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Plasmo-catalysis generation of green hydrogen for zero decarbonisation

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Abstract

Here we engineered photoactive plasmonic nanostructures with enhanced photocatalytic performance using non-noble metallic MgB_2 high-temperature superconductor which represents a new family of photocatalysts. this covalent binary metal with layered graphite-like structure could effectively absorb visible and infrared light by excitation of multi-wavelengths surface plasmon resonances. We show that a MgB_2 plasmonic metal-based photocatalyst exhibit fundamentally different behaviour compared to that of a semiconductor photocatalyst and provides several advantages in photovoltaics applications. Excitation of localised surface plasmon resonances in MgB_2 nanostructures allows one to overcome the limiting factors of photocatalytic efficiency observed in semiconductors with a wide energy bandgap due to the usage of a broader spectrum range of solar radiation for water splitting catalytic reactions conditioned by enhanced local electromagnetic fields of localised plasmons. Excitation of localised surface plasmon resonances induced by absorption of light in MgB_2 nanosheets could help to achieve near full-solar spectrum harvesting in this photocatalytic system. We demonstrate a conversion efficiency of ~5% at bias voltage of V_{bias} = 0.3 V for magnesium diboride working as a catalyst for the case of plasmon-photoinduced seawater splitting. Our work could result in inexpensive and stable photocatalysts that can be produced in large quantities using a mechanical rolling mill procedure.

Keywords: seawater splitting, plasmonic photocatalyst, plasmon resonances, green hydrogen, magnesium diboride.

Decarbonising the planet is one of the goals that countries around the world have set for 2050. To achieve this, decarbonising the production of an element like hydrogen, giving rise to green hydrogen, is one of the keys as this is currently responsible for more than 2 % of total global CO_2 emissions. Producing 'green' hydrogen through water electrolysis powered by renewable energy is a simple, proven technology that, most importantly, produces no carbon dioxide or other greenhouse gas emissions. Moreover, now, the attraction of the hydrogen economy is as a tool for fighting climate change, by replacing fossil fuels in some of the hardest parts of our economy to decarbonize.

The cleanest way to produce hydrogen is by using sunlight to directly split water into hydrogen and oxygen, namely photocatalytic water splitting is the most promising. Sunlight is a clean and inexhaustible energy gift from nature. The solar radiation reaching the Earth's surface comprises nearly 100,000 TW power, which is much more than that of the current global power consumption (~16.3 TW)[1,2]. Practically, the harvesting of solar energy takes place from only a 0.07% Earth's land surface area of the total amount solar. It was theoretically predicted that converting such amount solar energy into usable form of energy (hydrogen and electricity) with 10% efficiency could cater the global energy demand[3,4]. Unfortunately, currently the energy conversion efficiency of photocatalytic water splitting is still too low for large-scale applications (the H_2-production activities do not achieve a solar-to-hydrogen (STH) efficiency of over 10%) and a widespread usage of hydrogen as green energy. The present situation in green H_2-production demands further developments in nanomaterial engineering to potentially solve the problems of low photoanode effectivity[5]. Plasmonic photocatalysts show a great promise due to their high solar energy utilization efficiency 5-7]. There are several reasons why metallic catalysts with plasmonic response could be best suited for direct water splitting by sunlight. In contrast to semiconductors, which generally exhibit poor chemical and catalytic activity due to the lack of the electron density at the Fermi level, plasmonic NPs possess significant electron density at the Fermi level, and strongly absorb ultraviolet (UV), visible (VIS) and near-infrared (near-IR) light.[18] The amount of light absorbed by a plasmonic material (the molar extinction coefficient of metal NPs) is in the range of 10^8–10^{10} M^{-1} cm^{-1}, which is approximately 10^4–10^6 times higher than most of the light absorbing species known.[5] This essentially means that plasmonic nanostructures can generate large number of high-energy electron–hole (e^- - h^+) pairs upon irradiation with visible light ($\approx 10^{16}$ cm^{-2}). Moreover, some plasmonic nanostructures can effectively utilise photons across the near-IR region wavelengths (750–2000nm) which concentrates the approximately 50% of the solar energy spectra.

Here we report the room temperature water and seawater splitting on magnesium diboride (it is possible to use other materials such as binary layered metals, for example TiB_2, AlB_2, NbB_2 and $NbSe_2$) nanostructures using visible and near-IR light. We show that inexpensive MgB_2 nanostructures provide efficient plasmonic water splitting and could be a viable alternative to noble metal nanoplasmonics. (It is worth noting that noble-like plasmonic metals, such as Cu, Ag, and Au typically exhibit low intrinsic activities with surface-adsorbed molecules due to their fully filled *d* bands.) An introduction of nanostructures based on non-noble metals with high intrinsic direct water splitting activities could present a promising strategy to harvest the solar energy efficiently. In MgB_2 nanostructures (unlike in Au, Ag based) the localised surface plasmon resonances (LSPRs) are strongly coupled with interband excitations due to a spectral overlap of these processes.

In our previous works we have shown that at the surface properties of MgB_2 nanostructures can be actively involve into the process of water splitting in photoelectochemical cells (PECs) [5-7]. In this study, we demonstrate that interband damping of LSPRs is also an important channel for the formation of e^-–h^+ pairs. These e^-–h+ pairs are separated over two bands (namely, between the π and σ bands) have a longer lifetime and are thereby expected to harvest sun energy more efficiently and contribute to the generation of H_2 together with direct electron injection mechanism of hot electrons generated via LSPRs. We also demonstrate that, in sharp contrast to semiconductor photocatalysts, photocatalytic efficiency on plasmonic-like MgB_2 nanostructures increases for seawater splitting. More importantly, we suggest and test a new method of fabrication of plasmonic nanostructures with large area on flexible substrates for seawater splitting using mechanical rolling mill procedure which open up avenues to implement design that enable much-improved effectivity and costless of hydrogen production. This method provides stable and dense packed nanostructures.

The usage of seawater for effective production of hydrogen is one of the most important results of our work. Indeed, water becomes crucial resource in the World. Due to population growth, the availability of fresh water as a feedstock becomes problematic. Hence, the usage of abundant seawater for industrial production of H_2 is beneficial as the oceans and seas represent 96.5% of the total water reserves of the Earth providing almost unlimited resources[8]. Nowadays, the best strategy to produce H_2 from seawater is to split it into hydrogen and oxygen using electricity that comes from renewable energy sources, such as photovoltaic cells. Our work allows direct conversion of sunlight into hydrogen using seawater splitting by MgB_2 nanostructures.

In a designed photoelectochemical cell (PEC) water splitting occurs in next step: (i) Water reacts at the anode to form oxygen and positively charged hydrogen ions (protons). (ii) The electrons flow through an external circuit and the hydrogen ions selectively move across the PEC to the cathode, platinum electrode. (iii) At the cathode, hydrogen ions combine with electrons from the external circuit to form hydrogen gas. Anode Reaction: $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$ Cathode Reaction: $4H^+ + 4e^- \rightarrow 2H_2$.

The layered structure of metal diborides with their graphene-like boron sheets suggests the possibility of exfoliation into thin nanosheets down to a monolayer. The produced nanostructures have a distribution of lateral dimensions from tens of nanometers up to several micrometers (0.1-5 μm) and a distribution of thicknesses from as low as few up to tens of nanometers (1-30 nm), which were measured by high resolution optical and scanning electron microscopies (SEM), Fig. 1. The presence of LSPRs nature of fabricated MgB_2 nanostructures is confirmed by multiple colours in the optical image, Fig. 1. One can see that different areas of the sample changes colour from blue to red. In addition, one can see black spots corresponding to total light absorption. The multitude of colours can be explained by a variation of reflectivity characteristics due to excitation of multi-wavelengths LSPRs around the sharp edges of the nanosheets (Fig. 1).

We have tested the efficiency of a MgB_2 nanostructured photoanode in a two-electrode photo-electrochemical cell configuration with a Pt microwire serving as a cathode. The white light was provided by a solar simulator AM 1.5G (Newport) which has illumination intensity ~100 mW cm^{-2}. The current-voltage (IV) characteristics were recorded using a digital sourcemeter (Keithley, Model 2400) with and without an external potential bias (V_{bias}) applied across the cell. The measurements were carried out in 1 M NaOH aqueous solution at pH ~13.6 and in 0.5 M LiOH and 0.5 M NaCl (pH ~7-8). In the presence of electrolytes, the photocurrents were significantly enhanced for all the investigated MgB_2-based photoanodes (Fig. 2) as compared to the values for the case of DI water. We found that our inexpensive MgB_2 nanostructures submerged into a 0.5M LiOH –DI water solution under a small bias (0.4 V) promote the strong enhancement of light-to-photocurrent conversion.

PEC performance was also measured in a 0.5M NaCl electrolyte emulating seawater under maximal applied V_{bias}=0.4 V. The difference between photocurrent in "on" and "off" state reached its highest value of ~1.2 mA. Observed fluctuations and a slight drop of the measured currents on longer timescales under illumination are mainly caused by the bubble formation on the surface of the MgB_2 photoanode (which generated O_2) and the Pt (which generated H_2). The bubbles can be seen by naked eyes in a dark room under solar illumination. Optical images taken during the formation and growth of bubbles on the water splitting photoanode and cathode were used for the measurement of the gas-evolving reaction rate. The conversion efficiency has been calculated using bubble microscopy. These measurements confirmed 0.95% Faraday efficiency (each two electrons generated ~0.95 molecules H_2). Note that the decreasing of currents on longer timescales can be also caused by heating of solution during solar illumination. The dependences of current versus time are restored if change the electrolyte on the fresh (in this case the bubbles are removed and solution is at room temperature) and the measurements are repeated. Therefore, we found that MgB_2 nanostructures can effectively absorb solar energy facilitating the reaction of water/seawater splitting and deliver the electrons and holes required for generation of hydrogen and oxygen gases [5,6].

The enhancement of light-to-photocurrent conversion can be described by incident photon to current conversion efficiency (IPCE) calculated as [1]:

$$\mathrm{IPCE} = \frac{\mathrm{J_{SC}(mA\ cm^{-2})\times(1.23V-V_{bias})}}{\mathrm{P_{light}(mW\ cm^{-2})}},$$

where J_{SC} is short-circuit photocurrent density, V_{bias} is the applied potential between photoelectrode and counter electrode, P_{light} is the total irradiation input, and the redox potential of interest is equal to 1.23V for water oxidation. It was found that the maximal efficiency could be achieved by selection of optimal ions and their concentrations in the electrolyte that provide the maximal ion mobility. The evaluated efficiencies represent the normalised on the square A (cm^2) of the geometrical area of photo-anode or cathode. The highest efficiency of 6.5 % (normalised to the cathode area) for MgB_2 nanostructure was obtained in the case of PEC filled with solution of 0.5M of LiOH in the DI water. In the case of seawater splitting the highest efficiency was ~5 % and has been achieved under V_{bias}=0.3 V.

Our study demonstrates effective plasmon-induced seawater splitting with the help of the fabricated MgB_2 nanostructures. These plasmonic nanostructures consist only of metallic MgB_2 nanosheets and promise much better efficiency than that of semiconductor photocatalysts often restricted by their large bandgap. Thus, the field of plasmonics has impacted our ability to control light and its interaction with matter on the tiniest of scales for many years which opens up fascinating opportunities for developing new devices exploiting sunlight as the primary energy source. Plasmonics offers the possibility of transformational progress in key areas of catalytic science, including those relating to low carbon energy and environmental protection.

The world is betting on hydrogen. This simplest of elements is increasingly being regarded as a big part of the solution to global climate change. Ukraine must be ready to become the generator green hydrogen and it supplier of Europe. In the near future the Ukraine can be a prospective partner for the European Union to reach its ambitious hydrogen goals. The south of the Ukraine should become the most powerful place for building the hydrogen plants. On one hand, it has around 320 sunny days per year with average solar radiation of 1,600 kilowatts per square metre (kW/m^2). On the other hand, it can also count on significant water resources, Black see and the Danube and Dnipro rivers. Finally, the developed transport infrastructure of Odessa's port makes it possible to transport the produced hydrogen to many countries in the Europeans region. Perhaps most importantly, despite nearly 30 months of the war, the country's competitiveness in this area remains resilient. Nonetheless, aside from the security challenges arising from the war, Ukraine faces several key obstacles in seizing its potential in joint green hydrogen leadership on the continent. Hydrogen production in Ukraine can become a key tool for Ukrainian and European independence from russian energy resources, and the rapid transition to the use of “green” energy. For Ukraine, it is also a chance to become the main energy supplier of “fuel of the future” for Europe.

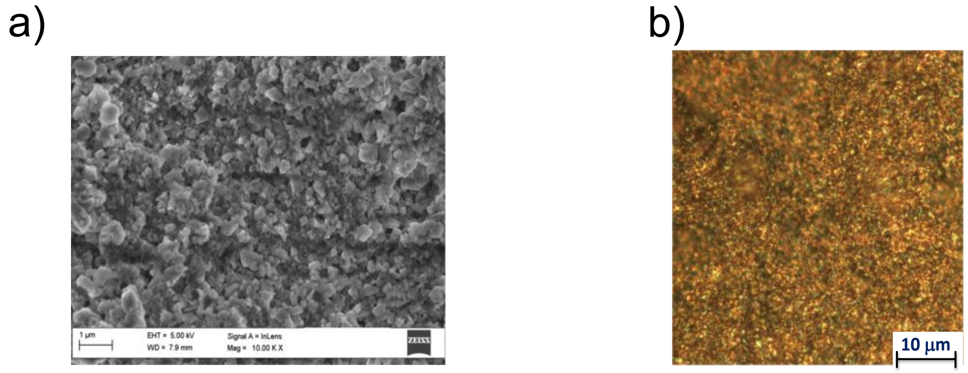

Figure 1. Magnesium diboride nanostructures as a model system for plasmonics photocatalys. (a) SEM image showing the assembly of MgB_2 nanostructured layers. (**b**) Optical image showing the assembly of MgB_2 nanostructured layers which exhibit different colors due to excitation of assemblies localised surface plasmon resonances.

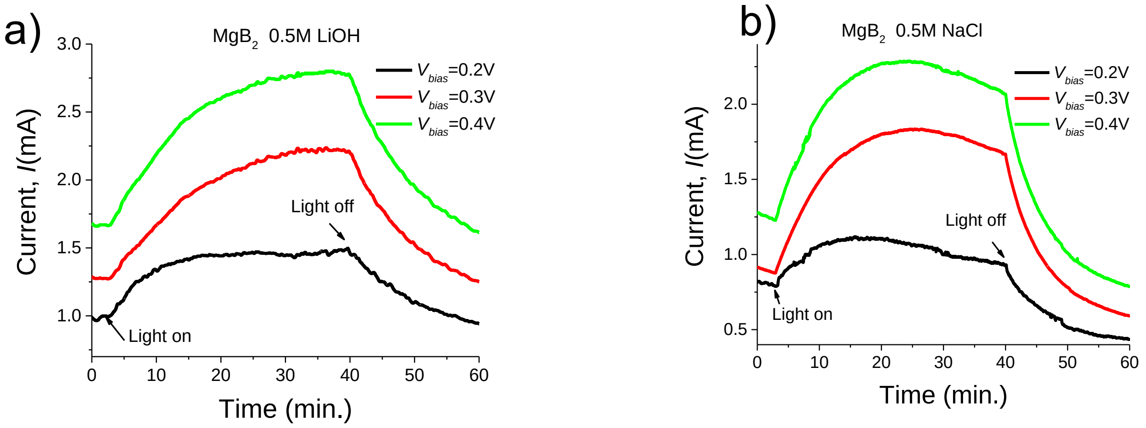

Figure 2. Solar water splitting. Photocurrent as a function of time and external voltage, V_{bias}, for the integrated water splitting device under illumination a solar light simulator: (**a**) nanostructured MgB_2 photoanode and the Pt cathode submerged in 0.5M LiOH electrolyte; (**b**) nanostructured MgB_2 photoanode and the Pt cathode submerged in 0.5M NaCl electrolyte – sea water.

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