromagnetic radiation with the material. When this occurs, the vibrational and electronic states of the material get excited. In the specific case of metal nanoparticles, the surface plasmon frequency falls in the visible region of the electromagnetic spectrum. Thus a feature appears in the absorption spectrum which is called as surface plasmon resonance (SPR).

In Fig 1 the typical Plasmon resonance spectra of gold nano particle and nano rods are given for two typical shapes namely a spherical particle and a nano rod.

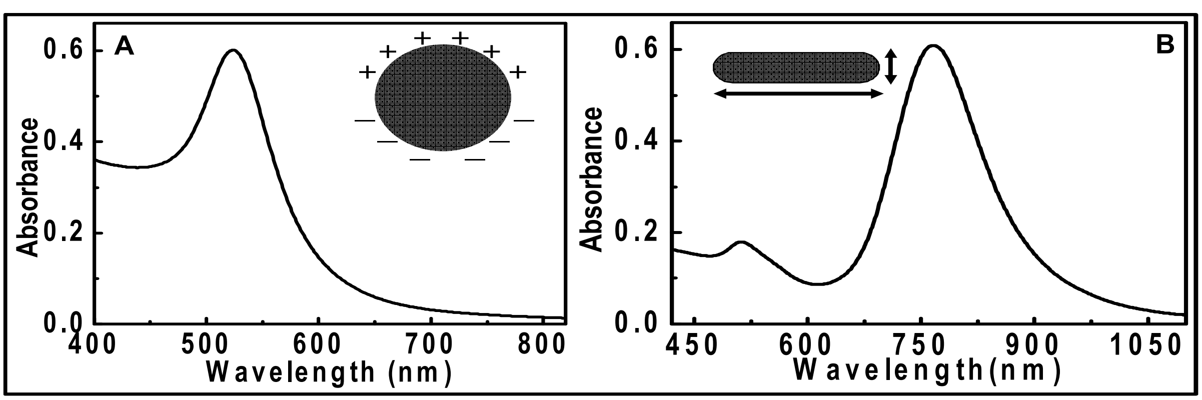


Fig.1. SPR of gold nano particle and nanorod. One can see two bands in the case of nanorod while it is a single absorption band for the spherical particle. gold nanoparticles (A) and nanorods (B). The arrows in B correspond to the electron motions

The position of the surface plasmon band in optical spectrum mainly depends upon the

- Nature of the metal
- Size and shape of the metal particles
- Nature of the capping agent
- Nature of the medium
- Average distance between the neighboring particles

It is not clear at present how or why all these factors affect the Plasmon resonance and it is hoped that we will come up with suitable reasoning for this observation that is available in literature.

In Fig 2 the SPR bands are shown as a function of the size and shape of the nanoparticles.

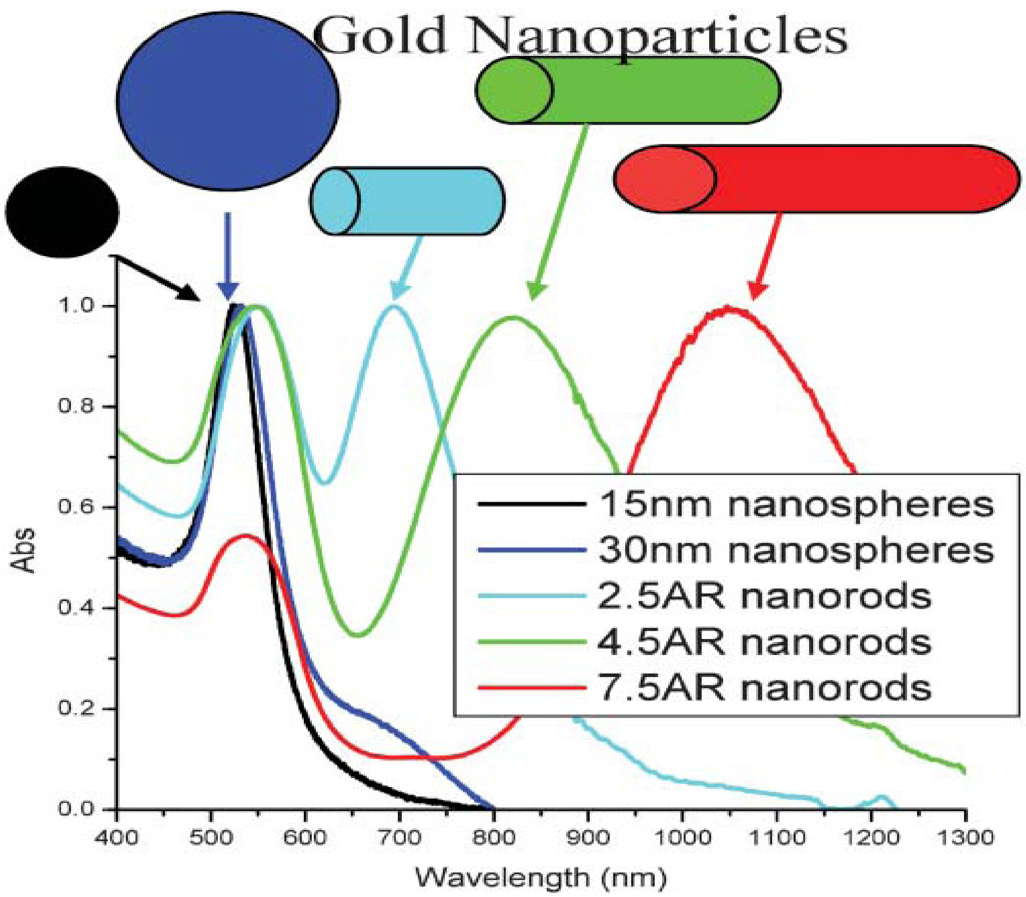


Figure 2. Gold nanoparticles – absorption of various sizes and shapes [M. A. El-Sayed et. al., Chem. Soc. Rev., 2006, 35, 209]

Some data available in literature is also compiled in Table 1.

Table 1. Position of the surface plasmon resonance peak in dependence of the particle diameter.

λspr (nm)	d (nm)	λspr (nm)	d (nm)	λspr (nm)	d (nm)
525.0	32	534.9	58	552.1	84
525.6	34	535.9	60	553.8	86
526.2	36	536.9	62	555.7	88
526.8	38	538.0	64	557.6	90
527.5	40	539.2	66	559.6	92
528.2	42	540.4	68	561.7	94
528.9	44	541.6	70	563.9	96
529.6	46	542.9	72	566.2	98
530.4	48	544.3	74	568.6	100
531.2	50	545.7	76	571.1	102
532.1	52	547.2	78	573.7	104
533.0	54	548.8	80	576.5	106
533.9	56	550.4	82	579.3	108

Data reproduced from W. Haiss et. al., *Anal. Chem.* 2007, 79, 4215

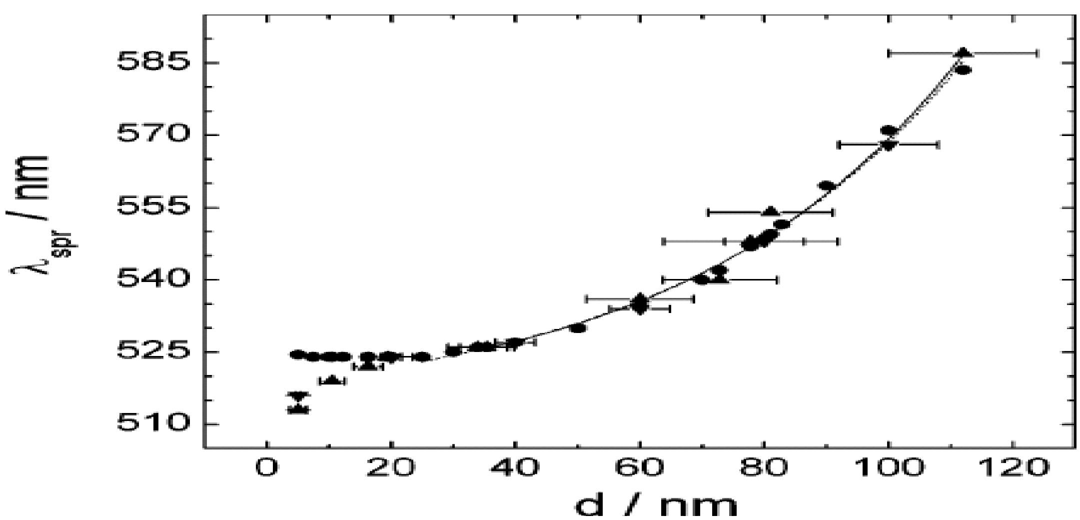
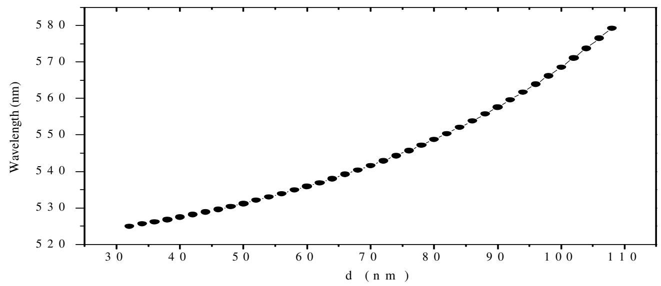


Figure 3. Position of the surface plasmon resonance peak (λspr) as a function of the particle diameter for GNPs in water: calculated (circles); experimentally measured (downwardpointing triangles, commercial GNPs; upward-pointing triangles, in-house synthesized GNPs). An exponential fit to the theoretical data for d > 25 nm is shown as a dotted (dashed) line.

In Fig.4. the variation of Plasmon resonance wavelength as a function of the size of the particle is given.



Position of the surface plasmon resonance peak (λspr) as a function of the particle diameter for Au nanoparticles

In Table 2 **Table 2. Sizes, Plasmon Wavelengths of Variously Shaped Au Nanoparticles**

Au nanoparticles	length (nm)	diameter (nm)	λspr (nm)
Cubes	44	-	538
Cube	66	-	550
Hexagon	70	-	550
Rods	40	17	653
Rods	55	16	723
Rods	74	17	846
Bipyramids	27	19	645
Bipyramids	50	18	735

J.Wang et. al., *Langmuir* 2008**,** *24,* 5233; C. J. Murphy et. al., *J. Am. Chem. Soc.*. 2004, 126, 8648.

Some results from the unpublished results from our laboratory is also given for comprehension of this topic.

Table 4. Sizes, Plasmon Wavelengths of speherical Au Nanoparticles

S.No.	λspr (nm)	d (nm)
1	538	14
2	532	12
3	526	11
4	520	8
5	518	7
6	517	6
7	515	4

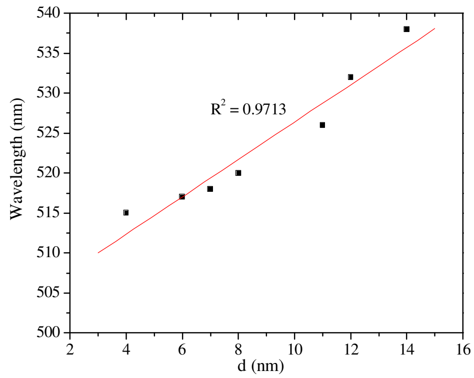


Figure 4. Position of the surface plasmon resonance peak (λspr) as a function of the particle diameter for Au nanoparticles

It is hoped that we will come out with more details soon.