

■ Electro, Physical & Theoretical Chemistry

AurOrGlass: ORMOSIL Sol-Gel Glasses Functionalized with Gold Nanoparticles for Advanced Optical Applications

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Dubbed *AurOrGlass* in this study for the first time, organically modified sol-gel glasses functionalized with Au nanostructures and atomic clusters are endowed with exceptional optical properties. The behaviour of these plasmons is governed by

key nanochemistry and physical principles addressed herein prior to their widespread adoption in several technological domains.

1. Introduction

Aptly defined by García as “the most outstanding optical property of metal nanoparticles”,^[1] surface plasmon resonance (SPR) is accountable for the strong scattering of incident light along with the orders of magnitude local amplification of scattered light, due to collective (coherent) oscillations of free electrons of noble metal nanoparticles resonating with a typical resonant frequency, dependent on the size, shape, composition, and dielectric of the surrounding medium and on the distance between the nanoparticles (NPs).

In 1908, Mie published in the *Annalen der Physik* the complete analytical solution of Maxwell's equations for the scattering of light by a homogeneous, isotropic sphere,^[2] describing the light extinction (absorption and scattering) from spherical particles of arbitrary sizes. The theory finally explained the colour effects of colloidal gold particles due to the SPR.

The article was almost ignored until about 1945.^[3] The increasing interest in colloids since the early 1950s led to its rediscovery, and when in 2008 Wriedt opened the conference organized by the Deutsche Forschungsgemeinschaft to celebrate the 100th birthday of Mie theory, he could report how the paper was still frequently cited with some 160 citations per year, and the theory being regularly applied to subjects as different as climate research, optical particle characterization and interstellar dust.^[4]

As further underlined by García, after Mie's work, the origin of the optical properties of metallic nanoparticles was understood, but further exploitation was limited by the capabilities to synthesise and manipulate NPs in a controlled way, requiring

the development of nanotechnology at the end of the XX century for the applications of SPR to expand to many fields.^[1]

Today, SPR finds application in a variety of fields encompassing biosciences and information technology.

For example, gold thin films 10, 50 and 100 nm thick, grown on glass microscope slides via high vacuum deposition using a magnetron sputtering technique, are commercialized as optical biosensors by nanotechnology companies for real-time observation of biomolecular interactions.^[5] The surface plasmon waves, indeed, are sensitive to changes at this interface induced by the adsorption of molecules to the metal surface.^[6]

Furthermore, as this study succinctly summarizes, the SPR can be successfully tuned by varying the composition of the organically modified glass. Hence, the name we propose for this versatile class of materials: *AurOrGlass* (*Aurum* Organically-modified Glass).

As it often happens in science,^[7] the importance of the aforementioned findings concerning the exceptional optical properties of *AurOrGlass* materials is eventually being rediscovered.

Which advances in nanochemistry can be applied to further expand control on the SPR and other optical properties of these glasses? Which hurdles need to be overcome to realize the potential of at least some of the “plethora of applications”^[8] mentioned in the introductory text of almost all optical research articles devoted to silica-based materials functionalized with Au nanocrystals?

2. From Silicas to ORMOSILS

Exploiting the glass transparency, the very first report of the sol-gel molecular entrapment phenomenon concerned the encapsulation of a fluorescent organic dye, when significant enhancement in the photostability of the fluorescent probe (“of important practical consequences such as for...dye lasers”) was reported by Avnir and co-workers in 1984^[9] inaugurating the science and technology of chemistry within sol-gel glasses.

Eight years later, MacKenzie and co-workers reported that the encapsulation of Au nanoparticles in ORMOSIL (Organically Modified Silicate) from a mixture of polydimethylsiloxane

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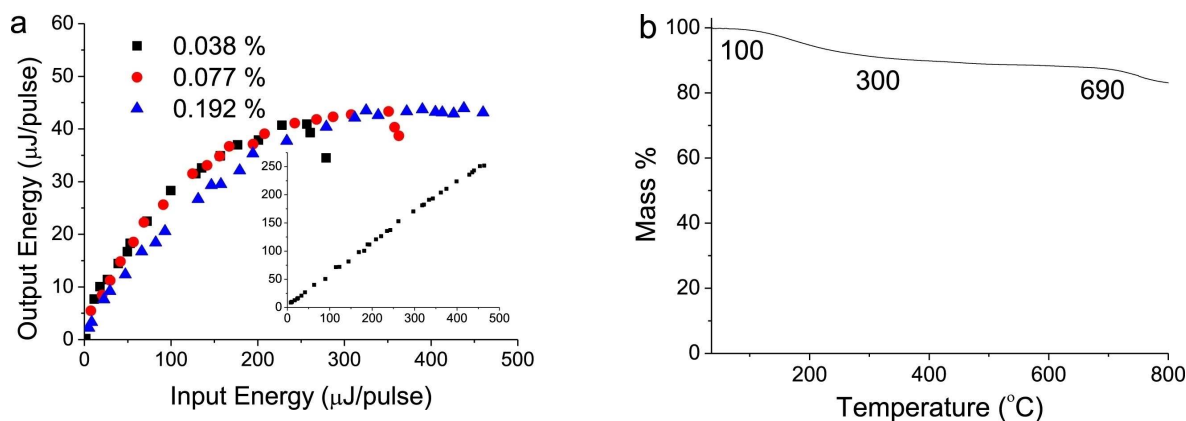


Figure 1. (a) Transmitted laser energy (output energy) vs. incident energy (input energy) from ORMOSIL glass sheets doped with Au nanorods (blank in the inset); (b) thermogravimetric analysis of glass doped with 0.192% Au nanorods. [Reproduced from Ref.16, with kind permission of Elsevier].

(PDMS) and tetraethyl orthosilicate (TEOS) resulted in “beautifully coloured disks with excellent transparency”.^[10]

The sol-gel entrapped Au^{3+} ions in the resulting yellow ORMOSIL materials were reduced to Au^0 NPs, via UV-irradiation or by thermal treatment of the aforementioned disks, originating samples in a wide range of colors, “from red, green to shades of purple-blue”,^[10] due to different resonance peaks in the wavelength region (400–800 nm) of visible light.

In the same report,^[10] the team first proposed that the response time of the doped ORMOSIL is expected to be very fast, in the subpicosecond to picosecond scale, since all attempts to measure the third order nonlinear response for the nanocomposites through the pump and probe technique failed.

Apparently, as testified by the relatively low number of citations of the aforementioned article,^[11] for about 25 years these important findings concerning ORMOSIL-entrapped Au NPs were met with limited interest by the scholarly community. On the other hand, especially thanks to pioneering work of Liz-Marzán since the mid 1990s,^[12] plentiful research attention has been devoted to Au NPs entrapped in SiO_2 .^[13]

Often referred to as “silica-coated” (a terminology which does not render the sol-gel entrapment chemical and physical phenomena),^[14] these materials possess large optical nonlinearities.^[10,12,13]

In general, the synthesis of Au@SiO_2 is easier than that of Au@ORMOSIL . For instance, Bharathi and Lev, in 1997, reported the sol-gel entrapment of Au NPs in an aminosilicate network starting from aminosilanes binding the Au^{3+} ions and stabilizing the Au nanoparticles, but “attempts to prepare gold colloids using TEOS or methyltrimethoxysilane (MTMOS) without aminosilane resulted in immediate aggregation of the gold particles during reduction with NaBH_4 ”.^[15]

3. Enhanced stable activity

Aiming at practical applications, the first finding recently rediscovered, concerns enhanced thermostability of Au nanoparticles once entrapped in an ORMOSIL matrix.

This is clearly shown by the behaviour of Au nanorods entrapped in an ORMOSIL obtained from 3-mercaptopropyl trimethoxysilane (MPS) and TEOS.^[16]

Employing an irradiation beam of 5.0 ns laser pulses at 532 nm, the ORMOSIL glass sheet (1.5 cm diameter and 2 mm thickness) doped with 0.192% Au nanorods showed both excellent optical limiting effect and high damage threshold (Figure 1).

Conversely, the ORMOSIL glasses with 0.038% and 0.077% Au content showed a sharp drop in the transmitted fluence at, respectively, input energies of 260 $\mu\text{J/pulse}$ and 340 $\mu\text{J/pulse}$, which is ascribed to laser induced surface damage of the glass surface (Figure 1a, where the blank ORMOSIL glass in the inset shows a linear relationship between the transmitted laser energy and the irradiation beam energy in whole experimental range).

The optical limiting (OL) effect of the ORMOSIL glass doped with 0.192% Au nanorods is similar to that of Au nanorods dispersed in silicone rubber matrix described by the same scholars in China in 2015.^[17]

Yet, the thermal stability of the ORMOSIL glass is considerably higher, as shown by the thermogravimetric analysis (a 10% mass loss between 100 °C and 300 °C due to the loss of organic groups linked to Si atoms, followed by combustion of the Si–C above 690 °C).

Noting the importance of protection materials against the laser damage, the team concluded that this nanocomposite material is a promising candidate for optical limiter, especially due to the enhanced thermal stability of the ORMOSIL glass matrix.^[16]

4. Tuning the surface plasmon resonance

Significant research efforts have been devoted to the synthesis of Au nanocrystals of different size and size distribution to tailor the SPR absorption band (peak position, shape and intensity). Yet, Stroyuk and co-workers lately argued,^[18] this approach led only to modest changes in the position of SPR band maximum over a broad range of Au nanocrystal size and

shape (a red shift of the SPR maximum of 50–65 nm when going from 5–10 nm to 100–110 nm nanoparticles).

4.1 Tuning the shape of the nanoparticles

A more successful approach to SPR tuning is based on altering the shape of Au nanocrystals, especially when replacing nanospheres with nanorods. As shown by El-Sayed and co-workers in 2006, using the Mie theory and a discrete dipole approximation, nanorods are the best photoabsorbing NPs offering the highest scattering contrast for imaging applications.^[19]

4.2 Altering the ORMOSIL hydrophilic-lipophilic balance

Another approach enabled by the ORMOSIL sol-gel chemistry for the entrapment of Au NPs consists in modifying the structure of the ORMOSIL embedding ceramic matrix. Klein and co-workers, for instance, recently reported the significant broadening and shift of the plasmon peak (“linked to the presence of the nanoparticles in a new medium”) for 16 nm gold citrate-capped monodisperse nanospheres entrapped in two ORMOSIL glasses.^[20]

In closer detail, Au nanoparticles were entrapped in glasses obtained via sol-gel processing of methyltriethoxysilane (MTES) and dimethyldiethoxysilane (DMDES). The monodispersed gold citrate-capped nanospheres with ~16 nm core diameter do *not* change their size during incorporation into the hybrid silica network.

Compared to the 520 nm relatively sharp peak of Au nanoparticles in solution, the same NPs encapsulated in 65 mol% MTES-35 mol% DMDES and 75 mol% MTES-25 mol% DMDES hybrid glasses with the same doping level, afford “fairly similar” spectra (Figure 2). A noticeable blue shift is evident from the

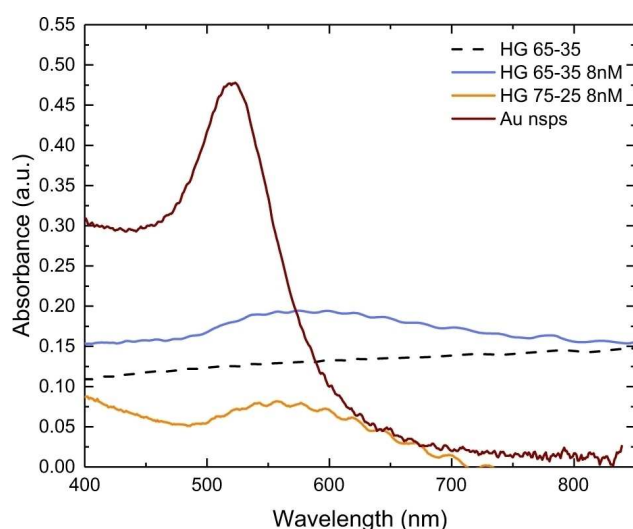


Figure 2. UV-Vis spectra of gold nanoparticles in water (brown), hybrid glass 65 mol% MTES-35 mol% DMDES without nanoparticles (dashed line), hybrid glass 65 mol% MTES-35 mol% DMDES with 8 nM gold nanospheres (blue), hybrid glass 75 mol% MTES-35 mol% DMDES with 8 nM gold nanospheres (orange). [Reproduced from Ref.20, with kind permission of Springer].

change of the NP color from red in aqueous solution to purple in sol-gel precursor solution and in the dried ORMOSIL matrices.^[20]

It is also relevant herein to notice another late 1990s finding mostly fallen into oblivion, namely that the refractive index (n) of highly transparent and crack-free ORMOSIL glasses can be tuned from 1.40 to 1.55 by tuning the ORMOSIL composition varying the relative amounts of phenyltriethoxysilane (PhTES) MTES and TEOS in the sol precursor mixture from 100% phenyl-modified silica having $n=1.559$ to organosilica of composition MTES/PhTES/TEOS=35/35/30 affording $n=1.490$.^[21]

We briefly remind that glasses with refractive index above the 1.46-1.50 range are required for good matching to standard optical fibre.

4.3 Ligand and co-dopant control of the SPR

Ending their comprehensive 2007 review on the interparticle coupling effects on the SPR of Au NPs, Pal and Ghosh concluded “that a wide range of different types of architectures of gold nanoparticles can be synthesized, and it is clear that further investigations will continue to design novel methodologies to enlarge the variety of such compounds available”.^[22]

Yet, an alternative, versatile and perhaps more convenient approach made possible by the unique versatility of the sol-gel route to functionalized silicas, is based on the introduction of a co-dopant interacting with the Au NPs.

The approach has been recently demonstrated by Stroyuk and co-workers using single layer carbon nitride (SLCN) nanosheets added at the stage of the formation of Au nanocrystals.^[18] Now, the key parameters of the SPR (absorption peak position, band shape and intensity) are tuned by chemical functionalization of the Au nanocrystals expanding control on the SPR and nonlinear optical (NLO) properties well beyond the “modest” changes observed when tuning the shape and size of the Au nanocrystals.

The SLCN nanosheets function as capping ligands at the surface of the Au NPs causing a decrease of the electron density on the noble metal nanoparticle surface. At the same time, the nanosheets suppress aggregation and direct interparticle interactions, inhibiting additional plasmonic features typical of Au nanoparticle aggregates. As a result, the method allows the SPR peak position of gold/SLCN composites to be tuned in the 520–610 nm broad range, with no distinctly shaped second SPR band in the absorption spectra of Au/SLCN nanocrystals.

Similarly, changes in the Au nanoparticle surface chemistry result in changes in the position of the SPR, as shown for example by the *slight* red-shift of the SPR upon ligand exchange for alkanethiolate-protected Au NPs (Figure 3).^[23]

In brief, we emphasize in this study, by adding to the ligand control over the electronic properties of Au NPs, the possibility to broadly tune the composition of the organically modified glass also thanks to the presence of a co-dopant, the *AurOrGlass* class of NLO materials are likely to find practical application in the numerous domains (optical communications,

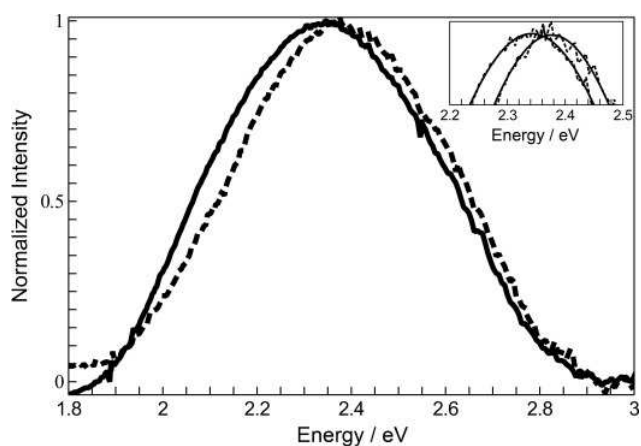


Figure 3. Isolated SPR bands for C6 (hexanethiolate-protected, dashed line) and C6/Br (hexanethiolate/4-bromothiophenolate-protected, solid line) Au nanoparticles. Inset: the experimental spectra (dashed line) and Gaussian curves (solid line) fit to these data. [Reproduced from Ref.23, with kind permission of Wiley-VCH].

optoelectronics, biosensors, photocatalysis, etc.) in which laboratory demonstration has been reported.

This has been shown in 2015 by Zheng and co-workers reporting a marked improvement of the optical limiting performance of ORMOSIL glasses co-doped with graphene oxide (GO) and Au NPs obtained through hydrolysis and polycondensation of TEOS, GPTMS, and APTES in 7:2:1 molar ratio.^[24]

Investigated via nanosecond open-aperture Z-scan technique at 532 nm, the significantly enhanced OL performance of GO/Au-doped ORMOSIL sol-gel glass at 532 nm was ascribed to SPR of the conduction electrons in the Au NPs on the surface

of GO. The TEM photographs show (Figure 4) the typical homogeneous sol-gel entrapment within the ORMOSIL inner porosity, with the 20–50 nm Au NPs (0.24 nm lattice spacing) attached to the GO surface.

5. Outlook and Conclusions

Frequently in science important scientific advances remain poorly used for years, or even decades.^[7] As succinctly shown in this study, this is the case for gold atomic clusters and nanoparticles incorporated in ORMOSIL ceramic matrices, here-in first dubbed *AurOrGlass*, in relation to their optical properties.

The rediscovered *AurOrGlass* class of materials is ready to find practical application in bioimaging, analytical chemistry, laser and photocatalysis for synthetic organic chemistry.

Demonstrating the industrial potential of the technology, noble metal (Pd, Pt) nanoparticles sol-gel entrapped in ORMOSIL matrices are widely employed as selective catalysts for multiple synthetic organic chemistry key conversions.^[25]

The sol-gel entrapment of Au nanocrystals in ORMOSIL matrices enhances the catalytic activity,^[26] making possible for instance the synthesis of valued oxygenated compounds in one pot under solvent-free conditions when the Au NPs are encapsulated within spherical ORMOSIL microparticles.^[27]

Hence, by exploiting the unique versatility of the sol-gel process, ORMOSIL xerogels doped with highly dispersed Au NPs, added during the sol-gel transition, can be obtained in any desirable shape and widely different composition,^[28] with much higher chemical stability than Au@SiO₂ materials.

Similarly, by exploiting the wide nanochemistry of Au nanocrystals (for example with the alkanethiolate chain length)^[29] the electronic and thus the optical properties of gold nanoparticles can be modulated in an ample range, whereas

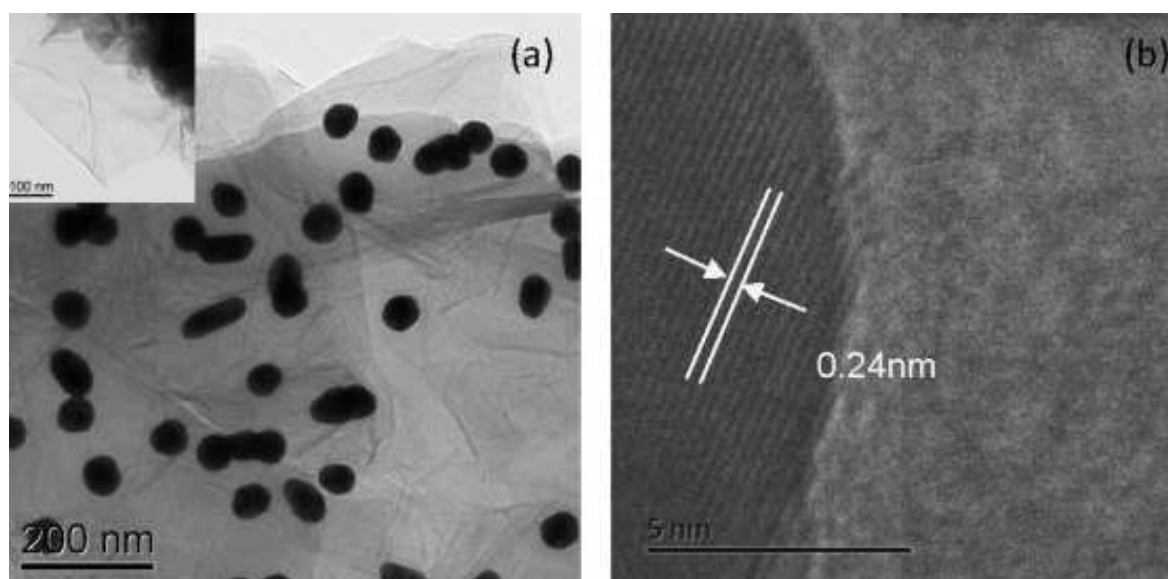


Figure 4. GO/Au@ORMOSIL glass with doping levels of 4.8×10^{-3} (mass ratio of GO/metal NP to SiO₂): (a) TEM image; (b) high resolution TEM image showing the lattice spacing of Au nanoparticles. [Reproduced from Ref.24, with kind permission of Elsevier].

the sol-gel entrapment in the ORMOSIL sol-gel cages provides the high photostability during prolonged illumination required for practical application.^[16]

In 2013 along with Béland and Pandarus we forecasted that, driven by low manufacturing cost, high reproducibility, and excellent environmental and health profile, sol-gel functional materials, and ORMOSIL xerogels in particular, were poised to find widespread use in the chemical, biotechnological, optical, construction, transportation, pharmaceutical, cosmetic, analytical, and medical industries.^[30]

Merging the “favorable electron-transfer kinetics common to gold surfaces” with the “versatility features of sol-gel-derived composite materials”, in 1997 Wang and Pamidi reported the exceptional properties of bulk Au microcrystals sol-gel entrapped in methyl-modified ORMOSIL along with glucose oxidase enzyme as glucose biosensor.^[31] Dry stored at 4 °C, strips of the new electrode retained their stable sensing activity over the period of 3 months, in which the strip was used every 3 days.

Twenty two years later, scholars in Italy replaced bulk gold with gold nanoparticles, directly formed within a 100% methyl-modified silica matrix containing graphite powder, obtaining an electrode of exceptional sensitivity and rapidity for the nonenzymatic contemporary detection of glucose, ascorbic acid and dopamine through their consecutive electrocatalytic oxidation on the surface of the Au NPs.^[32]

The “screen-printable gold biogel ink”^[31] fabricated by Wang in 1997 could now be replaced by a much cheaper xerogel ink incorporating a tiny amount of expensive gold in nanoparticulate form.

This single example of an electrochemical application of ORMOSIL-entrapped Au nanoparticles testifies how important is that “chemistry practitioners at all levels will increasingly need more education on sol-gel hybrid silicas”.^[30] Such education fostering creativity using contemporary research resources^[33] has a great deal to learn from the story of ORMOSILs functionalized with gold nanocrystals for optical applications critically reviewed in this study.

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Conflict of Interest

The authors declare no conflict of interest.

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