RamaCam: autonomous in-situ monitoring system of marine particles by combining holography and Raman spectroscopy

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***Abstract*—**

Suspended particles in the ocean play an important role in global nutrient cycles. In this paper, a novel technique for the non-contact fast identification of marine particles is reported. An integrated method of digital holography and Raman spectroscopy aiming at *in-situ* continuous monitoring of marine particles, particularly in the deep sea where the density of particles is extremely low, is proposed. A particle located in a 20 cm water channel was illuminated using a collimated continuous wave laser beam which is used to take both a hologram and Raman spectrum to identify the shape, size and composition of the suspended material. Using a compact system, we have demonstrated the morphological and chemical analysis of plastic particles in a large volume of water. Furthermore, we have developed the *in-situ* device and tested it in the deep sea at a water depth of 900 m for the first time. The technique will contribute to the understanding of global-scale marine particle distributions.

Keywords*—*Marine particles, Raman spectroscopy, Holography, In-situ optical sensing

I. INTRODUCTION

Marine suspended particles play an important role in nutrient cycles in the global ocean. Phytoplankton, the major primary producers in the marine ecosystem, absorb around 50 billion tons of carbon each year, accounting for 40% of atmospheric CO_2 removal [1, 2]. Removed carbon is transported through the food chain and stored as organic carbon (e.g., lipid) or biomineralised directly as inorganic (e.g., $CaCO_3$) carbon. These organisms, carcasses, faeces and aggregates transport nutrients from the surface to the bottom of the ocean when they sink.

Recently, thousands of tons of plastic waste are generated every year, and some of it ends up in the sea. The density of plastic debris in the ocean has been selected as an indicator of the Sustainable Development Goals set by the United Nations for the year 2030 [3]. In particular, understanding the distribution of microplastics, whose size is defined as less than 5 mm [4], is becoming an urgent global issue. The sources of microplastics are either manufactured plastic components such as powder particles for scrubbers and resin pellets for plastic product manufacturing (primary sources), or small pieces made while plastic items decompose (secondary sources) [5]. Microplastics behave similarly to natural particles and get transported to all parts of the oceans, including the deep-sea trenches [6]. They are ingested by animals, and their impact on the organisms is the subject of multiple biological studies [7].

The abundance of these particles has been important in the field of aquatic chemistry to understand the nutrient cycles as well as pollution control, and are designated as essential ocean variables, ocean parameters that require long-term global-scale monitoring [8]. Sampling surveys on the surface and bottom of the ocean have been widely performed using towed nets [9] and sediment traps [10]. While particles in deep water columns are also collected using multiple nets [11], sample collection devices [12], and remotely operated vehicles [13], deployment of these systems in deep water columns is largely constrained by sea conditions and the number of samples is limited to the capacity of the sampling device. In addition, since the numerical density of suspended particles in deep water columns is much lower than at the surface (several to several tens of particles /L [14]), data acquisition using this approach takes a significantly long time. Fast *in-situ* measurement techniques can increase survey efficiency. Conventional *in-situ* sensing techniques for particles use imaging, light scattering, and light absorption techniques. While the morphological or specific chemical (e.g. chlorophyll) information can be obtained in a non-contact manner using these sensors, they are often not sufficient to distinguish the different matters and materials such as aggregates and microplastics [15].

In this paper, we introduce a novel *in-situ* sensing device for suspended particles in deep water columns, "RamaCam", which is an integrated system of digital holographic and Raman spectroscopic techniques. In Section II, the concept of the measurement system is explained; in Section III, the demonstration of the proof of concept using a laboratory setup is shown, and in Section IV, the development of the *in-situ* device and its first sea trial are reported.

II. DESIGN

Digital holography is a focus-less imaging technique that can take monochrome images of suspended particles in a large water volume with high spatial (several tens of µm) and temporal (the order of µs) resolutions [16]. A hologram records the interference pattern formed by the waves scattered from an object in a collimated laser beam path, and those arriving directly at the detector. We combined a digital holography setup with transmission Raman spectroscopy, a molecular analytical technique that also observes forward-scattered light directed at an object, to enable fast particle identification with both morphological and chemical information in a single, large volume channel using a compact setup.

The concept of the experimental setup of the RamaCam is shown in Fig. 1. The measurement process is the following: a 20 cm measurement chamber where the water flows using a pump is constantly illuminated using a collimated continuous wave (CW) laser beam. Using the beam, holographic images are captured at a high frame rate (up to several tens of Hz) to detect a particle. When a particle is detected, the pump stops to trap the particle and a Raman measurement is initiated using the same beam as an excitation source, which takes several to several tens of seconds. After the Raman measurement, the pump and holographic imaging start again to wait for the next particle. The continuous holographic imaging is set up to store the hologram only when a particle is detected and also trigger the Raman measurement. This avoids unnecessary or "blank" data capture. The advantages of this measurement method are that both image and chemical information of particles can be taken in a large volume of water; the whole process can be fully automated; and the system is compact and simple without a filter or mesh to collect particles, which does not require frequent maintenance and is ideal for a long-term *in-situ* deployment.

III. LABORATORY EXPERIMENTS

A laboratory setup was built and two plastic pellets were measured. The details are reported in Ref. [17]. Polystyrene (PS) and poly(methyl methacrylate) (PMMA) pellets with a size of 3 mm, located in the water channel, were illuminated using a collimated CW laser beam with a diameter of 4 mm and wavelength of 785 nm. The resin pellets, which are materials in manufacturing plastic products and commonly found in surface waters and on beaches all over the world [18], were used for the experiment. PS and PMMA are typically found in aquatic environments [19] and both pellets are transparent, and similar in shape and size. Fig. 2 shows the reconstructed holographic images and Raman spectra taken for the pellets using the laboratory setup. While they look too similar to recognise the difference from the holographic images,

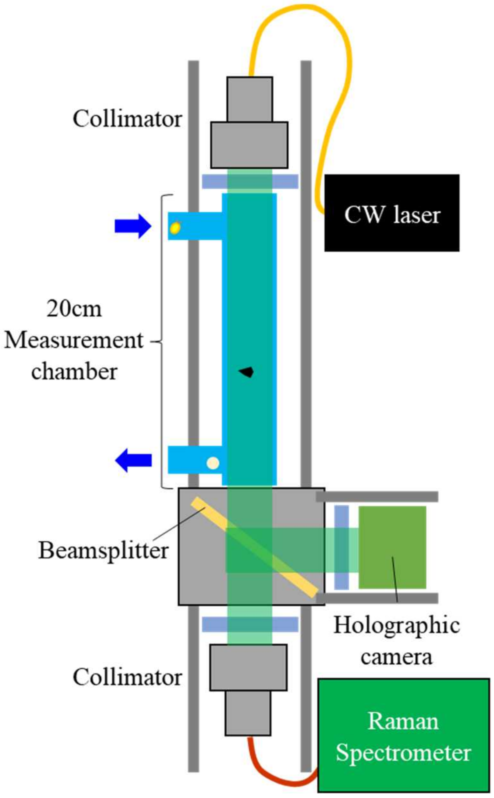

Fig. 1 Experimental setup.

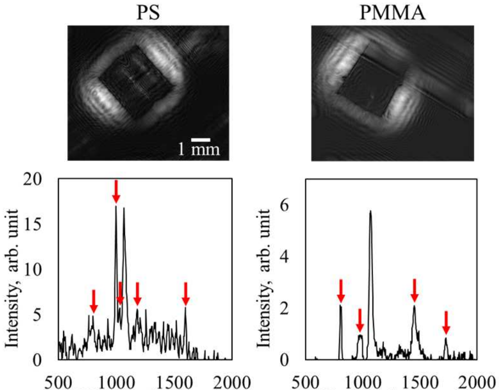

Fig. 2 Holographic images and Raman spectra of PS and PMMA pellets. Red arrows in the spectra show the corresponding Raman peaks to the materials [17] Copyright © 2020 The Authors. Published by Optica Publishing Group (spectra modified).

corresponding Raman peaks for the materials are clearly observed in the Raman spectra. The result shows the proof of concept that the identification capability of particles can be improved by the proposed method where holography and Raman spectroscopy are combined.

IV. IN-SITU RAMACAM SYSTEM

Based on the laboratory setup, the *in-situ* RamaCam device was developed. The device, shown in Fig. 3, is a 2000 m depth-rated *in-situ* suspended-particle monitoring device that has been developed at the Japan Agency for Marine-Earth Science and Technology (JAMSTEC), Japan, through collaborative work with the University of Tokyo, University of Southampton, and University of Aberdeen. The main hull is 500 mm long with a diameter of 250 mm. The total weight is 50 kg in air and 20 kg in water. While a laser with a wavelength of 785 nm and power of 150 mW was used for the laboratory setup, the wavelength and power were changed to 532 nm and 300 mW, respectively, as it generates stronger Raman peaks. The diameter of the collimated beam was extended to 10 mm from 4 mm as the excitation efficiency was improved due to the change of the laser. While strong fluorescence was a concern for the wavelength of 532 nm [20], it was experimentally confirmed that fluorescence does not suppress Raman signals and fluorescence can even add chemical information on particles when the laser with 532 nm wavelength was used for the setup. The laser, holographic camera, spectrometer, and CPU are mounted in the main hull. A laser beam is delivered to a small pressure hull where a collimator lens is mounted via a single-mode fibre cable protected by a pressure-resistant pipe. A 20 cm long measurement chamber is mounted between the main and small hulls.

The *in-situ* RamaCam device was mounted on the KM-ROV during the KM21-08 cruise of the R/V Kaimei (JAMSTEC) in October 2021. The power was supplied to the RamaCam device via a 100V AC line on the ROV. It was remotely controlled on the ship via an Ethernet communication line on the ROV and the measured data can be monitored in real-time. An inlet funnel, attached to the front side of the ROV, was connected to the measurement chamber, and an outlet was attached to the measurement chamber with a long hose. Between the measurement chamber and the outlet, a pump was connected to make the water flow. The seawater was continuously sucked through the inlet funnel and holographic images were continuously taken with a frame rate of 4 Hz. The trigger to stop the pump and initiate a Raman measurement was sent manually once a particle was observed in a raw holographic image. The acquisition time of the Raman measurement was first optimised by taking several test shots, then five Raman spectra were taken for each particle. After the Raman measurement, the pump automatically started again. While this measurement process has been already fully automated in the laboratory setup, during the sea trials, particle detection was performed manually since the illuminated area in the holographic image slightly fluctuated due to vibrations caused by the ROV during *in-situ* measurements, which may lead to false detection. RamaCam was deployed for the first time off Hatsushima, Sagami Bay, Japan (Lat. 35°00'N, Lon. 139°13'E). During the two dives of the ROV, RamaCam was successfully operated to take holographic images of natural particles in a water depth of 900 m. Fig. 4 shows examples of reconstructed holographic images taken during the dives. Most particles seen in holographic images had a size of several hundreds of μm, which are considered to be a fragment of organic matter, but they were too small for Raman measurements. While the dives were too short to catch a particle large enough to obtain the Raman spectrum, a cluster of dust particles showed a broad fluorescence pattern in the

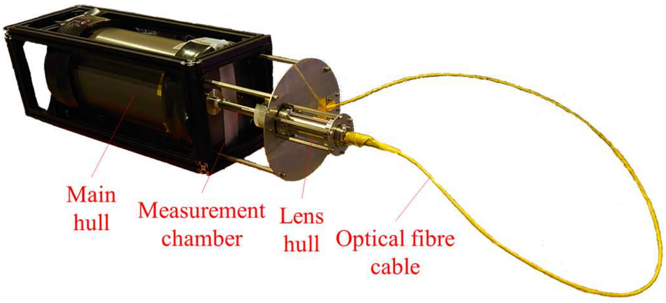

Fig. 3 *In-situ* RamaCam device.

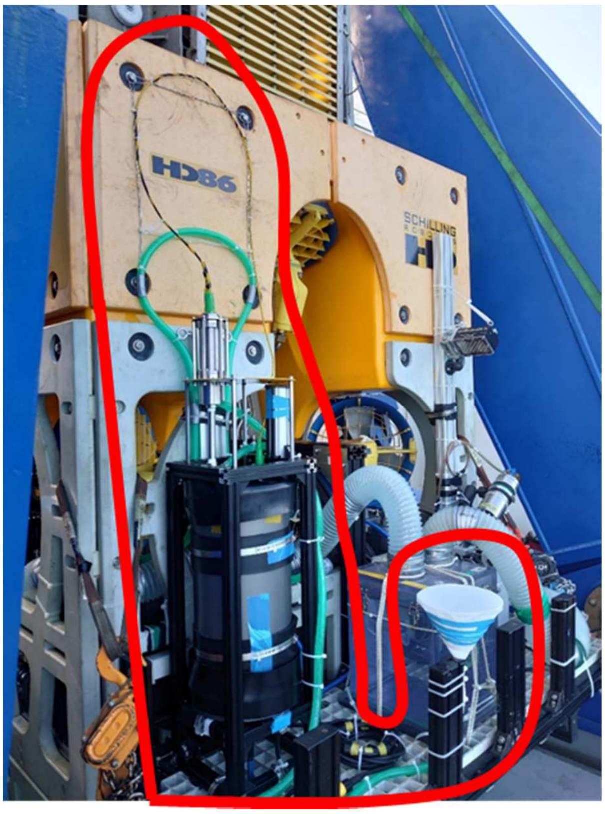

Fig. 4 RamaCam mounted on the back side of KM-ROV. The part marked in red is the *in-situ* RamaCam device.

spectra when the ROV landed on the seafloor as shown in Fig. 5, which indicates that the system worked properly.

In future works, the series of *in-situ* holographic images taken during the sea trials will be used for the development of an automatic particle detection algorithm. The system will be further improved for stand-alone operation, which is suitable for long-term observation by mounting it on autonomous platforms such as floats, landers and autonomous underwater vehicles.

V. CONCLUSION

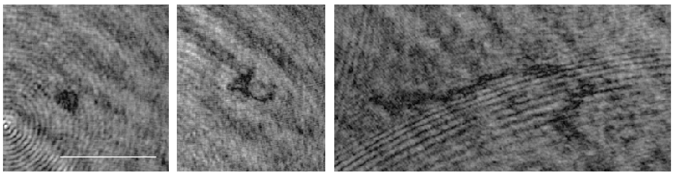

Fig. 5 Examples of in-situ holographic images. The scalebar indicate 1 mm.

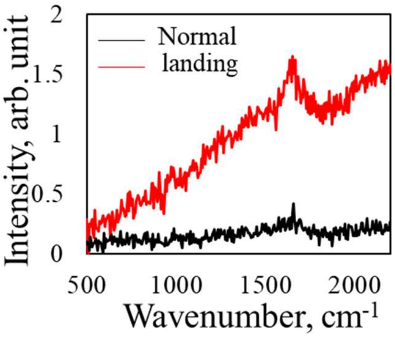

Fig. 6 Spectrum taken for a cluster of dust particles when the ROV was landing.

A novel technique for non-contact, fast identification of particles suspended in water without collection is reported by integrating digital holography and Raman spectroscopy. The proposed method demonstrates the potential for non-contact continuous *in-situ* monitoring of different kinds of marine particles such as plankton and microplastics. It is particularly promising for long-term measurements in deep water columns, where the density of particles is extremely low. Using the compact system, the morphological and chemical analysis of plastic pellets in a large volume of water was performed in the laboratory. The *in-situ* RamaCam device was developed and successfully deployed for the first time in the deep sea at a water depth of 900 m. Holographic images were continuously captured during the dives. This could be game-changing for current surveys of marine particles and will contribute to the understanding of global-scale nutrient cycles as well as microplastic pollution in the ocean.

ACKNOWLEDGEMENTS

The authors would like to thank the KM-ROV operation team and R/V Kaimei crew for their assistance during the KM21-08 cruise. The project is funded by the Japan Science and Technology Agency and Natural Environment Research Council under the SICORP program (grant number: JPMJSC1705, NE/R01227X/1). Kajima Foundation under the program of "Overseas Research Grant", and the Japan Society for the Promotion of Science (grant number: 18H03810, 18K13934).

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