Applicability of Photocatalytic Water Splitting, Electrolytic Water Splitting and Algae in Hydrophobic Nanostructures for the Prevention of Biofouling

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ABSTRACT

Background: Biofouling has been a problem in the ship industry ever since boats were first created. As a solution to biofouling, gas emitting hydrophobic nanostructures were envisioned by Dr. Chang-Hwan Choi. As a student under his mentorship, I was tasked to look into processes that would account for the gas emitting factor for the hydrophobic surfaces.

Objective: To determine the feasibility of either a photocatalytic or electrolytic water splitting system or algae as the gas producing factor for the hydrophobic nanostructures

Methods: To determine the feasibility of the said processes, I was tasked to scour research papers and the web for material relevant to the research. I was tasked to sift through the material and provide summaries of their basic concepts.

Findings: Electrolytic and Photocatalytic Water Splitting processes as well as Algal photosynthesis were defined and simplified. The basic concepts of the three were compared and examined to determine which one would deserve future research.

Conclusion: Algae as compared to the water splitting processes proves to be the best among the researched topics. Algae are not as limited as the two water splitting processes- that being a given, algae are not without their own limitations.

INTRODUCTION

The problem of biofouling as well as counter measures against biofouling has been around almost as long as ships have existed. Biofouling as defined by Encyclopedia Britannica is the "Gradual accumulation of water borne organisms [such] as bacteria and protozoa on the surfaces of engineer[ed] structures in water" (citation). Biofouling in moving vessels decreases maneuverability and increases drag. This thus causes a ship's fuel consumption to increase up to 30% and as fuel costs account for 50% of the cost of running ships, the economic implications are tremendous (citation). Biofouling has ecological implications as well. Biofouling on moving vessels facilitate the introduction of unknown species into new environments, causing an imbalance in the natural order.

Biofouling starts off by the development of a biofilm coating on a surface in often contact with or submerged in water. Biofilm is a film made of bacteria or other micro-organisms that develop under specific conditions. Biofilm develops depending on pH, surface material, nutrients available, etc. This biofilm layer "provides a foundation for the growth of seaweed, barnacles, and other organisms" (citation). Biofilm forms slime to which larger organism attach.

Currently Copper- Nickel alloys and TBT are being used as solution. Copper-Nickel alloys having high corrosion and biofouling resistance is often used as actual surface material or as surface coatings as paint additive. Triorganotin- or organostannic- or simply, TBT is a tin based coating that like its copper- nickel counter part degrades slowly and steadily kills microorganisms stopping the process of biofouling (citation - cornell).

The problem with TBT and Copper- Nickel coatings is that they do not discriminate between the organisms they target. Residual effects from TBT and copper-nickel coatings can cause significant environmental damage, affecting algae, fish and crustaceans inhibiting growth and causing abnormal characteristics to show.

Alternative solutions researched by Professor Chang-Hwan Choi are in hydrophobic nanostructures. Hydrophobic nanostructures are water resistant surfaces that when applied to metals, would make them corrosion resistant. Professor Choi envisions hydrophobic nanostructures that can emit gases intermittently which would thus prevent the development of biofilm and in turn, biofouling. Professor Choi's hydrophobic nanostructures are not only rust and biofouling resistant; it also carries no environmental risks in terms of toxicity. Its biofouling resistant aspect would prevent the unwanted transfer of organisms from one location to another.

FINDINGS

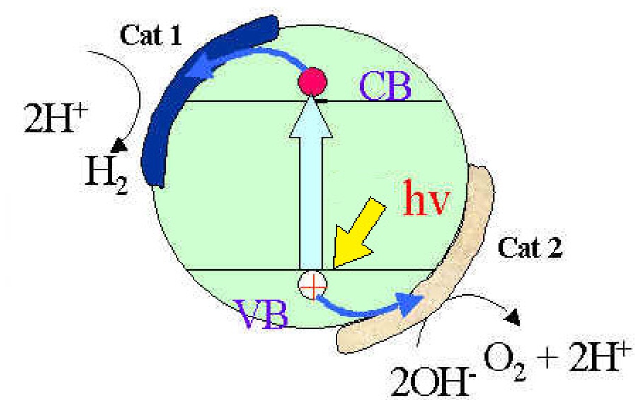
Hydrophobic Nanostructures

For Hydrophobic Nanostructures to become hydrophobic a contact angle of 156 degrees between the water droplet and the surface of the hydrophobic material has to be achieved. To obtain a contact angle of 156 degrees, nanostructures are made uniformly on the surface of a material. Either in the form of teeth or pores, the nanostructures may posses different shapes depending on the process through which they were made. In between the teeth and in the pores are pockets of air that deflect and prevent the seeping in and pooling of water.

Photocatalytic Water Splitting

Photo catalysts often come in powdered form, making them easily applicable to a wide variety of surfaces. Photocatalysis works by using the photons emitted by the sun as an energy source in the splitting of water into Hydrogen and Oxygen.

As the photocatalytic material is bombarded by photons, the photons cause Electrons to jump of the lattice of the photocatalytic material, freeing an electron. This process forms an electron hole while freeing an electron. This freed negatively charged electron causes a reduction reaction of water to form Hydrogen. The electron hole having a positive charge causes an oxidation reaction of water, forming Oxygen.



hV- photons/light energy
VB- valence band
CB- conduction band
Distance between CB and VB is the Band Gap

Shown here is the process of water splitting occurring as facilitated by a photocatalytic particle. Cat 1 facilitates hydrogen generation and cat 2 the oxygen creation

Jos Oudenhoven, Freek Scheijen, Martin Wolffs, "Fundamentals of Water Splitting by Visible Light"

For the splitting of water to occur successfully, the band gap of the photocatalytic material has to be enough to absorb both invisible light and has to be larger than 2.43eV. The Band Gap is the energy difference between valance band to the conduction band. The band gap is the amount of energy required to successfully split water. The band gap must be overcome to form hydrogen and oxygen from water.

Water splitting through photocatalytic means provides a constant supply of hydrogen and oxygen so long as there is sunlight to supply energy for the reaction. In terms of yield, by volume however, the conversion rate is not high enough to be called practical.

Another problem lies in the fact that current photocatalysts use ultraviolet light rather than visible light as their principle sources of energy as UV provides more potent energy. And due to the ozone layer deflecting the UV light, only a small amount of UV actually reaches earth's surface, making photocatalysis inefficient.

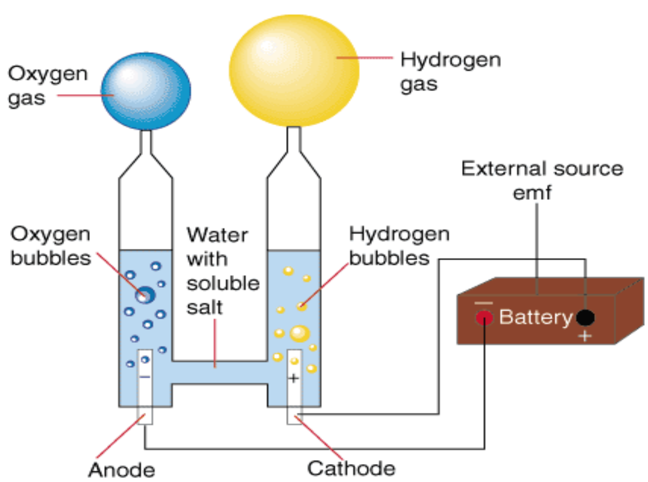
As applied hydrophobic nanostructures in the skin of ships, the problem with insufficient light is augmented by the effect of drag on the photocatalytic particle's adhesion to the nanostructures. Significant advancements in photocatalysts are needed to make this a feasible solution to biofouling.

Visible Light (2.43eV-3.0eV)	Ultraviolet Light (3.0eV+)
$(Ga_{.82}Zn_{.18})(N_{.82}O_{.18})$	$K_3Ta_3B_2O_{12}$
	$NaTaO_3$:La
	TiO2

Current photocatalysts available

Electrolytic Water Splitting

Electrolytic Water Splitting requires the use of an electric current in the splitting of water. The process as of yet is one of the more costly ways of producing hydrogen. Electrolytic water splitting requires the use of Platinum as an electrode, making the process uneconomical.



http://www.blewbury.co.uk/energy/images/electrolysis.gif

For Electrolytic Water Splitting to occur an electric source of energy, supplying 1.23 volts to inert electrodes is needed. The electrodes must be submerged in an electrolytic solution made of water and a soluble salt. Pure water cannot be used as it is not electronically conductive. With the positive end of the battery attached to an electrode, a cathode is formed. With the negative end of the battery attached to an electrode, an anode is formed. As the electricity gives charge to the electrodes, the cathode becoming positively charged and the anode becoming negatively charged, the water with in the electrolytic solution would begin to dissociate as hydrogen is attracted to the cathode and oxygen to the anode.

Electrolytic Water Splitting is a simple Redox reaction that uses energy input and would produce dissociation in water. If the source of electricity for the electrolysis was in renewable energy as solar power or wind power, then electrolysis could become a viable option.

The concept and idea of electrolytic water splitting could be applied to hydrophobic nanostructures. If electricity could be applied to the hydrophobic nanostructures in the skin of ships, the gas it would produce would prevent biofilm formation and thus eliminate biofouling.

Algal Photosynthesis

Algae produce oxygen through the process of photosynthesis. Algae derived oxygen accounts for most of the oxygen in our atmosphere today. Photosynthesis occurs with the use of pigments which function as light absorbers.

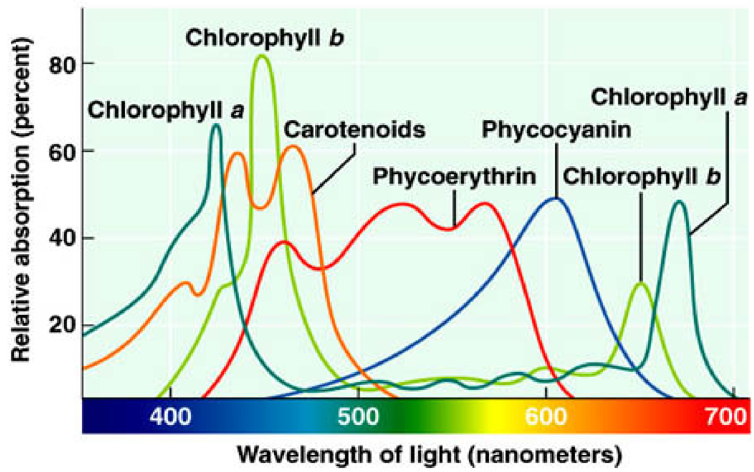
Pigments absorb light and the photons in the light cause electrons in the pigment to become excited. The excited electron passes through the photosynthethic systems of the algae and is eventually converted into ATP & NADP, forms of energy the plants can use. ATP & NADP are used then to convert CO_2 into glucose as food for plants. Oxygen results as a byproduct of this process.

$$6CO_2 + 6H_2O + \text{Energy (sunlight)} \rightarrow C_6H_{12}O_6 + 6O_2$$

Different pigments are adapted to absorbing different wavelengths. Chlorophyll the most common and often primary pigment in plants and algae is adapted to absorb 680 and 700nm best. Often plants and algae rely on more than one pigment. Pigments are responsible for the coloration in plants and algae.

The main problem concerning algal photosynthesis is the process' dependence on visible light as the primary source of energy. Visible light available in marine/fresh water environments decrease proportionally in relation to depth. Additionally unicellular algae, the ones most suited to the hydrophobic nanostructures live largely in near ocean surface environments. Algae that exist in deep water exist as seaweed.

The best thing about algae is that there are thousands upon thousands of species from which there is bound to be a perfect match for hydrophobic nanostructures.



Relative absorption in relation to Pigment type
http://scitec.uwichill.edu.bb/bcs/courses/Biology/BL05B/2_autotrophic%20nutrition.htm

Possible Algae Candidates for Research

Genus	**Commo n Name**	**Habita t**	**Depth**	**Pigment**	**Cellular Organizatio n**	**Nutrient**	**Product s**
Chlorophyt a	Green algae	fresh water	Shallo w water	chlorophyll a/b	unicellular Or Multicellular	CO2, sunlight Photosynthesi s	Oxygen, glucose
Phaeophyta	Brown algae	marine	Deep water – 160-200 feet	chlorophyll c1 + c2, fucoxanthin	multi cellular-seaweed	Photosynthesi s	Oxygen, glucose
Rhodophyt a	Red algae	marine	Deep water – 160-200 feet	phycoerythri n, phycocyanin Chlorophyll a	multi-cellular - Seaweed	Photosynthesi s	Oxygen, glucose
Cyanophyta	Blue-green algae	marine	Shallo w water	phycocyanin, phycoerythri n Chlorophyll a	unicellular	Photosynthesi s	Oxygen, glucose , Fixed Nitrogen

CONCLUSION

Electolytic and photocatalytic water splitting and algal photosynthesis when applied to the problem all seem to have their own solutions to biofouling, however the use of algae seems to be more advantageous against biofouling .

Currently the available photocatalysts are not efficient enough in their production of hydrogen and oxygen to become a viable option against biofouling. The specific need for uncommon UV light would limit its usability. Also the effects of drag on the photocatalyts attachment to the hydrophobic nanostructures would be something take into to consideration.

Electrolytic water splitting could be a possible solution, however the untold amounts of environmental damage releasing electricity from ship skins could be tremendous. Also the amount of energy needed to constantly dispose of biofilm would make the process inefficient.

The main problem concerning algal photosynthesis is the process' dependence on visible light as the primary source of energy. Visible light available in marine/fresh water environments decrease proportionally in relation to depth. Additionally unicellular algae, the ones most suited to the hydrophobic nanostructures live largely in near ocean surface environments. Algae that exist in deep water exist as seaweed.

Algae however, exist in a wide variety of the species. Algae would provide for an endless amount of choices each of which could possibly be immune from the problems aforementioned. Each can survive in different conditions, may have different light absorbing capabilities, oxygen production capacities and sizes.

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