Photoemission from small metal spheres: A model calculation using an enhanced three-step model

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A calculation of photoelectron emission from small particles in the photon energy range from threshold to 11 eV is presented. The calculation is based on a three-step model accounting for the spherical geometry. It explains the anomalous shape of the yield curve observed in previous experiments on 5-nm Ag particles. This size effect is understood to be solely due to the escape function being much different from the planar case. Geometrical arguments do not fully explain the yield enhancement observed for small Ag particles in previous work.

Since the experiment of Schmidt-Ott, Schurtenberger, and Siegmann (SSS),[1] where an enhancement of the photoyield Y near threshold of a factor of 100 compared to the yield Y_∞ of a flat surface was found for small Ag particles, many theoretical efforts have been made to explain this result.[2–9] These calculations mainly consider the surface plasmon, and cannot explain the experimental enhancement Y/Y_∞ in a satisfactory way. The calculation of Chen and Bates,[2] based on geometrical considerations, gives an enhancement mainly due to a work-function shift, which is of the order of the result of SSS. However, SSS had accounted for this shift, and their value therefore does not reflect this effect.

In the experiment of SSS the silver particles were suspended in an airlike N_2-O_2 mixture. Meanwhile, their result has been confirmed by an experiment by Müller,[10] where ultrapure helium was used as a carrier gas to avoid contamination.

In another experiment, Burtscher, Schmidt-Ott, and Siegmann[11] (BSS) measured the relative photoyield for small Ag and Au particles for photon energies from threshold to 11 eV. Whereas the Au particles showed the same behavior as bulk, significant differences occurred for Ag. The yield of Ag particles increases steeper near threshold and then exhibits a flat section between 7.5 and 8.5 eV. A calculation by Faraci *et al.*[12] of $Y(h\nu)$ showed good agreement for gold particles but failed to explain the flat section in the case of silver.

Here, a calculation based on the well-known three-step model by Berglund and Spicer[13–15] with a new formulation of the escape function is presented.

In a small particle with radius R much smaller than the penetration depth of the incoming light, the photoexcitation of electrons can be considered homogeneous. The light absorption of a small sphere with imaginary refractive index n is well described by Mie's theory.[16] In a first-order approximation the absorption probability of an incident photon is given by

$$P_{\rm abs}(h\nu)=C_{\rm abs}/\pi R^2 = (8\pi R/\lambda)\,\mathrm{Im}[(n^2-1)/(n^2+2)] , \quad (1)$$

with $C_{\rm abs}$ the absorption cross section of a sphere with radius $R \ll \lambda$ and λ the wavelength of the light.

If we assume a straight trajectory within the particle, the electron starting at a point $\mathbf{r}$ with an energy E reaches the particle surface in the direction $\mathbf{e}$ with a probability

$$p_t(E)=\exp[-d(\mathbf{r},\mathbf{e})/L(E)] , \quad (2)$$

where d is the distance it must travel and $L(E)$ is the mean-free path. According to a calculation by Krolikowski,[17] $L(E)$ can be approximated by

$$L(E)=K[E(\mathrm{eV})-E_F(\mathrm{eV})]^{-3/2} \quad (3)$$

for a free-electron s band with an overlapping valence d band. For silver, the Fermi energy $E_F=5.51$ eV and $K_{\rm Ag}=150$ nm. The range of validity is $4 \le E-E_F \le 15$ eV.

The averaged probability for the electron to reach the surface in any direction $\mathbf{e}$ starting at any point $\mathbf{r}$ in the sphere is

$$P_{\rm trans\,0}(E,R)=(4\pi R^3/3)^{-1}\int d^3r\, p_t(E) = \tfrac{3}{2}[L(E)/R]^4 f_0(R/L(E)) , \quad (4)$$

where $f_0(x)=2x-3+(2x^2+4x+3)e^{-2x}$. This has been derived by Chen and Bates.[2] In order to leave the particle, the electron has to overcome the surface potential barrier $W=E_F+\Phi$. According to Fowler,[18] it has to have a kinetic energy normal to the surface greater than W. This implies that the electron has to reach the surface under an angle α smaller than the critical angle α_c:

$$\alpha \le \alpha_c = \arccos(W/E)^{1/2} . \quad (5)$$

If this is fulfilled, we assume an escape probability of unity. The averaged probability for the electron to leave the particle starting at any point $\mathbf{r}$ traveling in any direction $\mathbf{e}$ is then given by

$$P_{\rm esc\,0}(E,R) = (4\pi R^3/3)^{-1}\int d^3r\, p_t(E)\Theta(\alpha_c-\alpha) = \tfrac{3}{2}[L(E)/R]^4 \times [f_0(R/L(E))-f_0(R\cos\alpha_c/L(E))] . \quad (6)$$

$\Theta(\alpha_c-\alpha)$ is the Heaviside unit step function. Equation (6) is the first trial escape function for a sphere. In con-

trast, Chen and Bates[2] use the escape cone $\frac{1}{2}(1-\cos\alpha_c)$ from the flat surface. As we will show below, this difference is crucial.

$P_{\text{sca }0}=P_{\text{trans }0}-P_{\text{esc }0}$ is the fraction of electrons reaching the particle surface without escaping:

$$P_{\text{sca }0}(E,R)=\tfrac{3}{2}[L(E)/R]^4 f_0(R\cos\alpha_c/L(E)) . \quad (7)$$

As Chen and Bates,[2] we assume that these electrons are elastically and diffusively scattered at the surface. The averaged probability to reach the surface in a second try in direction $\mathbf{e}$ starting at $|\mathbf{r}|=R$ is

$$P_{\text{trans }1}(E,R)=(1/4\pi)\int d\Omega\, p_t(E) = \tfrac{1}{2}[L(E)/R]^2 f_1(R/L(E)) , \quad (8)$$

where $f_1(x)=1-(1+2x)e^{-2x}$. The averaged escape probability for the second run is

$$P_{\text{esc }1}(E,R)=(1/4\pi)\int d\Omega\, p_t(E)\Theta(\alpha_c-\alpha) = \tfrac{1}{2}[L(E)/R]^2 \times[f_1(R/L(E))-f_1(R\cos\alpha_c/L(E))] , \quad (9)$$

and the fraction scattered again is

$$P_{\text{sca }1}(E,R)=\tfrac{1}{2}[L(E)/R]^2 f_1(R\cos\alpha_c/L(E)) . \quad (10)$$

Summing over all reflections yields the total escape function

$$P_{\text{esc tot}}(E,R)=P_{\text{esc }0}+P_{\text{sca }0}\sum(P_{\text{sca }1})^n P_{\text{esc }1} = P_{\text{trans }0}+P_{\text{sca }0}(P_{\text{trans }1}-1)/(1-P_{\text{sca }1}) . \quad (11)$$

The calculation neglects secondary electron emission.

Following Smith[15] the photoelectric quantum yield (PQY) per incident photon can be written as

$$Y_R(h\nu)=[P_{\text{abs}}(h\nu)/B] \times\int_{E_F}^{E_F+h\nu} dE\,\delta(E)\delta(E-h\nu) \times P_{\text{esc tot}}(E,R)\Theta(E-W) . \quad (12)$$

B is the normalization factor

$$B=\int_{E_F}^{E_F+h\nu} dE\,\delta(E)\delta(E-h\nu) . \quad (13)$$

$\delta(E)$ describes the optical density of states and $\delta(E)\delta(E-h\nu)$ is the joint density of states. $\delta(E)$ can be approximated by rectangular functions for silver:[19,20]

$$\delta_{\text{Ag}}(E)=\begin{cases}\frac{1}{4}, & E_F-4\text{ eV}<E\le E_F\\ \frac{10}{3}, & E_F-7\text{ eV}<E\le E_F-4\text{ eV}\\ 0, & E\le E_F-7\text{ eV} .\end{cases} \quad (14)$$

The integrals of δ over the s band and over the d band are normalized to 1 and 10, respectively. The use of the bulk density of states is justified by Wertheim, DiCenzo, and Buchanan,[21] who report visible changes in the d band width and position only for Ag particles with radii $R<1.5$ nm. For $E>E_F$ we use the same density of states as for the s band.

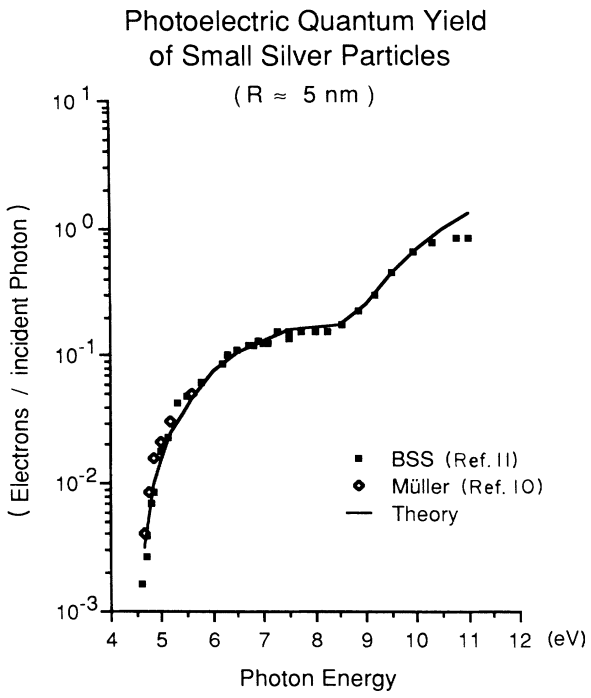

FIG. 1. Comparison of the shape of the theoretical curve with the experiment. The scale is the experimental one with an overall uncertainty of ±60%.

Figure 1 shows a comparison of the model calculation with the experimental data by BSS (Ref. 11) and Müller[10] for small silver particles 5 nm in radius. The data points from BSS were scaled to match the data by Müller near threshold. The theoretical curve was scaled by multiplying with a factor 40 to give the best conformity. The theoretical and experimental curves have identical shapes below 10 eV. Flattening of the experimental curve above 10 eV, where $Y\approx 1$, may thus be due to saturation.

Application of the model to a flat surface further corroborates the validity for Ag. The PQY per incident photon from a flat surface can be written in analogy to (12) as

$$Y_\infty(h\nu)=\{[1-R(h\nu)]/B\} \times\int_{E_F}^{E_F+h\nu} dE\,\delta(E)\delta(E-h\nu) \times P_{\text{esc tot}}(E,\infty)\Theta(E-W) . \quad (15)$$

$R(h\nu)$ is the reflectivity and $1-R$ the absorbed fraction of incident photons. The escape function $P_{\text{esc tot}}(E,\infty)$ for a plane surface has been derived by Berglund and Spicer:[13]

$$P_{\text{esc tot}}(E,\infty) = \tfrac{1}{2}\{1-\cos\alpha_c-(1/\alpha L)\ln[(1+\alpha L)/(1+\alpha L\cos\alpha_c)]\} \approx \tfrac{1}{2}[\alpha L/(1+\alpha L)](1-\cos\alpha_c) \quad (16)$$

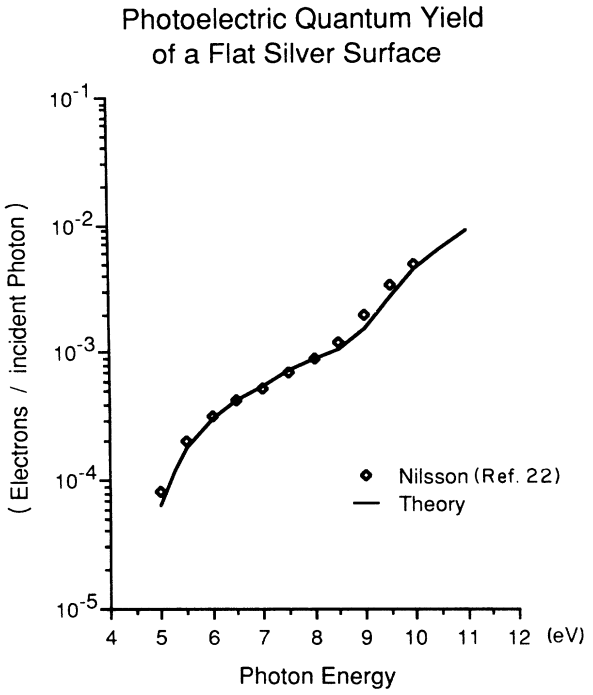

FIG. 2. Comparison of the experimental and theoretical yield of a flat silver surface.

with α the absorption coefficient given by $\alpha=(2\omega/c)\,\mathrm{Im}(n)$.

Figure 2 shows the comparison of the theory with the experimental data of Nilsson and Eastman[22] for Ag(111). They do not see any significant difference in the PQY from Ag(111) and Ag(100). The theoretical and experimental curve are in excellent agreement on an absolute scale. This result supports both the use of Eq. (4) for $L(E)$ and the approximation of the density of states. Note that our theory has no adjustable parameter.

The values of $L(E)$ are of the order of our particle radii. This has the effect that $P_{\mathrm{esc\ tot}}(E,R)\approx P_{\mathrm{esc}\ 0}(E,R)$, meaning that surface scattering hardly enhances Y. In a first-order approximation

$$P_{\mathrm{esc}\ 0}(R)\approx 1-(W/E)^2\ , \tag{17}$$

while for the flat surface

$$P_{\mathrm{esc\ tot}}(\infty)\sim 1-(W/E)^{1/2}\ . \tag{18}$$

This results in a much steeper rise of $P_{\mathrm{esc}\ 0}(R)$ compared to $P_{\mathrm{esc\ tot}}(\infty)$ with energy. $P_{\mathrm{esc}\ 0}(R)$ asymptotically reaches unity at $h\nu=7.5$ eV explaining the flat section, whereas $P_{\mathrm{esc\ tot}}(\infty)$ is still far away from its asymptotic value.

In the case of gold, this does not affect the shape of the PQY because of the much earlier onset of the d band contribution (≈ 2.4 eV below E_F) compared to silver (≈ 4 eV below E_F). Therefore particle and bulk yield are very similar as seen in the experiment.[11]

The model presented here is the first one to correctly reproduce the shape of $Y(h\nu)$ for particles as well as a flat surface of Ag. The absolute value obtained for particles is about 40 times lower than the experimental one over the entire range of photon energies considered. When the escape probability is set to unity which is equivalent to an infinite mean free path the yield increases only by a factor ≈ 7. At least the residual enhancement factor of 6 has to be explained by other arguments. We have thus shown that geometrical factors alone cannot explain the 100 times enhanced PQY of small particles. An increase of the Mie absorption cross section by an order of magnitude, constant over a wide energy range, also seems unlikely.

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