#### Research Assessment Exercise 2020 Impact Case Study

#### University: The Chinese University of Hong Kong Unit of Assessment (UoA): 7

**Title of case study:** Colloidal Plasmonic Metal Nanocrystals: A New Page in Food Safety and Various Photonic Applications

### (1) **Summary of the impact** (indicative maximum 100 words)

Professor Jianfang Wang's research group has developed robust methods for the synthesis of different noble metal nanocrystals at purities >90%, with responsive wavelengths widely variable from the visible (~400 nm) to mid-infrared (~10  $\mu$ m) region. This patented technology has been exploited by three spin-out companies, reaching over 1000 customers in more than 30 countries and regions. Impacts have been exerted on economy, R&D in medicine, diagnostics, biotechnologies, optical and optoelectronic devices, etc. Based on their metal nanocrystals, they invented smart tags and developed detection methods for monitoring the quality and safety of foods, beverages, drugs and explosives, etc.

## (2) Underpinning research (indicative maximum 500 words)

Materials such as gold and silver, when synthesized into nanocrystals of different shapes (sphere, rod, plate) and sizes (10 - 100 nm in at least one dimension), exhibit sharp optical spectra (**Figure 1**) because of the interplay between dielectric properties and the small dimensions (typically a fraction of an optical wavelength). In particular, their responsive wavelength bands are narrow and tunable by the shape and size, and optical intensity is strongly enhanced in regions just outside the nanocrystals. These properties open up many applications in a wide variety of areas.

Since 2006, the research team led by Prof. Wang (Professor, Department of Physics, CUHK [2005-]) has developed world-leading approaches of synthesizing noble metal nanocrystals with exquisitely controlled geometric shapes and sizes, including nanospheres [3.1], nanocubes, nanorods [3.2], nanobipyramids [3.3], nanoplates [3.4], nanocups, nanorings and nanowires, as well as multimetallic nanostructures, including Au–Ag [3.5], Au–Pd, Au–Pt and Au–Ag–Pd. By combining seed-mediated growth, oxidative etching and overgrowth, they successfully synthesized plasmonic metal nanocrystals with purity >90% and responsive wavelengths in narrow bands accurately adjustable with high precision (~5 nm) within the visible (~400 nm) to the infrared (~10  $\mu$ m) region. Three metal nanocrystal products are illustrated in Figure 2 as examples.



Figure 1: Normalized optical spectra of Au nanobipyramids of different lengths and waist diameters.



**Figure 2:** Three representative metal nanocrystal products in shapes of bipyramid [3.3], sphere [3.1] and rod [3.2]

Wang's team has demonstrated the practical uses of their high-quality plasmonic metal nanocrystals in various applications, as described below.

# Smart tags for indicating temperature history of perishable products

They invented *smart tags*, made of gold nanorods, silver ions and chemical reagents [3.6], to monitor the temperature history of perishable foods and medicines during transport and storage. The gold nanorods start out as red when affixed to the virgin samples. The silver ions gradually deposit on each nanorod, forming a shell layer, at a rate which depends very sensitively on temperature due to an activation potential. The thickness of the silver layer encodes the thermal history, and is revealed as altered colours. A period of elevated temperatures would lead to a final green colour, signifying the likelihood of spoilage or degradation. The colour-change response to temperature can be programmed using different chemical reagents, to produce customized and highly sensitive time-temperature indicators for food and medicine quality.

## Nanocrystal hot spots for molecular detection with portable spectrometers

Plasmonic metal nanocrystals focus light into nanoscale *hot spots* around the nanocrystal or in the gaps of the closely-spaced nanocrystals, with electric field intensity enhancements up to 10<sup>4</sup>. Wang's group realized the synthesis of plasmonic metal nanocrystals with carefully designed intense hot spots [3.3] and applied them for amplifying Raman signals of various target molecules, which allows for molecular detection with portable spectrometers and pushes molecular detection to parts-per-billion levels, at least an order of magnitude better than conventional methods. Their chemically synthesized, high-quality metal nanocrystal products for sensitive Raman detection are diverse, upgradable, inexpensive, and flexible for different application situations in foods, beverages, drugs and explosives.

- (3) **References to the research** (indicative maximum of 6 references)
- (\* indicates corresponding authors.)
- [3.1] Qifeng Ruan, Lei Shao, Yiwei Shu, Jianfang Wang\*, Hongkai Wu\*, "Growth of monodisperse gold nanospheres with diameters from 20 nm to 220 nm and their core/satellite nanostructures", Advanced Optical Materials 2014, 2, 65–73.
- [3.2] Weihai Ni, Xiaoshan Kou, Zhi Yang, Jianfang Wang\*, "Tailoring longitudinal surface plasmon wavelengths, scattering and absorption cross sections of gold nanorods", ACS Nano 2008, 2, 677– 686.
- [3.3] Qian Li, Xiaolu Zhuo, Shuang Li, Qifeng Ruan, Qing-Hua Xu, Jianfang Wang\*, "Production of monodisperse gold nanobipyramids with number percentages approaching 100% and evaluation of their plasmonic properties", Advanced Optical Materials 2015, 3, 801–812.
- [3.4] Feng Qin, Tian Zhao, Ruibin Jiang, Nina Jiang, Qifeng Ruan, Jianfang Wang\*, Ling-Dong Sun\*, Chun-Hua Yan\*, Hai-Qing Lin, "Thickness control produces gold nanoplates with their plasmon in the visible and near-infrared regions", Advanced Optical Materials 2016, 4, 76–85.
- [3.5] Ruibin Jiang, Huanjun Chen, Lei Shao, Qian Li, Jianfang Wang\*, "Unraveling the evolution and nature of the plasmons in (Au core)–(Ag shell) nanorods", Advanced Materials 2012, 24, OP200–OP207.
- [3.6] Chao Zhang, An-Xiang Yin, Ruibin Jiang, Jie Rong, Lu Dong, Tian Zhao, Ling-Dong Sun\*, Jianfang Wang\*, Xing Chen\*, Chun-Hua Yan\*, "Time-temperature indicator for perishable products based on kinetically programmable Ag overgrowth on Au nanorods", ACS Nano 2013, 7, 4561–4568.
- (4) **Details of the impact** (indicative maximum 750 words)

High-quality, high-performance plasmonic metal nanocrystals from Wang's team have been in continuous demand and distributed widely from research to industrial labs for various developments, leading to the following impacts:

**Impact on the economy:** Since 2006, Wang has been improving the synthesis of high-purity colloidal plasmonic metal nanocrystals. Seven Chinese patents were granted to his team from 2015 to 2019

[5.1]. Wang's spin-out company, NanoSeedz, established in 2011, provides low-cost, reliable and uniform colloidal noble metal nanocrystal products [5.2], which are widely adopted by research institutes from over 20 countries and regions [5.3]. The products are also sold to nearly every major university and research institute in mainland China [5.4]. NanoSeedz now has 3 full-time and 3 part-time employees, and yearly revenue of HKD 750K. From a latest report titled "Global Gold Nanoparticles Market 2019 By Manufacturers, Regions, Type and Application, forecast to 2024" from *Industry Research*, NanoSeedz is one of the world-leading gold nanoparticles manufacturers [5.5].

Smart tags, based on gold nanorods from NanoSeedz, successfully allow for accurate external visual check of freshness that is not readily accessible via conventional approaches. This invention received worldwide media coverage in 2014 (e.g. CBS News, Business Insider, Dairy Reporter, CBC News and Tech Times) [5.6]. The efficacy of the smart tag was revealed by CBC News, <u>"....tags could be more reliable than expiration dates if food is left exposed to higher temperatures before it's sold."</u> With the resultant commercial interest, another start-up company, Beijing Lantsai Technology Company Limited, was founded with a registered capital of RMB 20M in 2014 and investment of RMB 6.5M to commercialise the smart tags [5.7]. The company has now hired 10 full-time employees. Prototype smart tag products are being tested with food and milk companies.

The latest spin-off company, Advanced Plasmon Technologies Limited, was founded by Wang's team in 2018. The company was awarded TSSSU for HKD 0.6M in 2019, and has hired 2 people to develop a refined low-cost detection of additives in foods and beverages, and pesticides on fruits and vegetables. The invention received wide attention from the local media (e.g., Apple Daily, Headline Daily, Sing Tao Daily, Ming Pao Daily News, Wen Wei Po, Ta Kung Pao, Oriental Daily News, Metro Daily, Lion Rock Daily and Sing Pao) [5.8]. A quote from Apple Daily demonstrated its significance, <u>"This low-cost, high-precision nanochip enables more accurate detection of harmful substances in food in 30 seconds."</u>

**Impact on R&D:** Plasmonic metal nanocrystals produced by NanoSeedz have significantly helped national and international research in diverse areas, including medical diagnostics, nanomedicine, nanoparticle synthesis, photocatalysis, optics and optoelectronics. Representative works deploying NanoSeedz products are highlighted below [5.4]:

**Diagnostics:** Gold nanoparticles were employed as a novel contrast agent for breast cancer imaging (China) [5.4i]; Antibody-conjugated gold nanorods were used in innovative biosensors for the development of high-sensitivity multiplex serum cytokine immunoassays (USA) [5.4ii]; Gold nanorods were employed as biosensors for integration on a microfluidic platform to detect cytokine secretion for the development of personalized obesity treatment (USA) [5.4ii]; Thermosensitive polymer-capped gold nanorods were developed for rapid and highly sensitive spatiotemporal thermometry (China) [5.4iv].

**<u>Biomedical research</u>**: Polyethylene glycol-functionalized gold nanorods were used as ultrasound and photoacoustic imaging contrast agents to observe the neovascularization of tumors (China) [5.4v]; Polyethylene glycol-treated gold nanorods were used for the evaluation of bioaccumulation kinetics in vital mammalian organs (Spain) [5.4vi].

<u>Cancer therapy</u>: Photoresponsive gold nanorod-capped and (Chlorin e6)-doped mesoporous silica nanorods were used for photothermal and photodynamic therapy for breast cancer (China) [5.4vii]; Mesoporous silica-coated gold nanorods were adopted to achieve multi-modal ablation of breast cancer cells with photoacoustic performance (China) [5.4viii].

<u>Nanoparticle synthesis</u>: Innovative gold core–palladium shell nanoparticles were synthesized using *in situ* liquid cell transmission electron microscopy (Singapore) [5.4ix]; Gold nanobipyramids were employed to manipulate plasmon-induced polymerization process with precise local selectivity and directionality (China) [5.4x]; Polyvinylpyrrolidone-capped gold nanorods were used to prepare a large variety of core@shell nanostructures (Singapore) [5.4xi].

<u>Optics</u>: Janus nanosphere dimers consisting of gold and silicon nanospheres were applied to unidirectional light scattering (China) [5.4xii]; Multi-layered polyvinyl alcohol-functionalized gold nanorod films were used as optical data storage media (Australia) [5.4xiii].

**Impact on public welfare and education:** Prof. Wang has been actively engaged in communications to the public. Apart from the media coverage [5.6, 5.8], he was invited to exhibit his research works on metal nanocrystals in InnoCarnival 2018 [5.9] and won Bronze Medal at the 47th International Exhibition of Inventions Geneva [5.10]. The research works were showcased to the public globally and therefore achieved an extensive reach of audiences.

#### (5) Sources to corroborate the impact (indicative maximum of 10 references)

- [5.1] List of seven patents granted for Wang's colloidal plasmonic metal nanocrystals (2019)
- [5.2] NanoSeedz website: http://nanoseedz.com/
- [5.3] List of countries and regions adopting Nanoseedz products (2019): Australia, China, Canada, Germany, Hong Kong SAR, Israel, Italy, Japan, Netherlands, Saudi Arabia, Singapore, South Korea, Spain, Sweden, Taiwan, Thailand, UK, USA, Czech, United Arab Emirates and Macau SAR
- [5.4] List of diverse research works deploying Wang's colloidal plasmonic metal nanocrystals (2019)
- [5.5] Latest Gold Nanoparticles Market Report 2024 on NBC29.com (2019)
- [5.6] News coverage of the smart tags (2014)
- [5.7] Company brochure of Beijing Lantsai Technology (2019)
- [5.8] News coverage of the sensitive Raman molecular detection using the plasmonic metal nanocrystals (2018)
- [5.9] CINTEC Report InnoCarnival 2018, "Metal Nanoparticles" (2019)
- [5.10] CUHK Press release "CUHK Receives Fourteen Awards in the 47th International Exhibition of Inventions of Geneva" (2019)