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M.S. OSMAN[1,4*], M. ISMAIL[2], K. KHAIRUDIN[1,6], M. FATHULLAH[3,4], C. ROJVIRIYA[5], N.F. ABU BAKAR[5], M.R. MOHD RADZI[1], N. ISA[1]

CONCISE REVIEW OF LIGHT-DRIVEN MICROMOTOR SYNTHESIS AND ITS ENVIRONMENTAL APPLICATIONS

Light-powered micromotors are a new type of micromotor that can be used for water purification treatment. This paper focuses on the synthesis processes and its application in water remediation. This mini review will highlight the great potential of these light powered micromotor as well as the significance of preparing them for environmental applications. Photocatalytic micromotors or light-powered micromotors have been intensively researched over the last several years for several applications, such as environmental remediation, biomedicine and micropumps. It has been found that conventional wastewater treatment is commercially inefficient in water remediation. The emphasis then was on a new solution of using micromotor as a potential replacement for water remediation. Many studies have been carried out over the years on the synthesis of these light-powered micromotors, which revolves around the materials used, and applications. This paper, therefore, reflects on the advancement of light-powered micromotors and will be concentrating on the synthesis processes and its application in water remediation. This mini-review will highlight the great potential of these light-driven micromotors as well as the significance of preparing them for environmental applications.

Keywords: Photocatalytic; light-powered; micromotor; synthesis; environmental application

1. Introduction

Micromotors or nanomotors have been studied intensively for the past few years with an increasing number of publications from the year 2012 to 2017 [1]. Its unique material selection and mobility have become the factors in their wide applications such as sensing [2], environmental remediation [3-8], biological/chemical warfare agents [9,10], and cargo transportation [11,12]. Throughout the years, tremendous progress can be seen regarding the fabrication of micro/nanomotors to widen the applicability of its function. There are different types of micro/nanomotors which include polymer stomatocytes, helical microswimmers, biohybrids nanomotor, sporopollenin exine-based micromotors and Janus micromotors [1]. For example, Janus micromotor, as shown in Fig. 1, has received much attention due to its uniqueness. Janus micromotor usually involves two or more distinct physical properties which provide more efficient propulsion and also selective function [1].

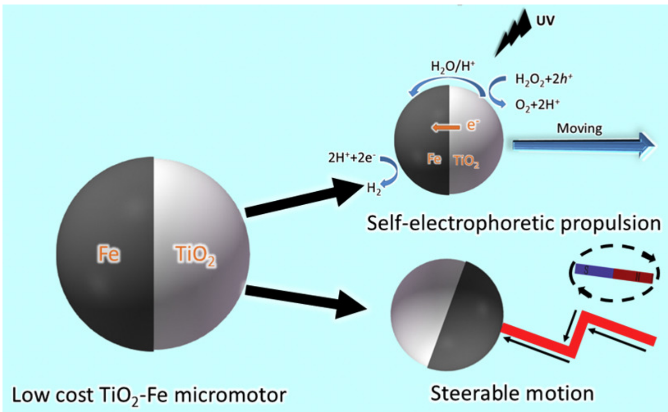

Fig. 1. Asymmetry structure of Janus micromotors [13]

All these micro/nanomotors are autonomously triggered through the usage of chemical fuels such as pure hydrogen peroxide (H_2O_2) and pure water [14]. Chemical fuels that are

1 UNIVERSITI TEKNOLOGI MARA EMZI-UITM NANOPARTICLES COLLOIDS & INTERFACE INDUSTRIAL RESEARCH LABORATORY (NANO-CORE), CHEMICAL ENGINEERING STUDIES, COLLEGE OF ENGINEERING, CAWANGAN PULAU PINANG, PERMATANG PAUH CAMPUS, 13500 PULAU PINANG, MALAYSIA
2 EMZI HOLDING SDN BHD, H-2, AVENUE 2/1, KEDAH HALAL PARK,08000 SUNGAI PETANI, KEDAH, MALAYSIA
3 UNIVERSITI MALAYSIA PERLIS (UNIMAP), SCHOOL OF MANUFACTURING ENGINEERING, PAUH PUTRA CAMPUS, 02600 ARAU, PERLIS, MALAYSIA
4 CENTER OF EXCELLENCE GEOPOLYMER & GREEN TECHNOLOGY (CEGEOGTECH), 01000 KANGAR, PERLIS, MALAYSIA
5 SYNCHROTRON LIGHT RESEARCH INSTITUTE (PUBLIC ORGANIZATION), NAKHON RATCHASIMA, 30000, THAILAND
6 UNIVERSITI TEKNOLOGI MARA SHAH ALAM, SCHOOL OF CHEMICAL ENGINEERING, COLLEGE OF ENGINEERING, 40450 SHAH ALAM, SELANGOR, MALAYSIA

* Corresponding author: syazwan.osman@uitm.edu.my

commonly used are usually unfriendly and toxic towards the environment. This can be exhibited by the use of hydrogen peroxide which is often used in high concentrations to form electrolyte or non-electrolyte gradient to propel the micro/nanomotor [15]. In a complex environment, the existence of fuel for micro/nanomotors might be a challenge in developing a more sustainable technology of itself. Hence, a fuel-free approach was considered such as light [16], magnetic [17,18], and acoustic [17]. Light specifically, which can be obtained from a natural source such as sunlight, has attracted quite the attention as it is more promising in terms of renewable energy and in general, is more environmentally friendly.

Moreover, compared to other actuation sources such as magnetic and acoustic, light itself has many variables that can be tuned and explored from the fundamental and application perspective. Some of the variables might include projection, wavelength and intensity. Light-driven micromotor or nanomotor often has wider applications and better performances because its motion can be remote by turning on/off the light, as well as alterable velocity [18].

For most light-driven micro/nanomotors published works assessed, micromotors can be triggered over a wide range of wavelengths such as UV, visible and near-infrared (NIR). In the current state, despite its overwhelming increase in publications, light-driven micromotors study is still scarce. For now, the focus of developing light-driven micromotors is to reduce the reliance on toxic fuels [15] and surface functionalization [19]. The fuel-free or light-driven micromotors itself is still wide in terms of collective behaviour and their applications depending on the light spectrum. Photocatalytic materials are usually responsive to a specific wavelength depending on their bandgap. High photocatalytic materials have a rapid response of approximately less than 0.1s, which has a huge potential in environmental remediation [20] compared to conventional water treatment. Therefore, a more photocatalytic material with a lower energy band gap has been used to synthesise the light-driven micromotor.

The objective of this concise review is to highlight the progress of developing light-powered micromotors. Intensive attention will be given to the different methods in the synthesis of micromotors which give out different structures of the micromotors. This review will also discuss the applications of these light-powered micromotors specifically in environmental applications.

2. Progress and Development in the Synthesis of Light-powered Micromotor

There are different combinations of micromotors fabricated over the years such as polymeric, polymeric/metallic, polymeric/metallic oxide, carbon/metallic and silica/metallic [1]. The development of light-powered micro/nanomotors has been significantly improving over the years. It can be seen when silica nanoparticles were the first to be used as the base for the preparation of Janus micromotors in most studies [21-23]. Metal and metal oxide nanoparticles were then studied as they can be driven by light. Photocatalytic materials were used to form light-driven micromotors due to their photocatalytic activity under the influence of different wavelengths.

Materials such as TiO_2 [24-28] and its adjacent becomes the main focus as it contains high photocatalytic activity [26] and is nontoxic [27]. However, due to TiO_2 huge energy band gap, a lower energy band gap materials have been looked upon such as Bismuth Oxyiodide (BiOI) [28]. However, the use of metal combinations has its drawback when it comes to larger-scale production. The incorporation of metal caused a higher cost to produce micromotors. Hence, a different approach is used recently, by incorporating graphitic carbon-nitride based micromotor [29]. However, the majority of light-powered micromotor is still in the need of high concentration fuels. The usage of toxic fuels such as hydrogen peroxide [30] is not favourable as it poses a threat to the environment. Hence, a more environmentally friendly or bio-based fuel was used such as glucose [29,31].

Looking into the synthesis aspect, these micromotors are fabricated with different structures such as tubular [32-35] and sphere [36,37] in which the propulsion and direction are varied as shown in Fig. 2.

Generally, in designing the micromotors, the structure of the micromotor can be categorized into two different structures. The micromotor is synthesized into asymmetrical shapes which are also called Janus structure as shown in Fig. 3. Janus structure consists of two symmetric hemispheres in which characterized by different surface properties. Asides from the Janus structure, there are other non-uniform shapes such as sphere, peanut-shaped, tubular, sheet-tube, rod-like, star-shaped, and others. The difference between this structure is that Janus structure has a uniform photo exposure on one side (photoactive material). Meanwhile, the others have a non-uniform exposure of lights

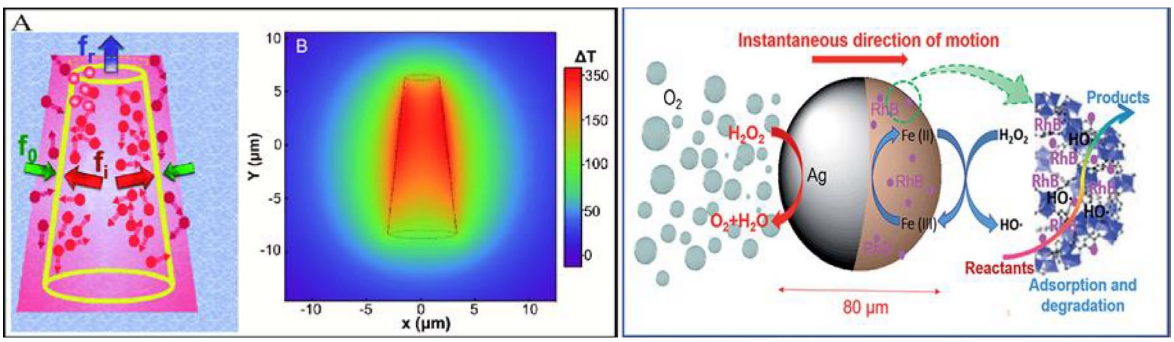

Fig. 2. Examples of tubular-shaped micromotor (left) and sphere micromotor (right) [37,38]

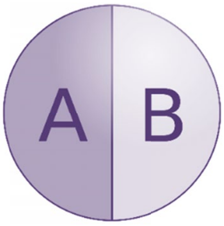

Fig. 3. Janus structure which consists of materials A and B

on the photoactive material. This could affect in a way of the propulsion or direction of the micromotors.

These different structural arrangements of the micromotors can be synthesised using different small-scale methods. Depending on the material itself, a certain synthesis method is needed to get a specific structure. Over the years, different methods have been approached to get a different structure that might affect the propulsion of the micromotors itself. The most common method in the synthesis of micromotor includes physical vapour deposition (PVD), template-assisted layer-by-layer assembly, and electrodeposition method. In the following subsections, the mechanism will be further discussed, and the works of each synthesis method will be reported.

2.1. Physical Vapor Deposition

This method involves the process of converting materials in solid or liquid form into gaseous state. A high temperature vacuum or gaseous plasma is usually involved in vaporizing the materials. The vaporized material will then be condensed into a thin film. There are different types of physical vapour deposition which include electron-beam physical vapour deposition, sputter deposition, pulsed laser deposition, and cathodic arc deposition. Each of the type uses different mechanisms to transport the desired material onto the surface of a material. In the synthesis of micromotor, a base material is first fabricated by using different methods such as ultrasonication which then will be coated with secondary material by using physical vapour deposition as shown in Fig. 4.

For Janus micromotor, this method is suitable as it requires a symmetric deposition of the coating on the surface of the substrates. Physical vapour deposition offers the ability to manipulate the tilt and rotation of the incoming vapour flux to produce different structures [40]. A method of physical vapour deposition using electron beam is illustrated by Ying et al. [36]. The research reported brush-shaped zinc oxide nanoparticles coated with platinum light-driven micromotor. A modified hydrothermal reaction was first used to synthesise ZnO arrays where three different substrates were used to produce zinc oxide nanoarrays (ZNAs) at different diameters. ZnO nanorods were then produced by the hydrothermal reaction by immersing the substrates vertically in the solution of ZnO precursor solutions. The ZnO micromotors were first etched and platinum is deposited on the surface of ZnO arrays by electron beam evaporation at a glancing angle of 55°.

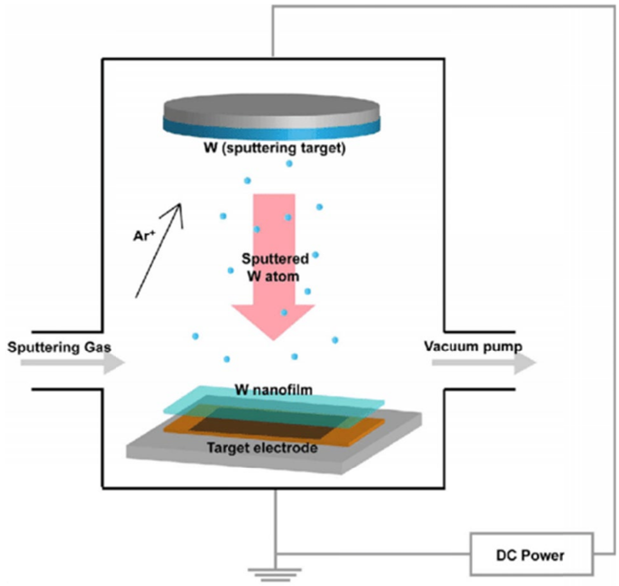

Fig. 4. Schematic diagram of physical vapour deposition method [39]

2.2. Template-assisted Layer-by-layer Assembly

Layer-by-layer is a technique in which charged materials are deposited alternatingly with its charge being opposite to each other [37]. This technique is suitable to incorporate a variety of materials and it is economically feasible other than easy to operate. On top of that, using this assembly method also offers the ability to encapsulate or incorporate desired components into another material [37].

Layer-by-layer assembly is commonly used to fabricate tubular-shaped micromotors by using a template as its non-spherical shape requires the deposition of different materials in alternative manners as shown in Fig. 5. A template-assisted layer-by-layer assembly method is demonstrated by Wu et al. [42] in the fabrication of tubular-shaped platinum-based micromotors. Two solutions of polyallylamine hydrochloride (PAH) and poly styrene-sulfonic acid (PSS) were used to immerse the template alternatively. Each immersion will form one bilayer. The template was immersed repetitively to form multiple bilayers. The additional material which is platinum nanoparticles (PtNPs) will be assembled in the innermost layer of the template.

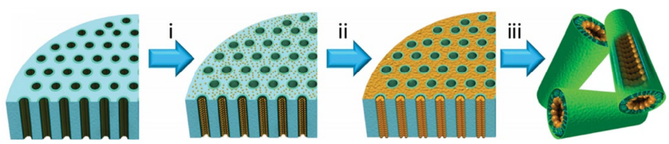

Fig. 5. Illustration of synthesis by layer-by-layer assembly method [41]

2.3. Electrodeposition

This method emphasizes the use of electric current on a conductive material in which it is immersed in a solution containing the metal to be deposited. Its ability to perform without costly equipment and sensitive environmental conditions make it easy to perform. Particularly in the synthesis of micromotors, the electrodeposition method usually comes with a template assisted as in Fig. 6. The use of template in electrodeposition allows the synthesis of desired tubes in each pore [37] which makes the fabrication can be done in mass production.

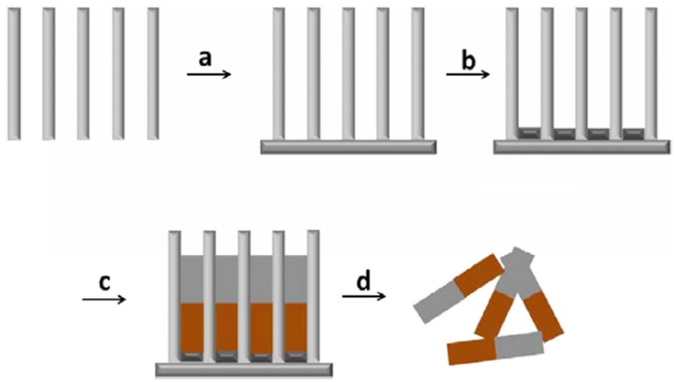

Fig. 6. Illustration of template-assisted electrodeposition [37]

Reported work by Enachi et al [11] illustrated the use of electrochemical deposition by anodization of titanium sheets. The TiO2 nanotubes were synthesized using a template. The usage of the template ensures the diameter and density of the micromotor stay constant throughout all samples. Hence, ensuring the consistent performance of all the samples.

3. Application of light-powered micromotor in Environmental Remediation

The deterioration quality of water in most cases is commonly caused by disposal, land use and industrial activities. Sources such as land disposal, animal feedlots, and use of pesticides are one of the contributors to water pollution [43]. Consequently, clean water sources for human usage were depleting over the years. Hence, a responsible step should be taken to improve the water quality. As for now, a few technologies were proposed for water remediation. As for now, there are three types of water remediation technologies which consist of physical treatment technologies, chemical treatment technologies and biological treatment technologies [44]. Norman Network has listed a total of 700 substances that are identified as emerging pollutants (EPs) being discharged in the aquatic environment [45]. Emerging pollutants are natural and synthetic compounds which pose threats to the environment, however, there is only limited information about emerging pollutants [46]. Asides from typical pollutants that are being treated and controlled before discharge, these emerging pollutants were discharged into the environment with high concentrations.

3.1. Water Treatment

Despite the advancement in water treatment process, these concentrations of EPs are still found in water bodies [47-49]. Hence, the advantages of these light powered micromotor in which can carry out a specific function can be utilized for the environmental remediation. Li et al. [10] synthesized a light-activated TiO_2-Au-Mg micromotors which have the capabilities of producing a highly reactive oxygen species. The species plays a vital role in the degradation of the cell membranes and mineralization of organophosphate nerve agents. The study demonstrated the use of light powered micromotors in degradation of pollutants which is hard to decompose. In other published work by Zhang et al. [19], a light powered Au-WO_3@C Janus micromotor shown a high sensitivity towards pollutant such as sodium-2,6-dichloroindophenol (DCIP) and Rhodamine B (RhB). The high sensitivity toward these pollutants can be utilized for detection and degradation of these pollutants. As fuel dependent light-powered micromotor is an issue in micromachines field, Tong et al. [50] synthesized an Iron phthalocyanine (FePc) with the addition of gelatin through emulsification process. This light-driven micromotor able to self-propulsion under the condition of water as fuel. This discovery proved the potential of micromotor in the environmental remediation. Meanwhile, Wang et al. [51] synthesized a novel light driven micromotor in which has the ability to carry out multipurpose function. A TiO_2-Fe micromotor. TiO_2 microspheres were first synthesized using microemulsion method which then sputter-coated with Fe. The micromotors were able to carry out photocatalysis and Fenton process in which suitable for the water treatment.

3.2. Water Purification Treatment

In the year 2020, Liu et al. [52] demonstrated a light powered bismuth bromide oxide (BiOBr) based micromotor doped with Fe^{3+}. It is found that the efficiency of degradation on methylene blue is approximately 97%. Later that same year, Zhan et al. [53] described a BiOI-AgI-Fe_3O_4-Au light driven micromotor a fabricated by simple hydrothermal method. Uniquely, the fabricated micromotor can be recoverable and reusable. Through the addition of AgI, the photocatalytic activity was increased to trigger a faster in motion speed and degradation of pollutants. Fe_3O_4 was added for the recoverability feature. Therefore, it is illustrated that a combination of different materials can provide a different functions or effects toward different pollutant. Hence, light powered micromotor has a wide application in water purification treatment.

4. Conclusion and outlook

Light powered micromotor have shown a lot of great potential in the application related to environmental remediation. The flexibility of materials combination allows the micromotors to have a different function according to each characterization. In past several years, light powered micromotors depending on high concentration and toxic fuels. Photocatalytic materials such as silica dioxide (SiO_2) and titanium dioxide (TiO_2) have been the main focus in fabricating light powered micromotors. The focus then turns towards a more efficient light driven micromotor with a lower energy band gap such as bismuth oxyiodide (BiOI). The use of polymer based micromotor also have been becoming an interest among researchers as it provides less threats to the environment.

In term of synthesis aspect, all the synthesis methods were in lab-scale application as to the best of our knowledge. In moving towards macro scale production, a more substantial progress should be made in the aspects such as interaction between the particles and interaction between the surrounding environment and micromotor itself. Even though there are promising novel light powered micromotor up to these dates, a combination of different actuation sources effect on micromotor is still at scarce. In real environment, the actuation sources can be found almost everywhere in which it might affects the motion behavior of the light powered micromotor. Hence, a combination study of all the actuation sources towards a group of micromotors should be studied to observe the behavior.

All in all, the light powered micromotor field is still in early stage of development. Without a doubt, light powered micromotor is one of the most exciting research projects in nanomaterials advancement with their flexibility in implementation of various kind of alteration. One of the future challenges in this area is the trade-off between performance and economical aspect of the micromotor development. Therefore, it is expected to grow at a faster pace in a few years to come, especially in moving towards macro scale production which might open plenty more door to explore.

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