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Active colloids: Progress and challenges towards realising autonomous applications

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ABSTRACT

Active colloids are small scale materials capable of producing enhanced motion within fluid environments. The field of active colloids has grown rapidly over the last ten years and is approaching maturity where viable applications are within reach. In this review, recent advances are surveyed with a strong emphasis on developments that can enable autonomous applications, where colloids execute useful tasks without external interventions. These applications are likely to prove transformative as the resulting technologies will be significantly less complex than current methods. A survey of the requirements to achieve autonomous applications is provided, considering guidance, solution compatibilities, manufacture and function; with reference to recent developments in these capacities. Following on from this, progress towards applications in environmental remediation, lab-on-a-chip microfluidics and in vivo drug delivery is highlighted.

1. Introduction

1.1. Background

Generating and controlling autonomous motion within a fluid environment is an essential component for many proposed nanometre and micron-scale technologies. While some ability to transport materials within a fluid environment is provided by Brownian diffusion and osmotic effects, in many cases these phenomena do not display the required speed or directionality. Fluidic transport problems are also faced in nature, as evidenced by the complex structures that have evolved to augment passive diffusion. For example, protein motors are used to transport attached cargo along microtubule tracks within cells [1], achieving directed motion at scales where trajectories are otherwise rapidly randomised by Brownian effects. In addition there are many examples of larger, micron sized cells, such as spermatozoa, *Escherichia coli* and algae, that can produce enhanced motion by "swimming" within fluids. These cells can also navigate based on well documented sensing mechanisms such as chemotaxis [2] and gravitaxis [3]. Partially inspired by these natural examples, and motivated by the burgeoning need to transport and organise material at small scales in order to realise new applications, attention has increasingly focused on producing synthetic devices capable of similar autonomous motion behaviour.

Two strands in the development of autonomously moving synthetic devices can be followed. At first it seemed that mimicking the deformation based swimming of the motile cells mentioned above is a promising strategy. This motivated the development of colloidal assemblies that could be manipulated to produce motion, that can be traced from a famous early example where a chain of magnetic beads executed spermatozoa like deformations [4], through simpler realisations involving fewer components [5]. However, so far the limitations imposed by low Reynolds number, requiring that deformation sequences are non-time-reversible [6], have necessitated the application of external actuating fields, such as magnetic fields or light, in order to generate synthetic motion from deformations. While these actuated colloidal devices are of significant fundamental interest, applying external field gradients to individual magnetic colloids also allows them to be efficiently transported, rotated, and manipulated [7], and so the unique benefits for using more complex deformation swimming to enable applications are hard to isolate. In this context, a second approach, which is less obviously, if at all, utilised in nature; based on the ability of chemically active colloids to modify their local environment, has proven to meet the requirement of autonomy. An early example for this concept, to produce motion by chemical activity, was reported by Whitesides, where asymmetrically distributed platinum catalyst allowed a centimetre scale device to autonomously move along a meniscus by generating a surface tension gradient while decomposing hydrogen peroxide fuel [8]. The general concept of an asymmetrically distributed reaction generating motion has subsequently been elaborated upon and miniaturised to lead to the development of the

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range of materials termed active colloids which are discussed here. Active colloids are so named to distinguish them from conventional passive colloids which exhibit purely Brownian transport behaviour.

1.2. Autonomous active colloids

The range of strategies by which surface reactions can produce motion has been the subject of several comprehensive reviews which the reader is directed towards, for example those by Kapral [9] and Sen [10]. As a broad classification, active colloids can be grouped according to geometry, and propulsion mechanism, however it is worth bearing in mind that for some examples the mechanism has been the subject of debate, and it is also possible that multiple mechanisms contribute to the observed motion. The earliest examples of small scale chemically active colloids were bi-metallic nanorods, Fig. 1a [11]. These rods produce enhanced motion by catalytically decomposing hydrogen peroxide fuel via an electrophoretic mechanism [12]. Many studies have reported a range of phenomena for these devices, including correlations between rod composition and motion velocity [13], the effect of solution properties on speed, and collective behaviour [14]. A further much studied category of active colloids, first postulated theoretically [15], are spherical Janus swimmers, Fig. 1b [16]. A common example of these devices is made by coating one hemisphere of a conventional colloid with a catalytic material, for example a platinum hemisphere decomposing dissolved hydrogen peroxide fuel. Janus colloids were initially thought to produce motion by pure self-diffusiophoresis, however recently experiments have suggested that an electrokinetic mechanism [17], related to that proposed for nanorods, may dominate. Again, extensive experiments have reported motion production across a range of colloidal sizes [18*, 19], for different materials [20], and investigated phenomena such as self-assembly [21]. For all reported bimetallic nanorod experiments, and the smaller sized examples for active Janus colloids, motion is produced without detectable bubble nucleation and release occurring at the colloid surface, despite the chemical reactions often producing a gaseous product. However, as devices get larger and less curved, the energetic penalty associated with bubble nucleation reduces [22], and examples of bubble propulsion, where motion clearly results from momentum transfer due to bubbles growing and detaching from the active surface are seen. Some examples of bubble swimmers include larger, more reactive spherical Janus colloids, Fig. 1c, made for example by partially masking an inner chemically active colloid with an inert overlayer [23]. In contrast to the smaller non-bubbling spherical colloids it has also been found that asymmetrical chemical activity is not a requirement to produce motion: uniformly chemically active colloids can also produce bubble propulsion [24,23]. The final much studied active colloid examples are rolled-up nanotubes [25], also termed nano-rockets, Fig. 1d. This swimmer type contains chemically active material localised inside a tubular structure, which generates bubbles that are expelled from one of the two open ends of the tube, resulting in rapid motion.

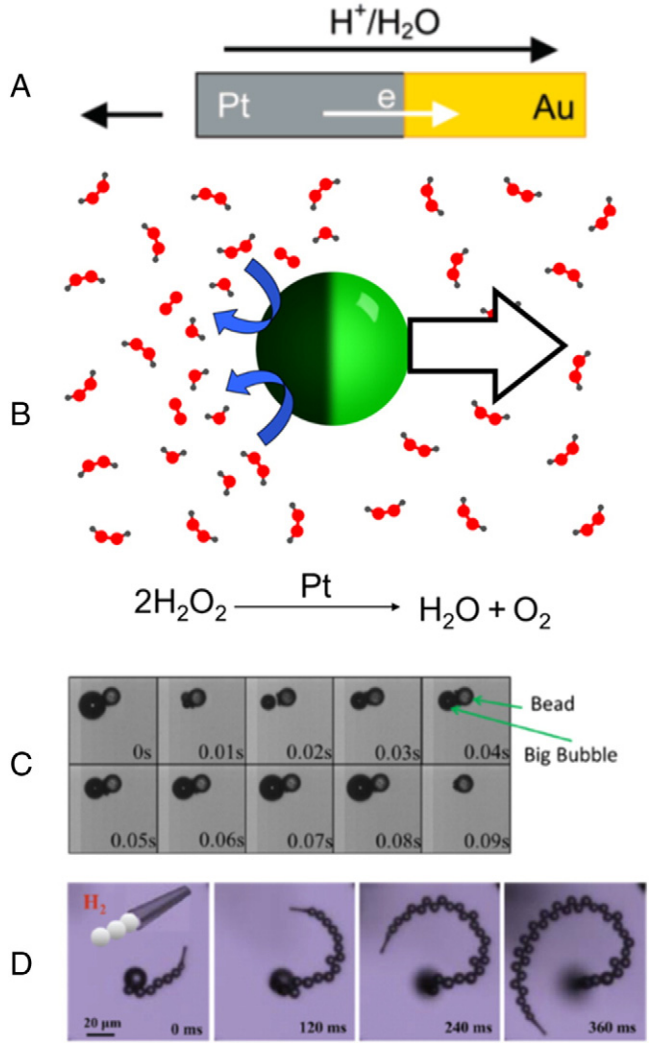

Fig. 1. Active colloids. (a) Schematic for a bi-metallic nanorod [12]. (b) Schematic for a spherical Janus active colloid. (c) Still frames from a video for a moving bubble producing spherical Janus active colloid [26]. (d) Schematic and still frames from a video for a moving bubble producing tubular active colloid [27*].

Despite this apparent diversity, all these active colloids possess the salient feature of producing motion powered solely by dissolved fuel and so offer the potential to be exploited for autonomous small scale transport applications.

1.3. Scope of review: emphasis on autonomy

This review focuses on advances made in the last three years that have the potential to contribute to the development of autonomous applications for active colloids. The remit of this review is consequently focused on active colloids that are not reliant on the application of external directing fields in order to perform a given task. This focus reflects the authors' viewpoint that any application that requires significant external control does not fully exploit the autonomous, unactuated motion capability that motivates interest in active colloids [28]. Due to this, the emerging class of active colloids that have a propulsion mechanism requiring external actuation are not discussed. These include examples such as thermophoretic devices [29] which are locally heated with a laser beam, and other examples based on de-mixing [30], electrophoresis [31], and ultrasonic agitation [32]. In addition, the review will endeavour to clearly indicate when tasks have to date only be achieved, by a "hybrid" approach: where an intrinsically autonomous motion producing device is steered or otherwise actuated by an external field [33]. While externally driven and controlled active colloids can enable applications, these are likely to be via relatively complex technologies requiring significant additional control and monitoring infrastructure. In contrast, by perusing the goal to retain autonomy in active colloid developments, simpler applications may be realised, and this is the strong focus of this perspective.

In this context, initially a "wish-list" for the functionality that will be required to produce fully autonomous applications is outlined. These features are compared with the currently reported behaviour for existing devices. Particular emphasis is placed on recognising that at present, as outlined above, there are a range of demonstrated active colloid propulsion mechanisms, each having relative advantages and disadvantages. Reviewing the state of the field without recognising this diversity has the danger of understating the challenges that must be met in order to implement a viable new technology based on active