Enhancement of bulk-type multipolar second-harmonic generation arising from surface morphology of metals

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Abstract. Gold films of 20 and 150 nm nominal thickness were characterized by two-beam second-harmonic generation to address their second-order nonlinear optical responses of surface (dipolar) and bulk (higher multipolar) origin. The surface response is enhanced by \(\sim 20\%\) in the case of the 20 nm film, as expected due to its higher surface roughness. Surprisingly, the bulk-type response is enhanced to a greater extent, exceeding 80\%, and this can be explained by effective quadrupolar nonlinearity arising from the field interaction with the local nonlinearity of nanoscale surface features.

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Second-order nonlinear optical processes are electric-dipole-forbidden in media with inversion symmetry. Such processes, for example second-harmonic generation (SHG), are thus allowed at material interfaces because of broken symmetry and have become useful tools to probe surfaces and thin films. When multipole (magnetic-dipole and electric-quadruple) effects are taken into account, however, second-order effects can occur even in the bulk of centrosymmetric materials [1]. The bulk response has two important parts. The first cannot be separated from the surface response, even in principle, and thus it contributes to the effective surface non-linearity [2]. The second can be separated from the surface response. However, the distinction of this separable bulk contribution from the surface response has been a long-standing problem [2–6], only recently achieved in a quantitative and unambiguous way [7, 8] by a new SHG technique based on the use of two non-collinear fundamental beams [7–11].

Noble metals can often be described as isotropic free-electron gases, and the origin of the metal nonlinearity has been widely discussed using models based on the free-electron approaches [1, 12, 13]. Most experiments on SHG from metal surfaces have focused on the determination of the surface response [14–18]. The surface origin of the nonlinearity has also been implicated for the case of metal nanoparticles [19–21] and nanodimers [22]. The bulk effects have received much less attention in general, but have recently been used to model SHG from metal nanostructures [19, 20], including split-ring resonators [23]. Nevertheless, the separable bulk contribution was identified only very recently by two-beam SHG for a gold film [24].

Surface morphology of metals can play an important role in their nonlinear response because the nanoscale features can attract strong local electromagnetic fields [25–31]. The local-field enhancement forms the basis for surface-enhanced Raman scattering [32] and has also been shown to enhance SHG of surface origin [33]. The morphology can be controlled by the nominal thickness of the film. The film growth starts with metal islands, at some point forming a percolated network, which then starts filling in to become a continuous film, first with a rough surface and finally with a relatively smooth surface.

In this paper, we demonstrate a counterintuitive result that the nanoscale surface morphology has a much stronger influence on the bulk-type multipolar second-order response than on the surface response. To do this, we use two-beam SHG to address the relative strengths of the surface- and bulk-type effects for gold films of 20 and 150 nm nominal thickness. Compared with the thick film, the surface response is found to be enhanced by ~20% for the thin film, whereas the bulk response is enhanced by over 80%. The result is explained by phase
retardation of the local field across the nanoscale features of the surface, which gives rise to an effective quadrupolar response.

2. Theoretical background

The geometry of two-beam SHG is shown in figure 1. Two non-collinear beams \( a \) and \( b \) at the fundamental frequency \( \omega \) are obliquely incident on the gold film in the same plane of incidence, and a joint SHG signal at frequency \( 2\omega \) is detected in reflection. We define the \( xz \)-plane as the plane of incidence and the positive \( z \)-axis along the surface normal. The \( y \)-axis is thus perpendicular to the plane of incidence. The unit vector \( \hat{s} \) is uniquely defined to be perpendicular to the plane of incidence for all beams, while \( \hat{p} \) is in the plane of incidence and depends on the propagation direction of each beam.

For isotropic surfaces, the effective electric-dipole-allowed SHG response is described by only three independent components of the surface susceptibility tensor (for details, see supporting information (available from stacks.iop.org/NJP/12/063009/mmedia)): \( \chi_{xxz} = \chi_{zzx} = \chi_{yzy} = \chi_{yyz} = \chi_{zxz} = \chi_{zyy} \) and \( \chi_{zzz} \) [2]. On the other hand, the effective bulk polarization from multipolar nonlinearities in isotropic and centrosymmetric bulk materials is [1]

\[
P_{\text{bulk}} = \beta \mathbf{e} [\nabla \cdot \mathbf{e}] + \gamma [\mathbf{e} \cdot \nabla \mathbf{e}] + \delta' [\mathbf{e} \cdot \nabla] \mathbf{e},
\]

where \( \mathbf{e} \) is the electric field at the fundamental frequency \( \omega \), and \( \beta, \gamma \) and \( \delta' \) are material parameters arising from the magnetic-dipole and electric-quadrupole effects. For isotropic and homogeneous materials, the first term \( \beta \) vanishes because \( \nabla \cdot \mathbf{e} = \varepsilon^{-1} \nabla \cdot \mathbf{D} = 0 \). The inseparable term \( \gamma \) is included in the effective surface susceptibility tensor components. \( \delta' \) is thus the only term separable from the surface response and will give rise to a non-vanishing signal only when two fundamental fields are used.

We showed earlier that the surface and bulk effects can be separated from each other by analyzing the dependences of the SHG signals on the polarizations of the two fundamental beams and of the SHG field [8]. The differences are particularly clear in s-polarized SHG signals whose functional forms for the effective surface and separable bulk contributions are [7, 8, 24]

\[
E_{s,\text{surface}} \propto \chi_{sxz} \left( a_p b_s + \kappa \frac{\sin \theta_b}{\sin \theta_a} a_s b_p \right),
\]
where \( a_j \) and \( b_j \) \((j = p, s)\) are the components of the fundamental fields; \( \theta_{a,b} \) denotes the propagation angle of the fundamental beam in air; the parameter \( \kappa \) is a combination of transmission Fresnel factors of the fundamental fields at the air–gold interface, i.e. \( \kappa = t^{s}_s t^p_p / (t^{s}_a t^p_p) \) where \( t^{s}_a \), e.g., is the amplitude transmission coefficient for the \( s \)-component of beam \( a \). The tensor components \( \chi_{x x z} \) in equation (2) and \( \delta' \) in equation (3) thus appear only as overall scaling factors. The polarization dependence of the surface SHG signal is completely specified by the two incident angles, while it does not depend on the experimental geometry for the bulk signal. Most importantly, the surface and bulk signals have a very different dependence on the polarizations of the fundamental beams when \( \theta_a \) and \( \theta_b \) have the same sign.

Proper use of equations (2) and (3) requires an additional consideration as to which medium the fundamental fields are evaluated in. The surface susceptibility can be defined equally well for fields internal or external to the metal, which are interrelated by the respective Fresnel factors [24]. The bulk response, on the other hand, should be evaluated in terms of the internal fields. In the present case, however, we are interested in the possible bulk-type response as modified by the rough surface, and the evaluation of the internal fields may be ambiguous. We therefore analyze our results using equations (2) and (3) for the limiting cases of fundamental fields fully in air and fully in the bulk of gold. We emphasize that this approach does not compromise our technique because the separation of the surface and bulk effects is fundamentally based on their different symmetry properties, as is evident from the functional forms of equations (2) and (3). The second-harmonic signals are therefore fitted to the model

\[
E_{s}^{\text{total}} \propto A_{\text{surface}} (a_p b_s + \kappa \frac{\sin \theta_b}{\sin \theta_a} a_s b_p) + A_{\text{bulk}} (a_p b_s - \kappa a_s b_p),
\]

(4)

Of course, when the fields are evaluated in air, \( \kappa = 1 \). Furthermore, when fitting our data, we take \( A_{\text{surface}} \) as real. The complex value of \( A_{\text{bulk}} \) thus also provides information about the relative phase of the surface and bulk contributions.

### 3. Experiments

The samples used were 20 and 150 nm thick gold films sputtered on microscopic glass slides (supporting information (available from stacks.iop.org/NJP/12/063009/mmedia)). Note that both films were chosen to be sufficiently thick to give rise to coherent and highly directional SHG signals, unlike nominally even thinner metal island films, which give rise to diffuse and dephased SHG scattering [28]. The surface quality of the films was determined by an atomic force microscope (AFM; supporting information). The results reveal that the 150 nm (20 nm) film has a root-mean-square surface roughness of 1.1 nm (1.5 nm), peak-to-peak roughness of 8.9 nm (11.3 nm) and a characteristic lateral feature size of 80 nm (50 nm). Peak-to-peak quality is an important characteristic, because strong fields can localize to individual features with appropriate properties [29]. In addition, the 150 nm film had isolated and relatively uniform terraces of 15 nm height and 60 nm diameter at the low surface density of about 10 terraces per \( \mu \text{m}^2 \). This number is more than an order of magnitude lower than the density of characteristic features. In addition, such randomly distributed isolated features are expected to contribute to incoherent SHG scattering rather than the coherent signal. We therefore believe that the terraces are unimportant from the point of view of the measured coherent SHG response.
Both films were isotropic in the plane of the substrate, as tested by doing measurements at different azimuthal orientations of the samples. The complex refractive indices of the 150 nm film were determined with a spectroscopic ellipsometer and found to be $n(\omega) = 0.21 + i7.26$ and $n(2\omega) = 0.45 + i2.25$ for the fundamental and SH frequencies, respectively.

The SHG measurements were performed using an Nd:YAG laser (1064 nm, 70 ps, 1 kHz, 0.15 mJ) as the source of fundamental light. The laser beam was weakly focused with a 20 cm focal length lens to yield a spot size of 0.3 mm at the sample. The beam was split into two beams, which were labeled as the control beam (a) and the probe beam (b), with nearly the same intensity. The beams were applied to the same spot of the metal film with incident angles of $\theta_a = 43.8^\circ$ and $\theta_b = 16.4^\circ$, respectively. This geometry results in the value $\kappa = 0.76 + i0.06$. The control beam was linearly polarized with a continuously rotating zero-order quarter-wave plate (QWP). A calcite polarizer was used to select s-polarized SHG signal in reflection before detection with a photomultiplier tube (PMT). The PMT signal collection angle is estimated to have a numerical aperture of 0.013. However, the SHG signals were found to be more directional than this in accordance with the coherent origin of the process. When the PMT was moved to the side of the coherent signal, any possible incoherent background was indistinguishable from the noise level determined to be at least two orders of magnitude lower than the actual signal levels.

It is straightforward to show, starting from equation (4), that, in the experimental setup described, the modulation of the probe polarization by the QWP gives rise to the following functional form of the measured SH intensity:

$$I_s^\text{total} = \frac{1}{4}[(c_1 - c_2 \sin 2\varphi - c_3 \cos 2\varphi)^2 + (-c_3 + c_4 \sin 2\varphi - c_1 \cos 2\varphi)^2]I_a I_b,$$

(5)

with $c_1 = (A^\text{surface} \sin \theta_b / \sin \theta_a - A^\text{Re bulk})$, $c_2 = A^\text{Im bulk}$, $c_3 = A^\text{surface} + A^\text{bulk}$, and $c_4 = A^\text{surface}$, where $A^\text{Re bulk}$ and $A^\text{Im bulk}$ are the real and imaginary parts of the coefficient $A^\text{bulk}$ in equation (4), respectively, $\varphi$ is the rotation angle of the QWP, and $I_a$ and $I_b$ are the intensities of the two fundamental beams. In the limit where the bulk contributions do not play a role, this reduces to the form

$$I_s^\text{surface} = \frac{1}{8}[3c_5^2 + c_6^2 + (c_2^2 - c_3^2) \cos 4\varphi - 2c_5c_6 \sin 4\varphi]I_a I_b,$$

(6)

with $c_5 = \kappa A^\text{surface} \sin \theta_b / \sin \theta_a$ and $c_6 = A^\text{surface}$. The surface-only signals should thus give rise to a pure fourfold symmetry as a function of the rotation angle, whereas only twofold symmetry is observed when surface–bulk interference plays a role.

4. Results and discussion

The experimental data and theoretical fits to equation (4) are shown in figures 2(a) and (b) for the 20 and 150 nm films, respectively. For both the samples, the fourfold symmetry is broken, and the surface-only models based on external or internal fields thus fail to explain the experimental results. However, excellent fits are obtained using the model of equations (4) and (5), which accounts for the interference between the surface and bulk effects. The results of figure 2 show that the maximum SHG signal from the thin, 20 nm film is about twice as high as that from the thick, 150 nm film. However, it is interesting to note that the enhancement is even higher.

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Figure 2. The s-polarized SH intensity as a function of the rotation angle of QWP. (a) A 20 nm thick gold film. (b) A 150 nm thick gold film. The data are fitted to surface-only models based on external (pink dot-dashed line) and internal (blue dashed line) fields and a model with both surface and bulk contributions (black solid line).

Table 1. The relative values of the surface and bulk contributions to the measured SH signals for the two samples. The two cases correspond to fits where the fields are evaluated in air (external) or inside gold (internal).

| Gold films | External field | Internal field |
|------------|----------------|----------------|
|            | $A_{\text{surface}}$ | $A_{\text{bulk}}$ | $A_{\text{surface}}$ | $A_{\text{bulk}}$ |
| 20 nm      | 0.2010         | 0.034 exp($-i37^\circ$) | 0.2118         | 0.033 exp($-i62^\circ$) |
| 150 nm     | 0.1664         | 0.019 exp($-i23^\circ$) | 0.1770         | 0.015 exp($-i62^\circ$) |

for the bulk-type response (over 80%) than for the surface-type response (20%) (table 1). It is also important to note that the quality of the fits and the enhancement factors for the two samples are essentially independent of whether the fits are based on external ($\kappa = 1$) or internal ($\kappa = 0.76 + i0.06$) fields. However, the enhancement factor for the bulk-type response is seen to be different (80% external; 120% internal), depending on the choice of the reference material. Note also that the enhancement factor for the surface response is typical for these types of samples and coherent signals [16].

Our results are in overall agreement with the known result that the surface morphology of metal films strongly influences the SHG response [30, 31]. However, this result has earlier been obtained only for the surface response because it has not been possible to address the bulk-type response. Due to surface roughness, the fragmented nanoscale features of the metal surface can provide plasmonic resonances for virtually any wavelength. Such resonances are associated with strong local fields, which thereby enhance the surface response.

When the nanoscale features become sufficiently large, however, we must also consider field retardation across such features. The retardation effects can lead to an effective quadrupolar response, as observed in incoherent hyper-Rayleigh scattering from individual nanoparticles [34, 35] and in coherent SHG from lithographically designed nanostructures [19, 20].
Figure 3. Schematic diagrams of two-beam SHG for a single nanosphere in a $(u,v,w)$ coordinate system. All beams are in the $u-v$ plane and the SH signal $E$ propagates along the $u$-axis. The p polarization is in the $u-v$ plane and the s polarization is along the $w$ direction. The system has reflection symmetry with respect to the $u-v$ and $u-w$ planes and rotation symmetry by $180^\circ$ about the $u$-axis. The polarizations of the two input beams are (a) the same (either p or s polarized) or (b) orthogonal. $a_j$, $b_j$ and $E_j$ ($j = p, s$) are the components of the fundamental and SH fields, respectively. The two configurations are interrelated by reflection with respect to the $u-w$ plane.

In the following, we show that, in the two-beam geometry, such a response must have the bulk-type characteristics of equation (3) instead of the surface-type response of equation (2).

We consider the simplest possible situation, where a nanoscale feature is described by a sphere. Such a sphere has a local SHG response at its surface [35], and the SHG signal emitted into the far field is obtained as a superposition of the local responses. For example, in the presence of only one fundamental beam, the responses from the opposite sides tend to cancel each other because of symmetry, and no coherent SHG is emitted in the far field. In the presence of two fundamental beams (figure 3), the coherent SHG signal is emitted along the bisector of the directions of propagation of the fundamental beams. It is thus possible that the local responses from opposite sides do not cancel, provided that the symmetry between the local field distributions is broken.

To treat this simple situation, we use a coordinate system specific to the sphere. We take all beams to be in the $u-v$ plane and the SHG signal to propagate along the $u$-axis. The p polarizations of the beams are also in the $u-v$ plane, while s polarization, which is the same for all beams, is along the $w$-direction. The geometry thus has reflection symmetry with respect to the $u-v$ and $u-w$ planes, and rotation symmetry by $180^\circ$ about the $u$-axis. We initially treat the cases where both fundamental beams are either p or s polarized (figure 3(a)), i.e. the signals $E_p \sim a_pb_p$, $E_s \sim a_pb_p$, $E_p \sim a_sb_s$ and $E_s \sim a_sb_s$. These signals are easily seen to be forbidden by reflections with respect to the $u-w$, $u-v$, $u-w$ and $u-v$ planes, respectively (supporting information (available from stacks.iop.org/NJP/12/063009/mmedia)). The SHG signals can therefore only exist when the fundamental beams have different polarizations.
We first consider the case where the fundamental field components are \(a_p\) and \(b_s\). In this case, the \(p\)-polarized SHG signal \((E_p \sim a_p b_s)\) is forbidden because reflection with respect to the \(u-v\) plane reverses the sign of the \(s\)-component, while \(p\)-components are unchanged. The remaining case of an \(s\)-polarized SHG signal \((E_s \sim a_p b_s)\), however, cannot be made vanishing by the symmetry operations. Nevertheless, the two fundamental beams can be converted to each other by reflection with respect to the \(u-w\) plane. This operation converts \(a_p\) to \(-b_p\), \(b_s\) to \(a_s\) and \(E_s\) to \(E_p\) (figure 3(b)). Hence, the overall \(s\)-polarized SHG signal must depend on \(a_p b_s - a_s b_p\), i.e. it resembles the bulk-type contribution of equation (4). A sufficient number of appropriate nanofeatures in unit wavelength then give rise to a contribution to the measured coherent signals. Of course, a more realistic description of the nanoscale features on a surface would also influence the surface response. Nevertheless, the present simplest possible description of a nanoscale feature proves that they can also strongly influence the bulk-type response. In the present case, the differences in the surface morphology of the two samples thus had a stronger influence on the bulk-type response than on the surface-type response.

We have also considered alternative possible explanations for our results. In particular, the transmission of the 20 nm film is significant for both wavelengths. As equations (2) and (3) are based on a single interface, it is important to consider whether the surface contribution (which is still stronger than the bulk contribution) from the gold–substrate interface could give rise to a significant bulk-type contribution of equation (3) to the measured signal. The answer is no (supporting information (available from stacks.iop.org/NJP/12/063009/mmedia)). We estimate that this contribution modifies the measured surface-type amplitude by about 10% and could thus explain the 20% change in the surface signal. In the present case, however, this contribution has such phase that the change in the dominant signal from the front surface is very small (supporting information (available from stacks.iop.org/NJP/12/063009/mmedia)).

It is also possible that the rough surface features could scatter light into propagating surface plasmons, whose propagation length is known to be sensitive to surface roughness [36]. However, there is no particular reason why such a mechanism would favor the bulk response rather than the surface response. In addition, increased roughness leads to two counteracting mechanisms: it improves the coupling to propagating plasmons but also decreases their propagation length. Even if such a mechanism, whose description is beyond the scope of this paper, was operative, it would still be related to differences in the surface morphology of the samples, which is our main result.

Our results show that higher multipolar responses can have a superior sensitivity to the nanoscale morphology of materials than the dipolar responses. In the present case, effective quadrupolar nonlinearity arises from the interaction of the field with the local nonlinearity of the nanoscale surface features. Our qualitative model based on a sphere shows that such a response exists even for nano-objects of very high symmetry. In particular, the response would be non-vanishing even when such objects are embedded in the bulk of a host material, thus producing an effective material with macroscopic centrosymmetry, but nevertheless a non-vanishing second-order response.

The results have potential implications for new sensing concepts. It is evident that the enhancement of the bulk-type signal achieved here is orders of magnitude lower than that for surface-enhanced Raman scattering. However, the present work is only the first demonstration of such an enhancement. It is possible that further enhancements could be achieved in optimized geometries and when the surface is functionalized by molecules. In addition, SHG provides a different contrast mechanism, which can be sensitive to, e.g., molecular orientation.
The possibility of accessing the response of nano-objects embedded in bulk samples is another interesting possibility for fluid samples. Finally, the technique gives rise to a coherent, highly directional signal, which can be detected even in cases where incoherent signals collected over large solid angles are buried in undesired background signals.

It will also be interesting to explore whether nanostructuring could be used to further optimize the higher multipole nonlinear responses. Such responses could pave the way to new types of multipolar second-order materials, not limited by the traditional non-centrosymmetry requirement. It is important to note, however, that even when the magnitude of the nonlinear parameter is optimized, signal growth and phase matching over long distances will provide additional challenges in the development of such materials. Nevertheless, we believe that this possibility presents a worthy goal because it would overcome a fundamental limitation of second-order materials.

5. Summary and conclusion

In conclusion, we have used the two-beam SHG technique to investigate the origin of the nonlinear response of metal films with different nominal thicknesses. For the thin and thick samples, both surface and bulk responses were found to contribute to the measured SHG signals, and both responses were enhanced for the thin film. However, the bulk-type response was enhanced to a greater extent than the surface-type response. This counterintuitive result was explained by field retardation across the nanoscale features of the rough surface, which gives rise to an effective quadrupolar nonlinear response. In the future, it will be interesting to investigate how the various multipolar nonlinear responses behave for the recently produced ultrasmooth metal films [36].

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Supporting Information Available. We provide supporting information regarding (1) the formalism of multipole effects in the nonlinear response of surfaces and bulk materials, (2) sample fabrication, (3) atomic-force analysis of the samples, (4) detailed symmetry arguments for a sphere and (5) exclusion of surface response from the gold–substrate interface. This includes additional figures and references.

References

[1] Bloembergen N, Chang R K, Jha S S and Lee C H 1968 Optical second-harmonic generation in reflection from media with inversion symmetry Phys. Rev. 174 813–22
[2] Sipe J E, Mizrahi V and Stegeman G I 1987 Fundamental difficulty in the use of second-harmonic generation as a strictly surface probe Phys. Rev. B 35 9091–4
[3] Shen Y R 1999 Surface contribution versus bulk contribution in surface nonlinear optical spectroscopy Appl. Phys. B 68 295–300
[4] Guyot-Sionnest P and Shen Y R 1988 Bulk contribution in surface second-harmonic generation Phys. Rev. B 38 7985–9
[5] Wei X, Hong S, Lvovsky A I, Held H and Shen Y R 2000 Evaluation of surface vs bulk contributions in sum-frequency vibrational spectroscopy using reflection and transmission geometries J. Phys. Chem. B 104 3349–54
[6] Held H, Lvovsky A I, Wei X and Shen Y R 2002 Bulk contribution from isotropic media in surface sum-frequency generation Phys. Rev. B 66 205110
[7] Cattaneo S and Kauranen M 2005 Polarization-based identification of bulk contributions in surface nonlinear optics Phys. Rev. B 72 033412
[8] Rodríguez F J, Wang F X, Canfield B K, Cattaneo S and Kauranen M 2007 Multipolar tensor analysis of second-order nonlinear optical response of surface and bulk of glass Opt. Express 15 8695–701
[9] Figliozzi P, Sun L, Jiang Y, Matlis N, Mattern B, Downer M C, Withrow S P, White C W, Mochan W L and Mendoza B S 2005 Single-beam and enhanced two-beam second-harmonic generation from silicon nanocrystals by use of spatially inhomogeneous femtosecond pulses Phys. Rev. Lett. 94 047401
[10] Larciprete M C, Bovino F A, Giardina M, Belardini A, Centini M, Sibilia C, Bertolotti M, Passaseo A and Tasco V 2009 Mapping the nonlinear optical susceptibility by noncollinear second-harmonic generation Opt. Lett. 34 2189–91
[11] Larciprete M C, Bovino F A, Belardini A M, Sibilia C and Bertolotti M 2009 Bound and free waves in non-collinear second harmonic generation Opt. Express 17 17000–9
[12] Rudnick J and Stern E A 1971 Second-harmonic radiation from metal surfaces Phys. Rev. B 4 4274–90
[13] Sipe J E, So V C Y, Fukui M and Stegeman G I 1980 Analysis of second-harmonic generation at metal surfaces Phys. Rev. B 21 4389–402
[14] Quai J C and Simon H J 1985 Second-harmonic generation from silver and aluminium films in total internal reflection Phys. Rev. B 31 4900–5
[15] Murphy R, Yeganeh M K, Song J and Plummer E W 1989 Second-harmonic generation from the surface of a simple metal, Al Phys. Rev. Lett. 63 318–21
[16] Chang C S and Lue J T 1997 Optical second-harmonic generation from thin films Surf. Sci. 393 231–9
[17] Krause D, Teplin C W and Rogers C T 2004 Optical surface second harmonic measurements of isotropic thin-film metals: gold, silver, copper, aluminum and tantalum J. Appl. Phys. 96 3626–34
[18] O’Donnell K A and Torre R 2005 Characterization of the second-harmonic response of a silver–air interface New J. Phys. 7 154
[19] Kujala S, Canfield B K, Kauranen M, Svirko Y and Turunen J 2007 Multipole interference in the second-harmonic optical radiation from gold nanoparticles Phys. Rev. Lett. 98 167403
[20] Kujala S, Canfield B K, Kauranen M, Svirko Y and Turunen J 2008 Multipolar analysis of second-harmonic radiation from gold nanoparticles Opt. Express 16 17196–208
[21] Canfield B K, Kujala S, Laiho K, Jefimovs K, Turunen J and Kauranen M 2006 Chirality arising from small defects in gold nanoparticles arrays Opt. Express 14 950–5
[22] Canfield B K, Husu H, Laukkanen J, Bai B, Kuittinen M, Turunen J and Kauranen M 2007 Local field asymmetry drives second-harmonic generation in noncentrosymmetric nanodimers Nano Lett. 7 1251–5
[23] Klein M W, Enkrich C, Wegener M and Linden S 2006 Second harmonic generation from magnetic metamaterials Science 313 502–4
[24] Wang F X, Rodríguez F J, Albers W M, Ahorinta R, Sipe J E and Kauranen M 2009 Surface and bulk contributions to the second-order nonlinear optical response of a gold film Phys. Rev. B 80 233402
[25] Wokaun A, Bergman J G, Heritage J P, Glass A M, Liao P F and Olson D H 1981 Surface second-harmonic generation from metal island films and microlithographic structures Phys. Rev. B 24 849–56
[26] Deck R T and Grygier R K 1984 Surface-plasmon enhanced harmonic generation at a rough metal surface Appl. Opt. 23 3202–13
[27] Boyd G T, Rasing Th, Leite J R R and Shen Y R 1984 Local-field enhancement on rough surfaces of metals, semimetals, and semiconductors with the use of optical second-harmonic generation Phys. Rev. B 30 519–26

New Journal of Physics 12 (2010) 063009 (http://www.njp.org/)
[28] Stockman M I, Bergman D J, Anceau C, Brasselet S and Zyss J 2004 Enhanced second-harmonic generation by metal surfaces with nanoscale roughness: nanoscale dephasing, depolarization, and correlations Phys. Rev. Lett. 92 057402

[29] Anceau C, Brasselet S, Zyss J and Gadenne P 2003 Local second-harmonic generation enhancement on gold nanostructures probed by two-photon microscopy Opt. Lett. 28 713–5

[30] Zavelani-Rossi M et al 2008 Near-field second-harmonic generation in single gold nanoparticles Appl. Phys. Lett. 92 093119

[31] Jin R, Jureller J E and Scherer N F 2006 Precise localization and correlation of single nanoparticle optical responses and morphology Appl. Phys. Lett. 88 263111

[32] Kneipp K, Wang Y, Kneipp H, Perelman L T, Itzkan I, Dasari R R and Feld M S 1997 Single molecule detection using surface-enhanced Raman scattering (SERS) Phys. Rev. Lett. 78 1667–70

[33] Chen C K, Heinz T F, Ricard D and Shen Y R 1983 Surface-enhanced second-harmonic generation and Raman scattering Phys. Rev. B 27 1965–79

[34] Russier-Antoine I, Benichou E, Bachelier G, Jonin C and Brevet P-F 2007 Multipolar contributions of the second harmonic generation from silver and gold nanoparticles J. Phys. Chem. C 111 9044–8

[35] Dadap J I, Shan J and Heinz T F 2004 Theory of optical second-harmonic generation from a sphere of centrosymmetric materials: small-particle limit J. Opt. Soc. Am. B 21 1328–47

[36] Nagpal C P, Lindquist N C, Oh S-H and Norris D J 2009 Ultrasmooth patterned metals for plasmonics and metamaterials Science 325 594–7