Acetylene bubble-powered autonomous capsule: Towards in situ fuel

Journal:	*ChemComm*
Manuscript ID:	CC-COM-09-2014-007218.R1
Article Type:	Communication
Date Submitted by the Author:	05-Oct-2014
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Journal Name RSCPublishing

COMMUNICATION

Acetylene bubble-powered autonomous capsule: Towards *in situ* fuel

Cite this: DOI: 10.1039/x0xx00000x

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Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

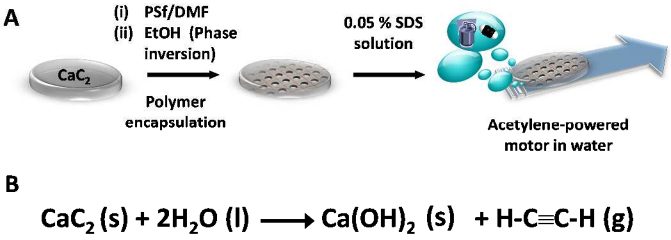
www.rsc.org/

A fuel-free autonomous self-propelled motor is illustrated. The motor is powered by the chemistry of calcium carbide and utilising water as the co-reactant, through a polymer encapsulation strategy. Expulsion of acetylene bubbles powers the capsule motor. This is an important step, going beyond toxic hydrogen peroxide fuel used normally, to find alternative propellants for self-propelled machines.

Self-propelled devices have been proposed to be fielded in numerous scenarios:[1] both in environmental remediation[2, 3] and biomedical applications.[4, 5] Thus said, the ability for the provision of fuel *in situ* is an important aspect in self-powered systems,[6-10] obviating the need for high concentrations of toxic hydrogen peroxide for oxygen bubble-propelled devices by catalytic decomposition reactions. Such fuel-free machines grant higher degrees of freedom and autonomy during their operations. The use of water as an *in situ* fuel under ambient conditions, utilising chemical reactions of reactive metals such as magnesium[7-9] and aluminum[10] have been demonstrated in hydrogen bubble-propelled motors. Alternatively, the Marangoni effect, which employs interfacial tension, minimizes changes towards the surrounding environment, through a self-contained and self-sustained device.[11-17] Pumera and co-workers illustrated the use of a slow asymmetrical release of entrapped DMF from a polysulfone capsule, being capable of moving at high velocities and has long life-spans in the order of minutes.[16] Later, Orozco *et al*. exemplified the use of the Marangoni effect with an encapsulation strategy, with the controlled release of surfactants from millimeter-sized vessels.[18] Both these works highlighted the need for a measured release of the reactants for propulsion to occur.

Thus far, the use of water as a fuel, has been limited to reactive metals to produce simple molecules of elemental hydrogen bubble for propulsion. The use of ionic and compound substrates have not been demonstrated for use as a potential source of fuel, where complex gaseous molecules could be used as a propellant for autonomous moving objects. In this study, we demonstrated that the use of an encapsulated calcium carbide motor is capable to demonstrate motion, which is propelled by the expulsion of acetylene bubbles. The study expands the scope of bubble-propulsion beyond hydrogen and oxygen bubble-propelled motors. The acetylene bubble-powered motor, utilizing water as a co-reactant, is an additional step towards fuel-free self-propelled devices in aqueous medium.

Designing an autonomous self-propelled motor such that it is independent from the environment and using the fuel source *in situ* has been a challenging task. In this report, we illustrate the use of a calcium carbide motor, exploiting water as a co-reactant. The devised motor is able to traverse the surface of an aqueous medium via acetylene bubble-propulsion.



Scheme 1 Depiction of (A) Polymer encapsulation of calcium carbide granule and operation of acetylene-powered capsule motor in water (B) Reaction scheme of calcium carbide in aqueous media.

As shown in Scheme 1A, the calcium carbide granule was encapsulated with a polymer layer through a phase inversion strategy. Namely, it was carried out via a sequential immersion in 10 % *wt.* polysulfone in DMF solution (PSf/DMF) followed by ethanol. The thin layer of polysulfone encapsulates the calcium carbide granule, hereby designated as PSf/CaC_2 capsule motor. It must be noted that the 10 % PSf/DMF mixture is the optimal encapsulation concentration. A 5 % *wt.* PSf/DMF concentration for encapsulation resulted in a rapid rupture of the PSf membrane and the consequent increase beyond, to a 15 % *wt.* concentration led to the sinking of the PSf/CaC_2. Previously, it has been demonstrated that such phase inversion membranes allows for the creation of nanoporous films.[16] These pores are important for the contact of the surrounding aqueous media with the encapsulated substrate. The reaction of the calcium carbide with water, leads to the formation of acetylene and calcium hydroxide salt as shown in Scheme 1B. This ensuing chemical reaction that occurs at the interface led to the formation of acetylene bubbles, which escapes and propels the capsule motor forward.

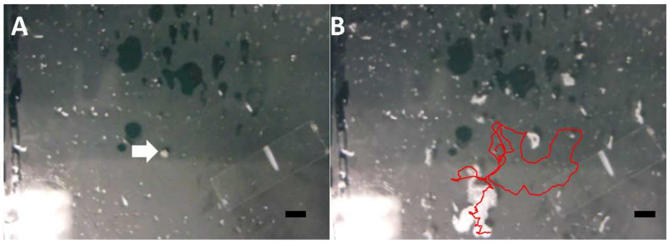


Fig. 1 Tracking image for the path of a PSf /CaC_2 capsule motor at (A) t= 0 s (B) t = 16 s on the surface of water with 0.05 % SDS. Translational motion was observed. Arrow indicates initial position of capsule motor. Scale bar indicates 1 cm.

At t = 0 s, the encapsulated PSf/CaC_2 was introduced into the 0.05 % SDS surfactant solution in Fig. 1A. The PSf/CaC_2 capsule motor is of millimetre-sized, with approximate dimensions of 3 mm across each end. The surfactant serves to lower the surface tension for ease of bubble formation and ensures the stability of the bubbles that are formed.[19] An almost instantaneous effervescence was observed. This corresponded to the water seeping past the PSf membrane to react with the core of calcium carbide. The chemical reaction between water and calcium carbide produces acetylene bubbles, via an acid-base reaction. A subsequent stream of bubbles was released from the PSf/CaC_2, where they aided the buoyancy of the PSf/CaC_2 capsule motor at the water/air interface.[20] This was followed by the translational motion of the PSf/CaC_2 across the surface of the solution in Fig. 1 B (See Video S1).

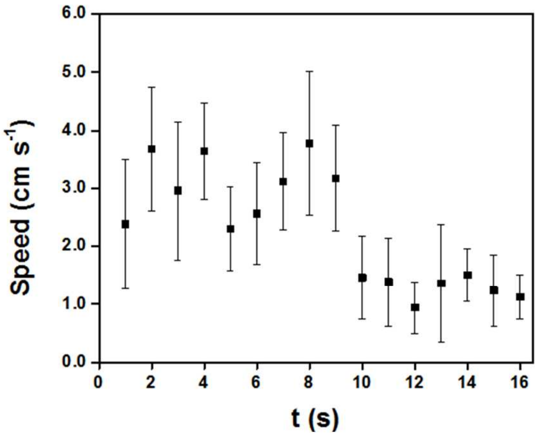


Fig. 2. Average speed profiles of PSf/CaC_2 capsule motor with Δ t =1. A total path length of 37 cm was travelled and the average speed was 2.3 cm s^{-1}.

In Fig. 2, the speeds of the PSf/CaC_2 capsule motor are described. The motor expressed an average speed of 2.3 cm s^{-1}, moving a total distance of 37 cm. This is approximately 8 body lengths per second. Two ranges of speeds were found for the PSf/CaC_2 capsule motor. From 0 to 9 s, the motor demonstrated speeds of between 2-4 cm s^{-1}. For the later part of the translational motion from 9 to 16 s, the PSf/CaC_2 motor demonstrated slower speeds of 1-2 cm s^{-1}. This is in part due to the consumption of the calcium carbide fuel and resulted in the decrease of propulsion force, leading to the reduction of speeds. Beyond the 16 s timeframe as shown in Figure 2, the motion of the capsule becomes limited with a retarded bubble formation.

The converse direct introduction of the PSf/CaC_2 into the aqueous medium without surfactant resulted in the motion of the capsule motor to be highly localized (See Video S2). The PSf/CaC_2, bobbed up and down the water/air interface. This exhibited the quintessential role of the surfactant for propulsion. The need for buoyancy of the PSf/CaC_2 capsule motor[20] and the sustenance of the bubbles[21] are required in order for translational movement to be observed. Separately, in the absence of the PSf membrane, an uncontrolled formation of bubbles due to the chemical reaction of the calcium carbide and water in direct contact resulted. The calcium carbide was rapidly expended and was accompanied with a foaming on the surface of the aqueous media. No significant propulsion behaviour was observed on the calcium carbide granule. Formation of the encapsulation film surrounding the capsule governs the motion of the PSf/CaC_2 capsule motor, where in the event of rupture, it resulted in a highly localized motion of calcium carbide fragments. This highlighted the need for the controlled reaction of the calcium carbide with water, in order to allow for the biased movement of the capsule motor, as reported by Zhao *et al.*[16] and Orozco *et al.*[18] The role of the PSf membrane as a binder to confer integrity and asymmetry to the particulate as a single entity is crucial for the biased movement for the bubble-propelled device.

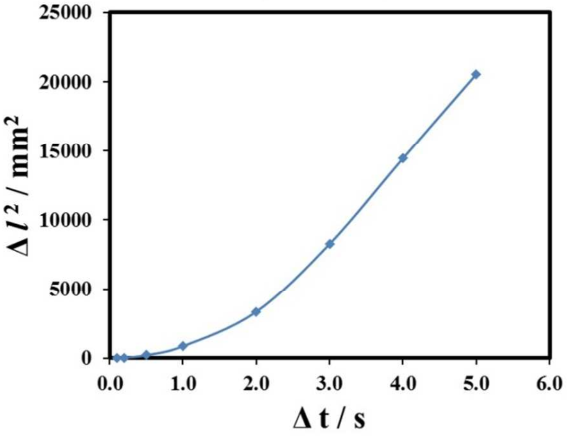


Fig. 3. Calculated mean-squared displacement (MSD) of PSf/CaC_2 capsule motor on the surface of water with 0.05 % SDS added.

In Fig. 3, the graph of mean squared displacement (MSD) against change in time intervals has been demonstrated to be an upward parabolic curve, indicative of an additional propelling force being present. [22, 23] This resulted in the millimetre-sized PSf/CaC_2 to move at an average of ~8 body lengths per second. This corresponded well with our hypothesis, that the production of a stream of bubbles powering the PSf/CaC_2 capsule motor, has given rise to the ballistic thrust needed for motion. The motion of the PSf/CaC_2 capsule motor changed direction multiple times during the course of 16 s as shown in Fig. 1, which was indicative of propulsion behaviour, eliminating any convective current effects.[23]

Conclusion

In conclusion, we have demonstrated the operation of a fuel-free autonomous self-propelled device based on the encapsulation of calcium carbide in polysulfone. The capsule motor runs on the basis of a controlled reaction with water, using acetylene bubbles as the means of propulsion. The extension of autonomous moving devices using alternative sources of *in situ* fuels is an important step towards widening the capabilities of such self-propelled machines. Alternative bubble-powered systems such as acetylene in our case and possibly other analogous complex molecules produced for bubble-propulsion may be possibly used as feedstock for further chemical manipulation in self-propelled autonomous systems.

Experimental Section

Calcium carbide (CaC_2), sodium dodecyl sulfate (SDS) and polysulfone (PSf) and *N, N'*-dimethylformamide (DMF) were purchased from Sigma-Aldrich.

The precursor encapsulation solution was prepared by mixing polysulfone with *N, N'*-dimethylformamide and dissolved into a clear solution using an ultrasonic bath for 30 min. The concentration of polysulfone (PSf) in DMF (PSf/DMF) was 10 % by weight.

Encapsulation of calcium carbide was carried out using a phase inversion strategy. Typically, a calcium carbide granule with an approximate dimension of 3 mm at each end was chosen. The granule was introduced into a 10 % *wt.* PSf/DMF solution, followed by the immersion into ethanol, where the phase inversion occurred. The encapsulated calcium carbide was left to dry for 5 minutes before being used for propulsion experiments.

The propulsion experiments were carried out in a glass container with dimensions 20 cm x 20 cm x 5.5 cm depth. An aqueous solution containing 0.05 % SDS was placed into the dish. A Casio HD video-recorder was placed over the glass container to capture the motion of the capsule motor. The video sequences were analysed using Nikon NIS-Elements software, where the average velocities were calculated.

Acknowledgements

M. P. acknowledges Nanyang Technological University and Singapore Ministry of Education Academic Research Fund AcRF Tier 1 (2013-T1-002-064, RG99/13) for the funding support. J.G.S.M. is supported by the National Research Foundation Singapore under its National Research Foundation (NRF) Environmental and Water Technologies (EWT) PhD Scholarship Programme and administered by the Environment and Water Industry Programme Office (EWI).

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† Electronic Supplementary Information (ESI) available: [Video S1, S2]