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Self-propelling capsules as artificial microswimmers

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ABSTRACT

The mimicry of natural microswimmers by artificial nano- and micro-devices is extremely challenging because it is hard to achieve and control nanoscale actuation reproducibly and reversibly. In the context of recent developments, we shall review the basic phenomena of artificial swimming objects in the micrometer scale. Typically, these swimming devices were rigid, and up to now, the mechanisms of self-propulsion have only rarely been adapted to soft particles as microcapsules. The high flexibility of capsules is an important feature for more realistic descriptions of the basic swimming processes of biological cells. Additionally, micro- and nanocapsules show the advantage that they can store a defined amount of chemical or biological compounds in their core regions. This offers a high potential for the realization of diverse biological or medical applications (e.g. cargo transport and controlled drug delivery). The discussed phenomena are based on different chemical reactions or flow and diffusion principles, including bulk- and surface rheology, and they can be used to develop new ideas concerning the construction of advanced types of self-propelling microcapsules.

1. Introduction

Life implies movement. Bacteria, algae, sperm and other cells use rotating organelles, wave propagating flagella or motile cilia in order to move forward in a certain direction [1–3]. The different types of these moving organelles are activated by motor proteins, whereas the biological energy is often created by the hydrolysis of biomolecules such as adenosine triphosphate (ATP) [4]. This leads to conformational changes of the surrounding molecules, and these variations are then amplified by complex cellular transfer mechanisms [3]. Together with diffusive effects this finally results in translation or swimming motions [4,5]. Due to the complicated cellular structures and corresponding mechanisms, swimming motions of biological cells are still insufficiently understood [4].

The current trend of miniaturization has caused a large interest in the creation of artificial nano- and micro devices which can move forward like living cells or microorganisms [3–8]. Due to the fact that these self-propelling particles are generally not in thermodynamic equilibrium, these artificial systems are often denoted as “active colloids” [3,9,10]. “Active colloids” are dispersed systems in dimensions from nanometers to micrometers that obtain free energy from their environment and use this as driving mechanism to execute non-equilibrium activities such as growth, replication and self-propelled motility [11,12]. A fundamental difference, however, exists between “active” and “driven colloids”. A “driven colloid” is in an extrinsic non-equilibrium state due to the action of an electric, magnetic or flow field. The external energy force leads to transport properties, but the individual particles themselves are more or less passive during this process. In contrast, an “active colloid” is not in an intrinsic equilibrium with its surroundings. Each active particle generates a flow field around itself which affects its own state and the properties of neighboring particles [13,14]. In biological and medical applications it is convenient if the swimming particles can operate autonomously without applying external forces [4]. For such processes “active colloids” are better qualified than “driven particles”, which solely move after applying external fields [4,14].

To achieve controlled motion or swimming of manmade microstructures, three different conditions need to be fulfilled. First, an asymmetric shape of the swimming device is inalienable to maintain orientation and to generate motion in a desired direction [4]. Secondly, energy should be injected and transferred into propulsion (e.g. by chemical or physical–chemical reactions or by a mechanical deformation of the device). The third requirement arises from the fact that fluid dynamics at the micrometer scale is dominated by viscous rather than inertial terms. This means that a purely reversible internal displacement is not associated with any net motion (the ‘scallop theorem’) [13] and that a propelled microscopic device must thus use a swimming strategy that breaks the time-reversal invariance [13–15].

Because of the general features of small moving objects like the absence of inertia effects and the dominant influence of friction and Brownian motion [3] a continuous motion of micro-swimming devices is generally associated with problems of energy dissipation. Due to these problems actively swimming particles need an effective energy source (fuel), in order to start and maintain their motion [3]. Chemical

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reactions, heat, electric or magnetic fields, surface treadmilling, diffusion and other processes have already been used to stimulate the swimming motion of artificial objects. A schematic sketch of different mechanisms is given in Fig. 1.

1.1. Self-diffusiophoresis

Many artificial swimming devices, which were synthesized in the last years, use a phoretic transport mechanism. The first pioneering demonstration of this phenomenon occurred in 2002 when Whitesides [16], and two years later Paxton [17] and Fournier-Bidoz [18] discovered the basic mechanisms of these transport properties. Typical examples for colloidal particles showing phoretic motions are asymmetric platinum–gold (PtAu) nanorods. At the platinum side, the hydrogen peroxide was catalytically decomposed into water and oxygen. This chemical reaction generated protons in solution and electrons in the wire on the Pt end. The protons and electrons were then consumed with the reduction of H_2O_2 on the Au end. The resulting ion flux induced motion of the particle relative to the fluid, propelling the particle toward the platinum end with respect to the stationary fluid [19]. Howse et al. were among the first who synthesized polystyrene Janus-beads, which are covered on one side with a thin layer of platinum and dispersed them in aqueous hydrogen peroxide solutions, which then served as fuel [20].

1.2. Bubble propulsion

An alternative mechanism was proposed by Gibbs and Zhao in order to explain the movement of spherical Janus particles, which consisted of one platinum side and one silicon dioxide hemisphere [21]. These authors observed the formation of oxygen bubbles at the platinum surface. This phenomenon was denoted as bubble propulsion mechanism [22]. Considerable efforts have been devoted to chemically powered micro- and nanoscale motors based on the catalytic decomposition of hydrogen peroxide at platinum surfaces. Sanchez et al. have demonstrated that self-propelled microjets provide enough force to move against flowing streams and to transport spherical microparticles to a desired location [23,24]. As an alternative to platinum Vicaro et al. synthesized spherical particles which were partly covered by a monolayer of synthetic manganese catalase [25]. The reaction of these organic molecules with hydrogen peroxide induced again the formation of oxygen bubbles. A combination of glucose oxidase and catalase was used by Pantarotto et al. in order to release oxygen at the surface of rod-shaped particles in aqueous solutions of glucose [26].

Besides these investigations in three dimensions, swimming motions of colloidal particles have also been analyzed in restricted systems of two-dimensions, for instance at the water surface. Whitesides and coworkers where probably among the first who constructed millimeter sized surface swimmers [16]. The energy source of the swimming particles was again based on the catalytic reaction between platinum and hydrogen peroxide. Mano and Heller developed more complicated surface swimmers which were powered by enzymatic biochemical reactions [27]. In these experiments carbon fibers or nanotubes where functionalized at opposite ends with glucose oxidase and bilirubin oxidase [27]. The catalytic reaction of these biomolecules with glucose served as driving power unit [27]. The influence of the exothermic nature of the described chemical reactions on the propagation of the described particles is still under debate [28].

1.3. Ultrasound propulsion

Hoyos and Mallouk describe exciting experiments in which ultrasonic acoustic waves can propel, align, rotate, and assemble metallic nanowires in aqueous solutions [29]. The acoustic wave induced a local pressure gradient at the concave end of the nanowires and this leaded to a directional motion. The significance of these findings lies

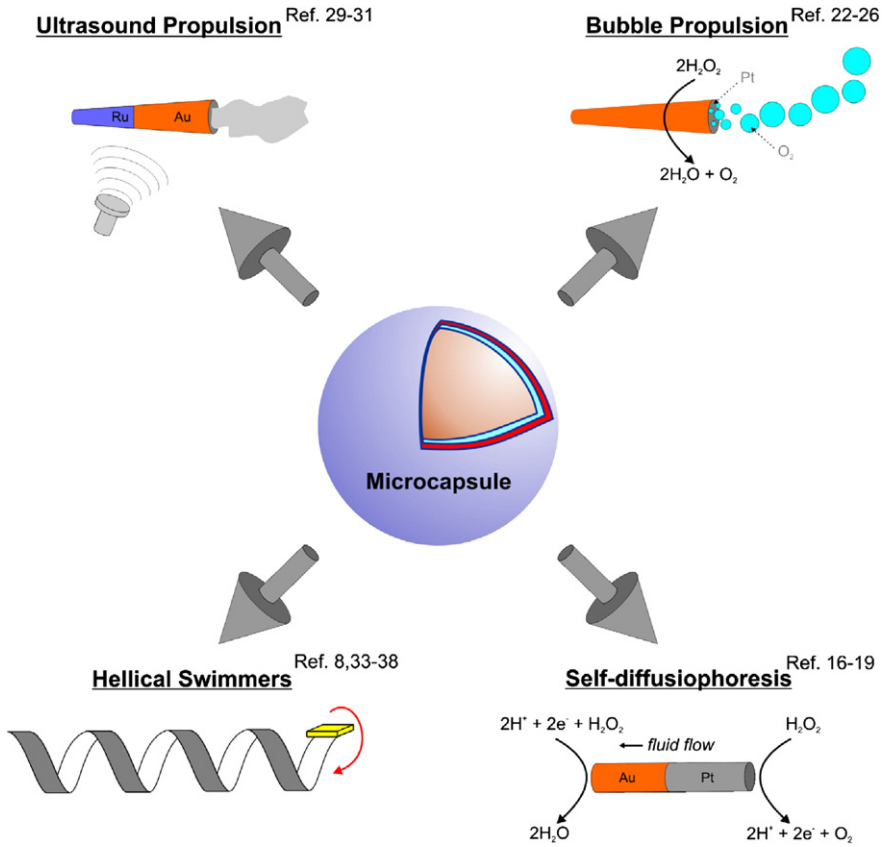

Fig. 1. Schematic drawing of different mechanisms for self-propelling microcapsules.