Surface plasmon resonance of Au-Cu bimetallic nanoparticles predicted by a quasi-chemical model

Yen-Hsun Su1,2* and Wen-Lin Wang1

Abstract

Au-Cu alloys are functional materials with nonlinear optical applications. However, the optical properties of such alloys are difficult to predict due to the random mixing of materials. In this paper, we present a quasi-chemical model to simulate the optical properties of Au-Cu alloy systems based on the mixing of Gibbs free energy. This model is also able to predict the position of the surface plasmon resonance peaks for Au-Cu alloy nanoparticles. The model can be applied to predict the optical properties of alloy systems in the fields of plasmonics and nanophotonics.

Keywords: Dielectric properties; Gibbs free energy; Nanostructures; Metals; Optical properties

Background

Metal nanoparticles (NPs) have attracted much research interest due to their unusual chemical and physical properties, such as catalytic activity, novel electronics, optics, and magnetic properties, and they have potential applications in solar cells and biosensors [1-7]. Alloy nanoparticle systems have been found to exhibit optical limiting properties due to surface plasmon resonance and have been used in biodiagnostic applications [8,9]. Alloy nanoparticles are materials used to tune the position of surface plasmon resonance, and thus help to produce materials for use in nonlinear optical applications [10-14]. Au-Cu alloy system is a completely dissolvable alloy. The position of surface plasmon resonance for Au NPs is about 520 nm. The position of surface plasmon resonance for Cu NPs is 570 ~ 580 nm [15]. At low temperatures, Au, Au3Cu, AuCu, AuCu3, and Cu exist and order easily in Au-Cu alloys system. The prediction of the optical properties of such alloy systems are difficult to predict because of the random mixing of materials.

The quasi-chemical method is a statistical approach for predicting the short-range-order of Au-Cu alloys system according to Gibbs free energy. While the optical properties of Au-Cu alloys can be computed by the quasi-chemical model based on the energy potential between the electric field and induced dipole, few works have attempted to do this.

In this study, we thus simulate the optical properties of Au and Cu using a quasi-chemical model, based on the energy potential between the electric field and induced dipole. We then used this quasi-chemical method to modify the statistics for the short-range-order of Au-Cu alloy system. Then the optical properties are simulated by combining the Gibbs free energy and electric potential energy. The light extinction of nanoparticles is calculated by using Mie theory. The results show that the model is suitable for predicting the position of surface plasmon resonance peaks.

Methods

Model

Regular solution

Au-Cu alloy system refers to a solid solution. Properties of a regular solution are best examined based on the concept of excess function [16]. The excess value of an
extensive thermodynamic solution property is simply the difference between its actual value and the value that it would have if the solution were ideal based on the Gibbs free energy of the solution,

\[ G = G^{\text{id}} + G^{\text{XS}} \]  

(1)

In which \( G \) is the molar Gibbs free energy of the solution, \( G^{\text{id}} \) is the molar Gibbs free energy that the solution would have if it were ideal, and \( G^{\text{XS}} \) is the excess molar Gibbs free energy of the solution. Because the two components have equal molar volumes and do not exhibit a change in molar volume when mixed, their regular solution behavior can be understood by the application of a statistical mixing model, i.e., a quasi-chemical model.

**Quasi-chemical model**

The energy of the solution is the sum of its interatomic bond energies. Consider 1 mol of a mixed crystal containing \( N_A \) atoms of A and \( N_B \) atoms of B such that

\[ X_A = \frac{N_A}{N_O} \quad \text{and} \quad X_B = \frac{N_B}{N_O}, \]

(2)

where \( N_O \) is Avogadro’s number. The mixed crystal, or solid solution, contains three types of atomic bond: A-A bonds, B-B bonds, and A-B bonds. A-A bonds the energy of each of which is \( U_{AA} \), B-B bonds the energy of each of which is \( U_{BB} \), and A-B bonds the energy of each of which is \( U_{AB} \). If in the solution, there are \( p_{AA} \) A-A bonds, \( p_{BB} \) B-B bonds, and \( p_{AB} \) A-B bonds, the energy of the solution \( U \) is obtained as the linear combination

\[ U = p_{AA}U_{AA} + p_{BB}U_{BB} + p_{AB}U_{AB} \]  

(3)

and the problem of calculating \( U \) becomes one of calculating the values of \( p_{AA} \), \( p_{BB} \), and \( p_{AB} \). Thus,

\[ \Delta U^M = p_{AB}[U_{AB} - \frac{1}{2}(U_{AA} + U_{BB})]. \]  

(4)

The change in volume is negligible. Since \( \Delta V^M = 0 \),

\[ \Delta H^M = \Delta U^M = p_{AB}[U_{AB} - \frac{1}{2}(U_{AA} + U_{BB})]. \]

(5)

Ideal mixing requires the condition \( U_{AB} = U_{AA} = U_{BB} \). If \( \Delta H^M = 0 \), the mixing of the \( N_A \) atoms with the \( N_B \) atoms of B is random.

\[ \Delta S^M = \Delta S^M_{\text{id}} = -R(X_A \ln X_A + X_B \ln X_B). \]

(6)

The quasi-chemical model is a statistical mixing model in Gibbs free energy. According to Equations 5 and 6, the mixing Gibbs free energy will be presented. In the ‘Results and discussion’ section, the dipole energy in Gibbs free energy was utilized to consider the optical properties with different frequencies of incident light.

**Results and discussion**

The probability that a neighboring pair of sites contains an A-B pair is \( 2X_AX_B \), while an A-A pair is \( X_A^2 \), and a B-B pair is \( X_B^2 \). If in the solution, there are \( p_{AA} \) A-A pairs, \( p_{BB} \) B-B pairs, and \( p_{AB} \) A-B pairs, the energy of the solution

\[ G = G^0 + \Delta G^M = \frac{X_A^2}{2}G_{AA}^0 + \frac{X_B^2}{2}G_{BB}^0 + 2X_AX_B[U_{AB} - \frac{1}{2}(U_{AA} + U_{BB})] + RT(X_A \ln X_A + X_B \ln X_B). \]

(7)

Combining Equations 5 and 6 with Equation 7 produces the following:

\[ \Delta G^M = p_{AB}[U_{AB} - \frac{1}{2}(U_{AA} + U_{BB})] + RT(X_A \ln X_A + X_B \ln X_B). \]

(8)

Because \( p_{AB} = 2X_AX_B \),

\[ \Delta G^M = 2X_AX_B[U_{AB} - \frac{1}{2}(U_{AA} + U_{BB})] + RT(X_A \ln X_A + X_B \ln X_B). \]

(9)

The Gibbs free energy of the solution is as follows:

\[ G = G^0 + \Delta G^M = \frac{X_A^2}{2}G_{AA}^0 + \frac{X_B^2}{2}G_{BB}^0 + 2X_AX_B[U_{AB} - \frac{1}{2}(U_{AA} + U_{BB})] + RT(X_A \ln X_A + X_B \ln X_B). \]

(10)

After applying the electric field \(-E\),

\[ G(-\vec{p}_{\text{mixing}} \cdot \vec{E}) = X_A^2(G_{AA}^0 - \vec{p}_A^2 \cdot \vec{E}) \]

+ \( X_B^2(G_{BB}^0 - \vec{p}_B^2 \cdot \vec{E}) \)

+ \( 2X_AX_B(U_{AB} - \vec{p}_{AB} \cdot \vec{E}) - \frac{1}{2}(U_{AA} - \vec{p}_A^2 \cdot \vec{E}) \)

+ \( (U_{BB} - \vec{p}_B^2 \cdot \vec{E}) \)

+ \( RT(X_A \ln X_A + X_B \ln X_B) \).

(11)

where \( \vec{p}_{\text{mixing}} \) is the induced dipole moment of metamaterial, \( \vec{p}_A \) is the induced dipole moment of material A, \( \vec{p}_B \) is the induced dipole moment of material B, and \( \vec{p}_{AB} \) is the induced dipole moment due to the interaction of materials A and B.

The Gibbs energy was subtracted when applying an electric field from that without applying one, as follows:

\[ G(-\vec{p}_{\text{mixing}} \cdot \vec{E}) = X_A^2(G_{AA}^0 - \vec{p}_A^2 \cdot \vec{E}) \]

+ \( X_B^2(G_{BB}^0 - \vec{p}_B^2 \cdot \vec{E}) \)

+ \( 2X_AX_B(U_{AB} - \vec{p}_{AB} \cdot \vec{E}) - \frac{1}{2}(U_{AA} - \vec{p}_A^2 \cdot \vec{E}) \)

+ \( (U_{BB} - \vec{p}_B^2 \cdot \vec{E}) \).

(12)
Because $\overrightarrow{p} = (\varepsilon - \varepsilon_0) \overrightarrow{E}$, the above equation can be rewritten as follows:

$$
\begin{align*}
(e_{\text{mixing}} - \varepsilon_0) \overrightarrow{E} \cdot \overrightarrow{E} &= X_A^2 \left( (\varepsilon_A - \varepsilon_0) \overrightarrow{E} \cdot \overrightarrow{E} \right) \\
&+ X_B^2 \left( (\varepsilon_B - \varepsilon_0) \overrightarrow{E} \cdot \overrightarrow{E} \right) \\
&+ 2X_A X_B \left[ \left( (\varepsilon_{AB} - \varepsilon_0) \overrightarrow{E} \cdot \overrightarrow{E} \right) - \frac{1}{2} \left( (\varepsilon_A - \varepsilon_0) \overrightarrow{E} \cdot \overrightarrow{E} \right) \\
&+ \left( (\varepsilon_B - \varepsilon_0) \overrightarrow{E} \cdot \overrightarrow{E} \right) \right]
\end{align*}
$$

(13)

$$(e_{\text{mixing}} - \varepsilon_0) = X_A^2(\varepsilon_A - \varepsilon_0) + X_B^2(\varepsilon_B - \varepsilon_0) \\
+ 2X_A X_B \left[ \left( \varepsilon_{AB} - \frac{1}{2}(\varepsilon_A + \varepsilon_B) \right) \right]
$$

(14)

The dielectric function of the mixed material includes the interaction term $\left[ (\varepsilon_{AB} - \frac{1}{2}(\varepsilon_A + \varepsilon_B) - \varepsilon_0) \right]$ and independent terms $\varepsilon_A X_A^2$ and $\varepsilon_B X_B^2$. When $\left[ (\varepsilon_{AB} - \frac{1}{2}(\varepsilon_A + \varepsilon_B) - \varepsilon_0) \right]$ is assumed to be an experience constant, $A$, the dielectric function of mixing material is reduced to the following form:

$$
\varepsilon_{\text{mixing}} = \varepsilon_A X_A^2 + \varepsilon_B X_B^2 + 2X_A X_B A
$$

(15)
The Newton formula [17] is used to apply these concepts to the clustered material. The dielectric functions refer to these clusters and the embedding matrix,

$$\epsilon_{\text{Newton-mixing}} = f \epsilon_A + (1-f) \epsilon_B.$$  \hspace{1cm} (16)

The quasi-chemical model describes the mixing of clusters in which the interaction term is approximated by Newton formula mixing. Combining the probability of neighboring pairs with the Newton formula, the optical model of the regular solution is as follows:

$$\epsilon_{\text{eff}} = X_A^2 \epsilon_A + 2X_A X_B (\epsilon_{\text{Newton-mixing}}) + X_B^2 \epsilon_B.$$  \hspace{1cm} (17)

The effective dielectric complex of the alloy is presented in Figure 1.

According to Mie theory [18,19], the resonances denoted as surface plasmon were relative with the onset of the quantum size and shape effects of Au NPs. There is one SPR band for metal NPs, and this is shown as follows [20,21]:

$$\epsilon_i = \epsilon_h + f \frac{\epsilon_h (\epsilon_h - \epsilon_m)}{\Gamma_i \epsilon_m + (1-\Gamma_i) \epsilon_h},$$  \hspace{1cm} (18)

where $\epsilon_h$ is the dielectric constant of the host medium embedding Au NPs, $\epsilon_m$ is the dielectric constant of Au NPs, $f$ is the volume fraction of Au NPs, $\epsilon_i$ is the total dielectric constant, and $\Gamma_i$ is a set of three parameters defined along the principal axes of the particle characterizing its shape. $\Gamma_1 + \Gamma_2 + \Gamma_3 = 1$ and the other parameters range from 0 to 1. The frequencies of the surface plasmon of nonspherical metal NPs have two or three bands, depending on their shape. The extinction coefficients of alloy metal NPs with different sizes and environments are presented in Figures 2, 3, 4.

![Figure 3 Extinction of different sized NPs. (a) Au, (b) Au₃Cu, (c) AuCu, (d) AuCu₃, and (e) Cu alloy nanoparticles (n = 1; Q_{abs} is the extinction coefficient).](image-url)
The quasi-chemical model is used to calculate the optical properties of Au-Cu alloys. The real part of the dielectric complex is negative for Au-Cu alloy system. The imaginary part of dielectric constant for Au-Cu alloy system shows the peaks that appear in range from 430 to 520 nm due to the electronic transition between the d band and sp band. The real and imaginary parts of the dielectric complex for Au-Cu alloys system are as shown in Figure 1a,b, respectively.

We use Mie theory to predict the spectrum and position of surface plasmon resonance. Figure 2b shows the extinction of a 10-nm diameter Au-Cu nanoparticle in different refractive index surroundings. For \( n = 1.4 \), the surface plasmon resonance peaks are 532, 538, 561, 567, and 578 nm for Au, Au$_3$Cu, AuCu, AuCu$_3$, and Cu, respectively, and these results which are in agreement with those of other experimental results [22].

The extinction spectra of Au-Cu bimetallic nanoparticle with size effect are presented in Figure 3. As the size of nanoparticles increase, the peak of surface plasmon resonance red-shifts. When the size is less than 50 nm, the size effect becomes more significant. The higher the ratio of Cu to Au of is, the more the surface plasmon resonance red-shifts. When the size is greater than 50 nm, the size effect is less significant due to the small increase in the cross section. The refractive index effect is shown in Figure 4. As the refractive index increases, the surface resonance peak will red-shift and become increasingly sharp. Based on this, it is possible to predict the surface plasmon resonance peaks of regular solution alloys, such as Au-Cu, Cu-Ag, Ag-Cu, and Au-Cu-Ag systems.

**Conclusion**

In this work we used the quasi-chemical model to compute the optical properties of Au-Cu alloy system. The results show that it is possible to use this approach to predict the positions of surface plasmon resonance...
peaks. This model is thus a useful tool in the development of future applications of alloy nanoparticles for plasmonics and nanophotonics.

Competing interests
The authors declare that they have no competing interests.

Authors’ contributions
YHS and WLW contribute in writing and model setting in all these works. Both authors read and approved the final manuscript.

Authors’ information
YHS is an assistant professor and WLW is a student in the Department of Materials Science and Engineering in National Cheng Kung University, Taiwan.

Acknowledgements
This work was financially supported by the National Science Council of Taiwan. This research was, in part, supported by the Ministry of Education, Taiwan, Republic of China and the Aim for the Top University Project of the National Cheng Kung University (NCKU).

Received: 17 July 2013 Accepted: 28 August 2013
Published: 2 October 2013

References
1. Banholzer MJ, Osberg KD, Li S, Mangelson BE, Schatz GC, Mirkin CA: Silver-based nanodisk codes. ACS Nano 2010, 4:5446.
2. Wustholz KL, Henry AI, McMahon JM, Freeman RG, Valley N, Piotti ME, Natan MJ, Schatz GC, Van Duyne RP: Structure-activity relationships in gold nanoparticle dimers and trimers for surface-enhanced Raman spectroscopy. J Am Chem Soc 2010, 132:10903.
3. Zhang XL, Song JF, Li XB, Feng J, Sun HB: Sun Optical Tamm states enhanced broad-band absorption of organic solar cells. Appl Phys Lett 2012, 101:243901.
4. Sen A, Lin CJ, Kaun CC: Single-molecule conductance through chiral gold nanotubes. J Phys Chem C 2013, 117:13676.
5. Su YH, Ke YJ, Cai SL, Yao QY: Surface plasmon resonance of layer-by-layer gold nanoparticles induced photoelectric current in environmentally-friendly plasmon-sensitized solar cell. Light Sci Appl 2012, 1:e14.
6. Stratakis E, Kymakis E: Nanoparticle-based plasmonic organic photovoltaic devices. Mater Today 2013, 16:133.
7. Su YH, Hsu CY, Chang CC, Tu SL, Shen YH: Ultra-thin titanium nanolayers for plasmon-assisted enhancement of bioluminescence of chloroplast in biological light emitting devices. Appl Phys Lett 2013, 103:063703.
8. Cao YW, Jin R, Mirkin CA: DNA-modified core-shell Ag/Au nanoparticles. J Amer Chem Soc 2001, 123:7961.
9. Nair AS, Suryanarayanan V, Pradeep T, Thomas J, Anjia M, Philip R: AuxAgY@ZrO2 core-shell nanoparticles: synthesis, characterization, reactivity and optical limiting. Mater Sci Eng B 2005, 119:173.
10. Isipaisou RG, Sahoo L, Varavski OP, Tornalia DA, Goodson T: Large optical limiting from novel metal-dendrimer nanocomposite materials. J Am Chem Soc 2000, 122:11005.
11. Sun WF, Dai Q, Worden JG, Huo Q: Optical limiting of a covalently bonded gold nanoparticle/polylysine hybrid material. J Phys Chem B 2005, 109:20854.
12. Wang GC, Sun WF: Optical limiting of gold nanoparticle aggregates induced by electrolytes. J Phys Chem B 2006, 110:20001.
13. Francois L, Mostafavi M, Belloni J, Deloix JS, Delaire I, Feneyrou P: Optical limitation induced by gold clusters. J Phys Chem B 2000, 104:6133.
14. Philip R, Kumar GR, Sandhyarani N, Pradeep T: Picosecond optical nonlinearity in monolayer-protected gold, silver, and gold-silver alloy nanoclusters. Phys Rev B 2000, 62:13160.
15. Yeh YH, Yeh MS, Lee YP, Yeh CS: Formation of Cu nanoparticles from CuO powder by laser ablation in 2-propanol. Chem Lett 1998, 11:1183.
16. Gaskell DR: Introduction to the Thermodynamics of Materials. 5th edition. New York: Taylor & Francis; 2008:249.
17. Theiss W: Optische Eigenschaften Inhomogener Materialien. Dissertation, RWTH Aachen; 1989.
18. Templeton AC, Pietron JJ, Murray RW, Mulvaney P: Solvent refractive index and core charge influences on the surface plasmon absorbance of alkanethiolate monolayer-protected gold clusters. J Phys Chem B 2000, 104:564.
19. Fuchs R: Theory of the optical properties of ionic crystal cubes. Phys Rev B 1975, 11:732.
20. Prasad PN: Nanophotonics. Hoboken: Wiley; 2004:130.
21. Fox M: Optical Properties of Solids. London: Oxford University Press; 2001:151.
22. Kim MJ, Na HJ, Lee KC, Yoo EA, Lee M: Preparation and characterization of Au-Ag and Au-Cu alloy nanoparticles in chloroform. J Mater Chem 2003, 13:1789.