

Research Assessment Exercise 2020
Impact Case Study

University: The Chinese University of Hong Kong

Unit of Assessment (UoA): 09-Chemistry

Title of case study: Novel Fabrication of Hollow Particles Deployed in White Inks and Sunscreen Products

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

Prof. To NGAI's team has developed novel methods for synthesis of submicron hollow based on particle-stabilized emulsions, which had extensive beneficial impact through applications in ink and cosmetic industries. The hollow particle has revolutionize white ink fabrication with less sedimentation and high white opacity. Xianhong Science has successfully applied this hollow particle technology to formulate white ink in digit printing, widely sold them to electronic industries, including Lenovo, ZTE, etc. with revenue [text removed for publication] in 2018. This hollow particle technology also attracted the investment from leading chemical company BASF for developing sunscreen and daily cosmetic products.

(2) Underpinning research (indicative maximum 500 words)

Hollow particle is a kind of powder contained interior hollow structure with dimensions from nanometer to micrometer. Owing to the special properties, such as high contrast optical and excellent light scattering properties, they have been widely applied in industrial coatings that require white opacity and brightness. In addition, hollow particles are useful in other technologies such as microencapsulation and controlled drug release. However, conventional methods for preparation of hollow particles with defined properties such as size, permeability, mechanical strength, and biocompatibility are still challenging. The development of new methods to manufacture hollow particles, thereby is of ever-increasing importance.

In 2008, research group led by Prof. Ngai (Professor, Department of Chemistry, [2006-]) at CUHK has developed a novel simply strategy to fabricate liquid core-polymer shell microcapsules by first templating an oil-in-water (o/w) emulsion stabilized by an interfacial monolayer of polymer latex particles and subsequently locking the assembled particles into a robust polymeric shell through the precipitation of a polymer at the interface [3.1]. The resultant hollow particles were stable, and their final structures were preserved even after directly drying in air. They further demonstrated that colloid particles microcapsules could be produced by combining the particle-stabilized emulsion template and a solvent-mediated diffusion method, which provides an innovative and general method for making hollow particles with a high yield at room temperature [3.2].

In 2014, Ngai's group further optimized the fabrication method and described for the first time the preparation of uniform-sized hollow particles based on particle-stabilized emulsions by combining a membrane emulsification technique and polymer deposition [3.3]. This opens the doors to fabrication of functional carrier/delivery systems for active ingredient encapsulation and controlled release. They then further studied the producing of biocompatible hollow particles and evaluated their potential use as drug delivery carriers for oral insulin. The formulated hollow particles showed high drug encapsulation efficiency (up to 96.7%), a pH-triggered release profile, and a long-term hypoglycemic effect in animal testing [3.4].

In 2018, Ngai realized the synthesis of sub-micron hollow particles is even more attracting and wide-ranging interests for applications. Ngai's group further developed world-leading approaches of synthesizing all-silica hollow particles with exquisitely controlled dimensions varying from ~300 nm to tens of micrometers based on the particle-stabilized emulsions [3.5] which exert

impacts on industry and economy. Since the coatings industry has long recognized the utility of hollow latex particles as effective hiding additive for water-borne inks due to its excellent light scattering properties, Ngai has been invited to provide expert service to the Xianhong Science (Hong Kong) Co. Ltd. in the development of white ink with less sedimentation and high white opacity using his developed method in producing hollow titanium oxide (TiO₂) nanoparticles (Detailed in section 4). In addition, the global chemical company BASF has been attracted in such technique and collaborated with Ngai's group at CUHK to develop the hollow particles in formulating new sun care and daily cosmetic products.

(3) References to the research

[3.1] Zhuo Ao, Zhi Yang, Jianfang Wang, Guangzhao Zhang, **To Ngai**, "Emulsion-Templated Liquid Core-Polymer Shell Microcapsule Formation", *Langmuir* 2009, 25 (5), 2572-2574.

[3.2] Zhuo Ao, Zifu Li, Guangzhao Zhang, **To Ngai**, "Colloidosomes Formation by Controlling the Solvent Extraction from Particle-Stabilized Emulsions", *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 2011, 384 (1-3), 592-596.

[3.3] Guanqing Sun, Feng Qi, Jie Wu, Guanghui Ma, **To Ngai**, "Preparation of Uniform Particle-Stabilized Emulsions Using SPG Membrane Emulsification", *Langmuir* 2014, 30 (24), 7052-7056.

[3.4] Feng Qi, Jie Wu, Guanqing Sun, Fangfang Nan, **To Ngai**, Guanghui Ma, "Systematic Studies of Pickering Emulsions Stabilized by Uniform-Sized PLGA Particles: Preparation and Stabilization Mechanism", *Journal of Materials Chemistry B* 2014, 2 (43), 7605-7611.

[3.5] Hang Jiang, Liangzhi Hong, Yunxing Li, **To Ngai**, "All-Silica Submicrometer Colloidosomes for Cargo Protection and Tunable Release", *Angewandte Chemie International Edition* 2018, 57 (36), 11662-11666. (indicative maximum of 6 references)

(4) Details of the impact (indicative maximum 750 words)

Innovation of fabricating submicron hollow particles by Ngai's group opens new opportunities and distributed widely from research to industry for various developments, leading to the following impacts:

Impact on white ink industry

The demand for the crisp, clean and opaque white ink has been elevating as it serves as a base for printing different colour onto it. Titanium dioxide (TiO₂) nanoparticle is the major white opacifying pigment used in ink formulation, added because of its high refractive index and excellent light scattering properties, e.g., high hiding power. However, a significant challenge in formulating white ink with TiO₂ pigment is its propensity to sedimentation due to the high density of TiO₂ (4.0 – 4.5 g/cm³), which not only leads to lose the hiding power but also causes nozzle blockage during inkjet printing. There is no remediated solution to tackle this problem in the current market.

Since 2008, Ngai's group has been developing the synthesis strategy to fabricate submicron inorganic/polymer hybrid hollow particles [3.5]. His technology received attention from the Xianhong Science (Hong Kong) Co. Ltd and Ngai has been invited to provide expert advices relating to make new, stable white ink in 2018 with **consultancy service contract at [text removed for publication]** [5.1]. Ngai has helped the company to synthesize a novel, submicron sized hollow TiO₂/polymer composite nanoparticle, which finally been applied in producing white inks with "***much better dispersion stability, whiteness, better compatibility with the different types of resins and printing stability***", exerting impact on product development and economy. This breakthrough technology helped the company to **expand its white ink market**

share [text removed for publication] (the total market size of TiO₂ revenue in the world is around USD17.7B), and **widely adopted by electronic industries, such as BOE, Lenovo, ZTE, Hisense, and Oppo** [5.2]. In 2018, the company has a revenue of [text removed for publication] related to the white ink business, and among them, [text removed for publication] **revenue contributed from Ngai's invented technology** [5.2]. The company has expected that there would be a [text removed for publication] in yearly revenue related to their white ink business because of the newly developed white ink formulation which has a good printing stability in inkjet printer [5.2].

Impact on product development and ecosystem from the novel UV filters of topical sunscreen.

The active constituents in topical sunscreen products against harmful sunlight ultraviolet radiation (UVR) are UV filters. However, photodegradation of certain UV filters may occur under the sunlight exposure, producing harmful free radicals and phototoxic substances. More seriously, UV filters may penetrate through the skin and cause bioaccumulation, resulting in allergic reactions or/and contact dermatitis. A recent study in 2019 revealed the application of some sunscreens on large skin areas can cause significant amount of chemical UV filter to enter the blood stream which exceeded the FDA threshold. These filters also significantly exacerbate marine environment and threaten ecosystems.

Ngai's group invented sub-micron hollow particles from particle-stabilized emulsions and have been tested as carries to encapsulate and controlled release of active ingredients [3.5]. The invention received attention from the leading chemical company, **BASF**. A collaborative agreement with **financial support of [text removed for publication]** from the BASF was established to revolutionize hollow particles in existing sunscreen products [5.3]. According to the group leader of BASF Functional Polymers Research Asia Pacific, "*The development of inorganic hollow particles based on silane monomers and Pickering Emulsion originated from Ngai's research [3.5], may pave a faster and more flexible route, adding a valuable and environmentally-friendly new product in an already extensive sun care portfolio*" [5.4]. The new formulation possesses **high sunscreen efficiency which can minimizing the skin contact and penetration of UV filters. Meanwhile, the issue of microplastics is resolved thus eradicating the harmful effects of existing hollow particles sunscreen products to environment** [5.4]. Considering of rising global demands of sunscreen market (Estimated [text removed for publication]), Ngai's invention has provided a market solution for current formulation problems of new sunscreen and daily cosmetic products. "*The potential commercialization of Prof. Ngai's technology in inorganic hollow particles will not just bring economic impact to BASF, but also a long term impact in the conservation of aquatic ecosystems.*" [5.4].

Summary

In summary, Ngai's team has developed robust synthesis methods that enable the production of reliable and reproducible submicron hollow particles that have useful practical applications such as making new white ink and encapsulation of chemical filters in sunscreen products which have been commercialized and adopted by Xianhong Science (Hong Kong) Co. Ltd. and BASF, respectively, resulting in impact on product development, economy and marine ecosystem.

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

[5.1] Consultancy Service Contract between Prof. To Ngai and Xianhong Science (Hong Kong) Co. Ltd. (2018) (nondisclosure)

[5.2] Testimonial from Xianhong Science (Hong Kong) Co. Ltd. (2019) (nondisclosure)

[5.3] Finance support from global chemical company BASF – "Pickering approach for hollow silica spheres as UV sun lotion booster" (2018) (nondisclosure)

[5.4] Testimonial from global chemical company BASF (2019) (nondisclosure)