TECHNICAL DIGEST

Summaries of papers presented at the

Conference on Lasers and Electro-Optics

Conference Edition

Baltimore Convention Center

Baltimore, Maryland

May 6–11, 2001

CLEO® 2001 SPONSORED BY

IEEE/Lasers and Electro-Optics Society

OSA-Optical Society of America

In Cooperation with:

Quantum Electronics Division of the European Physical Society and Optical Society Japanese Quantum Electronics Joint Group

OSA®

using this system in an *in vivo* environment for the delivery of therapeutic agents.

1. L.C. Dong, A.S. Hoffman, Thermally reversible hydrogels: III. immobilization of enzymes for feedback reaction control, J. Contr. Rel. 4, (223–227) 1986.
2. R. Averitt, D. Sarkar, N. Halas, Plasmon resonance shifts of Au-coated Au_2S nanoshells: insight into multicomponent nanoparticle growth, Phys. Rev. Lett. 78, (4217–4220) 1997.

CThF7 **11:45 am**

Metal nanoshells: a novel substrate for immunoassays

L.R. Hirsch, J.L. West, J.B. Jackson,* C.E. Moran,** N.J. Halas,† *Department of Bioengineering, Rice University, P.O. Box 1892, MS-142, Houston, TX 77251; Email: lrhirsch@rice.edu., jwest@rice.edu; *Department of Physics, Rice University, P.O. Box 1892, MS-61, Houston, TX 77251; email: jjackson@rice.edu; **Department of Chemistry, Rice University, P.O. Box 1892, MS-100, Houston, TX 77251; email: cristin@rice.edu; †Department of Electrical and Computer Engineering, Rice University, P.O. Box 1892, MS-366, Houston, TX 77251; Email: halas@rice.edu*

1. Introduction

Metal nanoshells are a novel class of nanoparticles with unique optical properties, including a tunable optical absorption and substantial enhancement of Raman scattering. Conventional roughened metal SERS substrates demonstrate optimal SERS enhancement at a single wavelength due to their fixed plasmon resonance. Metal nanoshells, however, possess a tunable plasmon resonance—permitting SERS in the Near-IR "water window" of 800–1300 nm, where deep optical penetration into biological samples should permit retrieval of Raman signals across tissue boundaries. This study examines the use of metal nanoshells as a substrate for the rapid, solution-based optical detection of analytes in complex biological solutions such as whole blood, using near-IR surface-enhanced Raman scattering.

2. Methods

Gold silica nanoshells are composed of a silica nanoparticle core, surrounded by a thin gold shell, which were manufactured as previously described.[1,2] Briefly, the silica cores were fabricated by the Stöber method.[3] The surfaces of the silica particles were aminated by reacting with aminopropyltriethoxysilane. The activated core was then seeded with gold colloid, and additional gold was reduced onto these colloid nucleation sites by chemical reduction in solution, which coalesces into a complete nanoshell.

Nanoshell-antibody activity was assessed by AFM analysis of antibody-labeled nanoshell binding to antigen-coated glass surfaces. Anti-rabbit IgG (1 mg/ml) was adsorbed onto nanoshell (2.9×10^9/ml) surfaces through chemoadsorption. Glass surfaces were coated with different concentrations of antigen. Antibody-labeled nanoshells were incubated over the antigen-coated glass for 1 hr, rinsed and examined by AFM. An Enzyme Linked Immunosorbent Assay was performed on the surfaces to determine the surface concentration of antigen.

Anti-rabbit antibody (AR) was conjugated with the Raman dye dimethylaminoazobenzine isothiocyanate (DAB). DAB-AR was adsorbed onto nanoshells (1.08×10^9/ml) at different concentrations. Spectra of the samples were collected using a Nicolet FT-Raman module (1064 nm, 700 mW, 64 scans).

Spectra were also collected in complex biological solutions. Nanoshells (1.62×10^{10}/ml) were labeled with DAB-AR and suspended in phosphate buffered saline (PBS), fetal bovine serum (FBS) and whole blood (heparinized). Spectra were collected at 700 mw, 15 scans.

3. Results

Uv-Vis spectra confirmed the synthesis of near-IR resonant nanoshells possessing a 198 nm diameter core, 13 nm shell and a peak plasmon resonance at 1064 nm. AFM revealed that antibody-labeled nanoshells successfully bind to antigen-coated surfaces of different concentration, confirming the presence of active antibody on nanoshell surfaces. These findings are in good agreement with ELISA results on the same surfaces. Near Infrared SERS detection of labeled proteins has also been demonstrated. DAB-AR labeled nanoshells produce defined peaks. Intensity analysis at the 1136 cm^{-1} peak reveals a good correlation between protein concentration and Raman intensity, with saturation occuring at ~200 µg/ml [Fig. 1]. Signals collected in FBS solutions demonstrated no attenuation compared to PBS samples, confirming that serum proteins do not interfere with the Raman signal. Spectra collected in whole blood showed minimal attenuation (31%) likely due to scattering from cellular components; however, these samples still possess sharp, defined peaks, with no increase in noise.

1. S.J. Oldenberg, R.D. Averitt, S.L. Westcott and N.J. Halas, "Nanoengineering of Optical Resonances," *Chem. Phys. Lett.*2 **88**, 243–247 (1998).
2. S.L. Westcott, S.J. Oldenberg, T.R. Lee, and N.J. Halas, "Formation and Adsorption of Clusters of Gold Nanoparticles onto Functionalized Silica Nanoparticle Surfaces," *Langmuir* **14**, 5396–5401 (1998).
3. W. Stöber and A. Fink, "Controlled growth of monodisperse silica spheres in the micron size range," *J. Coll. Interface Sci.*2 **6**, 62–69 (1968).

CThG

10:15 am–12:00 pm
Room 316/317

Optical Instrumentation and Measurements II

Brent C. Stuart, *Lawrence Livermore Natl. Lab., USA, Presider*

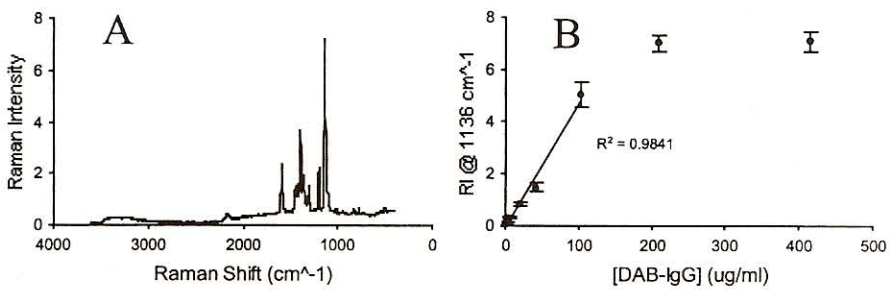
CThG1 **10:15 am**

Collisional ionization dynamics of the excited state of neon in a gas discharge plasma via time-resolved optogalvanic spectroscopy

P. Misra,* H.E. Major, C. Haridass,** *Laser Spectroscopy Laboratory, Department of Physics & Astronomy and The Center for the Study of Terrestrial & Extraterrestrial Atmospheres, Howard University, Washington, DC 20059, U.S.A.; email: pmisra@fac.howard.edu; NASA Administrator's Faculty Fellow, Aeronautics & Space Engineering Board, The National Academy of Sciences, 2101 Constitution Ave., N.W., #HA 292, Washington, DC 20418, USA. **Department of Physical Science, Belfry High School, Belfry, Kentucky, 41514 U.S.A.; Email: ksh3091@mikrotec.com*

Optogalvanic (OG) spectroscopy is a method that detects changes in the energies of atoms or molecules caused by variations in optically-induced currents. Whenever the wavelength of a laser coincides with the absorption of an atomic or molecular species in a plasma, the rate of ionization of the species momentarily increases or decreases due to laser-assisted acceleration of collisional ionization. The change in ionization rate is monitored as a variation in the transient current when a high voltage electrode is inserted into the plasma. In our work, a record of the time-resolved optoglavanic waveform helped identify the dominant physical processes and provided quantitative information on the rates of the excited state collisional processes.

A dye laser is pumped by the second harmonic of a Nd:YAG laser running at 10 Hz. The tuning range in the visible region was covered by several laser dyes. The laser beam entered a commercial Fe-Ne hollow cathode lamp. A high voltage power supply and a ballast resistor of 20 KΩ were used. The variations in the voltage across the lamp were coupled via a capacitor to a boxcar



CThF7 Fig. 1. A) SERS spetrum of DAB-IgG adsorbed onto nanoshells, and B) Raman Intensity analysis at 1136 cm^{-1} for different concentrations of DAB-IgG. Regression shows good correlation prior to saturation at 200 µg/ml.

integrator. Temporal evolution of the signal was recorded by a digital oscilloscope. Outputs of the boxcar and the photodiode were recorded using a computer aided data acquisition system.

Figure 1 shows the experimental time-resolved OG waveform for a range of discharge currents (0.6 – 1.2 mA) and extending in time from 0 to 40 μs, along with the corresponding fitted curves. The observed intensity of the OG signal, due to the $1s_2$-$2p_2$ (in Paschen notation) transition at 659.895 nm, as a function of time is given by the sum of the signals originating from all the energy states (S_2, S_3, S_4 and S_5) involved, and is given by[1]

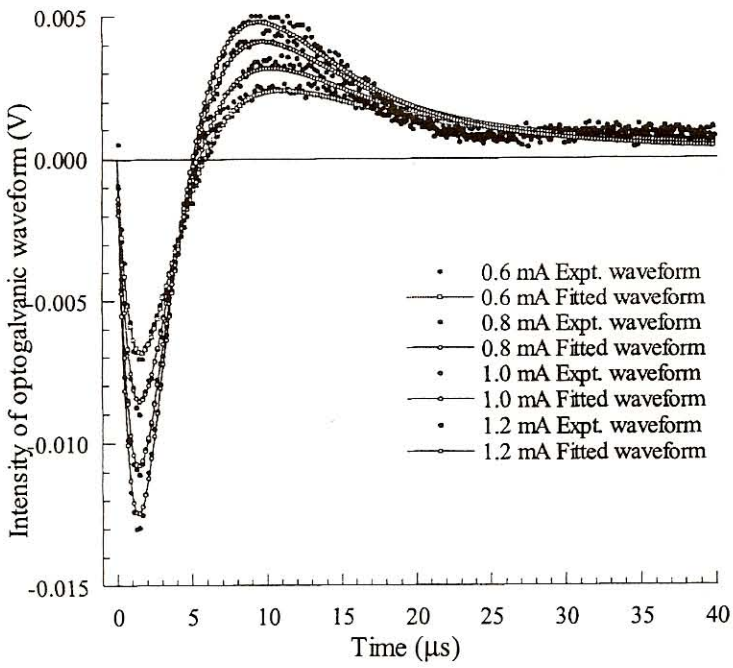
$$S(t) = \frac{a}{1-b\tau}\left(e^{-bt} - e^{-\frac{t}{\tau}}\right) - \frac{c}{1-d\tau}\left(e^{-dt} - e^{-\frac{t}{\tau}}\right)$$

$$+ \frac{e}{1-f\tau}\left(e^{-ft} - e^{-\frac{t}{\tau}}\right) + \frac{g}{1-h\tau}\left(e^{-ht} - e^{-\frac{t}{\tau}}\right) \quad (1)$$

where a, c, e and g are in turn the appropriate amplitudes and b, d, f and h are the decay rate constants for the four states involved in the transition, respectively. τ is the instrumental time constant. A non-linear least-squares fit program was used to fit Eq. (1). The values of the fitted constants, along with the standard deviations, for the four currents are given in Table 1. Owing to a high correlation between the amplitudes, the values of a, e, g and h have been fixed in the least-squares fit.

Reference

1. X.L. Han, W. Wisehart, S.E. Conner, M.-C. Su and D.L. Monts, "Collisional Ionization of Excited State Neon in a Gas Discharge Plasma," Contrib. Plasma Phys. 34, 439–452 (1995).



CThG1 Fig. 1. Fitted and observed OGE waveforms of the neon $1s_2$-$2p_2$ transition at 659.895 nm for four (0.6, 0.8, 1.0 and 1.2 mA) currents.

CThG1 Table 1. Fitted parameters of the observed optogalvanic signal of the neon $1s_2 - 2p_2$ transition for currents 0.6, 0.8, 1.0 and 1.2 mA.

	Value			
Parameter	0.6 mA	0.8 mA	1.0 mA	1.2 mA
τ (μs)	30(3)	26(2)	24(2)	22(2)
a(V)*	-7.41×10^{-1}	-8.29×10^{-1}	-8.29×10^{-1}	-8.34×10^{-1}
b(μs^{-1})	$6.84\ (45) \times 10^{-1}$	$7.25\ (38) \times 10^{-1}$	$6.93\ (55) \times 10^{-1}$	$6.71\ (66) \times 10^{-1}$
c (V)	$9.35\ (39) \times 10^{-1}$	$9.70\ (32) \times 10^{-1}$	$9.93\ (49) \times 10^{-1}$	$1.095\ (60) \times 10^{0}$
d (μs^{-1})	$2.83\ (18) \times 10^{-1}$	$2.84\ (13) \times 10^{-1}$	$3.09\ (14) \times 10^{-1}$	$3.20\ (14) \times 10^{-1}$
e(V)*	-5.01×10^{-1}	-5.01×10^{-1}	-3.80×10^{-1}	-3.80×10^{-1}
f (μs^{-1})	$2.32\ (15) \times 10^{-1}$	$2.28\ (10) \times 10^{-1}$	$2.23\ (11) \times 10^{-1}$	$2.22\ (11) \times 10^{-1}$
g(V)*	-2.51×10^{-1}	-2.76×10^{-1}	-2.59×10^{-1}	-3.91×10^{-1}
h (μs^{-1})*	7.17×10^{-1}	7.82×10^{-1}	9.64×10^{-1}	9.26×10^{-1}

*Fixed parameter in the least-squares fit.

CThG2 **10:30 am**

High-resolution spectral hole-burning spectroscopy at 580nm with an ultra-stable cw OPO

R.S. Conroy, T. Petelski, J. Mlynek, K. Bencheikh,* S. Schiller,** *Fachbereich Physik, Universität Konstanz, D-78457 Konstanz, Germany; E-mail: Richard.Conroy@uni-konstanz.de; *Laboratoire CDP, FTRD—CNRS (URA 250), B.P. 107, 92225 Bagneux Cedex, France; **Institut für Experimentalphysik, Universität Düsseldorf, D-40225 Düsseldorf, Germany.*

In order to test the Equivalence Principle of general Relativity, which encompasses the time invariance of fundamental constants and the universality of the gravitational red-shift, ultra-stable frequency sources are required with a fractional frequency instability of $<10^{-17}$. For comparison, the best current frequency standards typically have frequency instabilities of $\sim 10^{-15}$.

An important aspect in the push forward towards lower levels of instability is to use optical transitions in atoms with ultra-narrow linewidths as frequency references. The narrowest known optical transition in a solid is the $^5D_0$-$^7F_0$ (580 nm) transition in Eu^{3+}: Y_2SiO_5 at 4 K, with a linewidth of ~120 Hz.[1] With proper shielding and temperature stability of such a crystal, a transition frequency stability better than 10^{-16} appears possible. This is an attractive possibility for laser stabilisation. We have carried out the spectroscopy of this transition and burnt persistent spectral holes into the homogeneously broadened absorption with a hole linewidth <1 MHz. This is the first demonstration of high-resolution spectroscopy with a cw OPO in the visible spectral region.

The laser source used is a frequency-doubled, doubly-resonant optical parametric oscillator pumped by a monolithic CW frequency-doubled Nd:YAG. The 3.8 mW output is coarsely tunable 565–590 nm. We achieved 20 hours continuous operation in a single signal-idler mode pair without stabilisation of the pump laser. The output can be tuned via the frequency of the Nd:YAG crystal in two ways: over 18 GHz without mode-hops by slowly changing the laser crystal temperature, and quickly over 200 MHz by using a PZT attached to the Nd:YAG crystal or externally with an AOM in the 580 nm beam path (320 MHz).

We have investigated the spectroscopy of the two main sites of the Eu^{3+} ion in Y_2SiO_5. at 77 K and 4 K, as illustrated below. In addition, we have observed at least eighteen other absorption lines in agreement with the fluorescence measurements reported by Reedy et al.[2] A wavemeter (Burleigh 1500) was used to measure the frequencies at 4K as: Site 1: ν = 517178 GHz Δν = 3 GHz; Site 2: ν = 517333 GHz Δν = 2.5 GHz.

At 4 K phonon relaxation mechanisms in this crystal are reduced greatly and therefore spectral holes have been observed with lifetimes of at least several days.[3] We found that in our crystal (0.1% Eu^{3+}, 5 × 5 × 10 mm) 2 mJ of power from the free-running laser is sufficient to burn a hole of width < 1 MHz in the inhomogeneous absorption profile of Site 2 to a depth of 60%. Using a 5 μW beam, scanning continuously at 10 MHz/s over 5 GHz, the hole was still observed after 15 hours, having diminished to a depth of 8% in agreement with theoretical expectations. By