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ORAL PRESENTATIONS

SESSION 7. (Un)expected uses of gold

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Aulana®: Novel Nanogold Coloured Wool Textiles for Luxury Markets

Selective adsorption of 1,3-dimethyltrisulfane (DMTS) responsible for aged odor of Japanese sake with supported gold nanoparticles

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The research on the flavor of alcoholic beverages including Japanese sake have been investigated in the field of agricultural and food chemistry. The major methodologies currently used in the field to control the flavor concerns brewing process techniques and biotechnological improvements.

We introduce an approach using supported gold nanoparticles for selective removal of aged off-flavor of Japanese sake by a collaboration with sake- and catalysis researchers.

During the storages of Japanese sake, an aged odor often emerges, which is so-called *hineka* in Japanese. Dr. Isogai, one of the authors, disclosed that 1,3-dimethyltrisulfane (DMTS) is responsible for the smell. Traditionally, activated carbon has been used to reduce that but the carbon also decreases fruity flavour, so-called *ginjoka*, which arises from esters such as ethyl hexanoate. We demonstrate here, gold nanoparticles effectively adsorb DMTS without the detracting from its fruity aroma both in model solutions and real Japanese sake samples. The silica supported gold nanoparticles (Au/SiO₂) were prepared by impregnation using Au–amino acid complexes as precursors¹.

Adsorptive desulfurization using a model solution containing 4.7 mg L⁻¹ of DMTS in ethanol elucidated that smaller size of Au exhibited higher rate and equilibrium of adsorption. Langmuir-type monolayer adsorption is expected based on an adsorption isotherm experiment. Then adsorptive desulfurization were carried out with several kinds of aged odor emerged-Japanese sake samples: *daiginjo*, *junmai*, and *jukusei* in 5 L-scale. The results of instrumental analyses and sensory evaluations were most remarkable for the *daiginjo* sample, which has both strong fruity aroma and aged odor (Figure 1). DMTS concentration was 0.67 μg L⁻¹ for control, but was decreased to 0.29 μg L⁻¹ with activated carbon and 0.10 μg L⁻¹ with Au/SiO₂. On the other hand, ethyl hexanoate reduced to half with activated carbon but remained intact with Au/SiO₂. Sensory evaluation well reflected the results of the instrumental analyses.

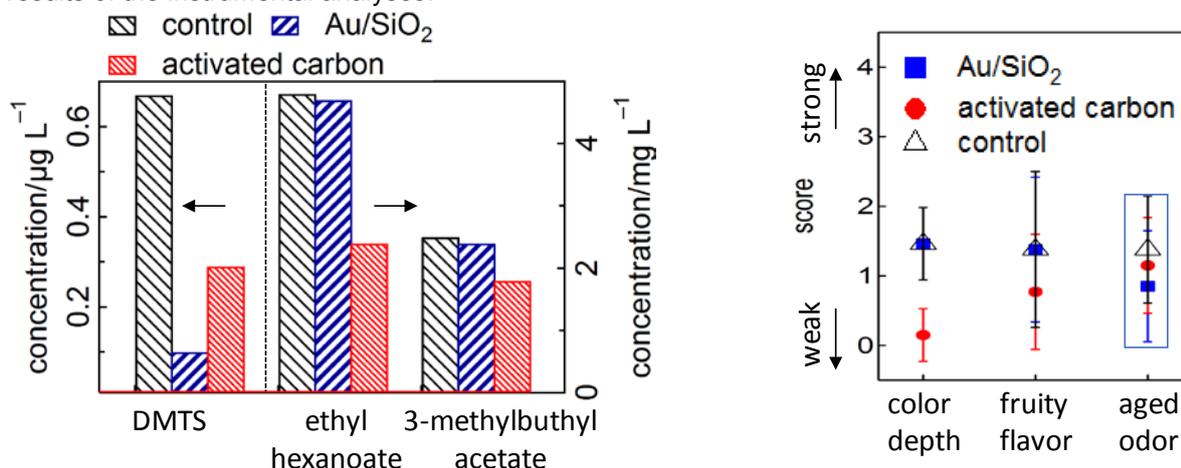


Figure 1. Instrumental analyses (left) and sensory evaluation (right) of an aged odor emerged-Japanese sake sample (*daiginjo*).

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Historically-based preparation of gold clusters supported on mesoporous materials for liquid-phase oxidation catalysts

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Gold nanoparticles and clusters have been synthesized from a two-liquid phase system by using essential oils as organic phase and a solution of gold in *aqua regia* (a solution of ammonium chloride in nitric acid) as metal source.¹ These gold entities have been immobilized on SBA-15 ordered mesoporous materials functionalized with varying amount of thiol and amino groups, which have been characterized by a variety of techniques (N_2 adsorption, TEM, UV-Vis, MAS NMR, XPS). Pore diameter of the resulting Au-materials is 6 nm. STEM-HAADF reveals the presence in the solids of gold nanoparticles, clusters and even isolated metal atoms, whose relative abundance depends upon experimental synthesis conditions and the nature of the essential oil. As an example, no nanoparticles are observed in the Au-material derived from rosemary oil, while eucalyptus oil led to both nanoparticles and nanoclusters, for metal content in the range 0.5-10 wt%. These Au-materials have been used as catalysts for the liquid-phase oxidation of cyclohexene with molecular oxygen at atmospheric pressure.^{2,3} It has been found that the activity is very much depending of the specific synthesis conditions of the gold precursor (Figure 1). Initial catalytic activity is generally low, but it increases substantially with the reaction time, while a concomitant increase of the gold particle size is also observed. This dynamic behavior of the gold entities in the reaction media, as well as the catalytic activity, seems to be governed by the chemical nature and density of the functional groups interacting with gold in the mesoporous support. However, in all cases the allylic oxidation pathway dominates over the double bond epoxidation, and 2-cyclohexeny hydroperoxide is the major product at low conversion, which transforms to the corresponding and stable enone and enol as the reaction proceeds

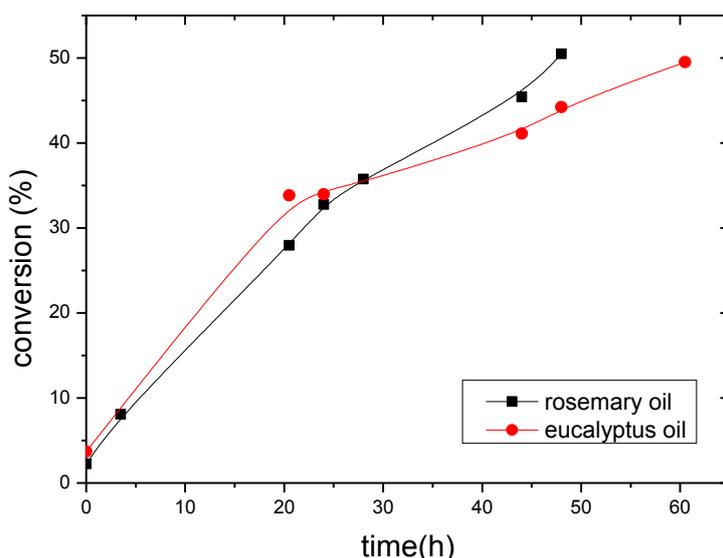


Figure 1. Conversion vs time for Au-SH-materials derived from rosemary and eucalyptus oil

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Antique black bronze; influence of Au and Ag Surface Plasmon Resonance on optical properties

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Black bronze is a surface treatment applied on bronze and copper artefacts since the Egyptian Middle Kingdom in order to produce for aesthetical effect a black colour onto copper alloys surface¹⁻³ (figure 1). It is obtained by chemical means which produce at the surface a Cu₂O (cuprite) oxide layer. If the copper alloy is completed with small additions of gold or silver or both elements, the red natural colour of cuprite is transformed to a black or bluish black colour. The development of that spectacular effect was propagated in the Aegean world and also in the Greek and Roman empires. More recently the same kind of alloys and procedure was used by the Japanese art workers since the 14th century and even in the present period. The antique chemical recipes used to obtain that effect are not precisely known, but the Japanese recipes are still used by the bronze art workers.

In the present study the Japanese recipes were used to patinate several common copper alloys containing gold and/or silver additions (a few weight percent) in order to produce the black bronze effect. For one of those, electrochemical data were collected during the patination process. Observation of the black oxide layer was done in transmission electron microscope (TEM), with the help of the EMAT (director professor D Scryvers, Antwerpen University) laboratory. The electrochemical data explained why the oxide grown on the surface during the process is majorly cuprite (Cu₂O).

TEM observations showed the occurrence of gold and/or metallic nanoparticles embedded in the oxide layer (fig. 2). Those nanoparticles are responsible for the black colour of that oxide, thanks to the Surface Plasmon Resonance effect. The size of the particles is small enough (a few nm) to produce an absorption of light reflexion. The resulting Mie peak is large enough to mask the red emission plateau due to the natural red colour of the cuprite. The reason of the black colour of the black bronzes is consequently explained for the first time.



Fig. 1. Black bronze Egyptian object. New Kingdom Sobekl:
Louvre museum, inv. E 11520. L. 18,75 cm.
© RMN-Grand Palais (musée du Louvre) /H. Lewandowski



Fig. 2 TEM micrography on a recreated black bronze
Silver or gold nanoparticles imbedded in cuprite
The inserted electron diffraction shows gold or silver
© EMAT Anvers/E. Grieten

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Aulana®: Novel Nanogold Coloured Wool Textiles for Luxury Markets

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Aulana® is a new technology and luxury nanogold-wool textile product suite, which innovatively combines the nanoscience of gold with wool fibres to produce nanogold-wool textiles in a boutique colour range for high value international luxury markets.

Aulana® captures the exciting and unique opportunity whereby the prestige and high value of gold are linked directly to the high quality of New Zealand wool through the use of nanogold as novel stable colourfast colourants in the wool, for the international high quality fashion apparel, luxury textiles and rug markets ¹ (Figure 1). This utilises the localised surface plasmon resonance properties of nanogold wherein the colour exhibited by the gold is dependent upon the size and shape of the nanogold particles and the dielectric constant of the surrounding material ^{1,2}. These nanoparticles are chemically bound to the sulfur and nitrogen containing amino acids in the wool fibre proteins on the cuticle surfaces and edges (Figure 2). Spherical particles of gold about 10-20 nm are pink-red in colour ¹⁻³. Precise control of the particle size enables the colour to be changed progressively through shades of pink, red, purple, blue-grey to grey (Figure 3). Gold nanorods potentially offer shades of blue, green and red colours, depending upon the aspect ratio of the gold nanorods ⁴, however their commercial production is problematic. We have developed an alternative synthesis for blue nanoparticles ⁵. Nanogold colourants cannot fade or denature in sunlight and hence the nanogold coloured wool products exhibit excellent lightfastness. Electronmicroscopy and associated X-ray elemental mapping and X-ray photoelectron spectroscopy show the nanogold is primarily bound to N and S entities on the cuticle edges.

The proprietary Aulana® technology and product suite have been developed on a laboratory scale and progressed to pilot and commercial scale production using combed top wool, yarn (Figure 3) and fabric, in stainless steel textile dyeing equipment. Noble Bond Ltd which owns the Aulana® brand, is commercialising Aulana® products in luxury apparel, upholstery textiles and bespoke rugs.

Aulana® is a world first technology and product suite, which has attracted interest from UK, Italian and French fashion houses. The journey along this pathway, together with the nanoscience and nanotechnology are presented here.



Figure 1: Aulana® scarf and 'Midas' rug



Figure 3: 500kg hanks of Aulana® yarn for rugs

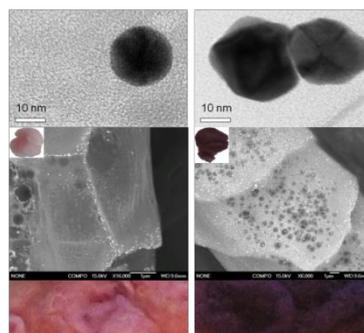


Figure 2: TEM and SEM images of gold nanoparticles on the cuticle surfaces and edges for pink and purple nanogold coloured wool

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