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Water Splitting

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Solar Water Splitting at $\lambda = 600$ nm: A Step Closer to Sustainable Hydrogen Production**

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photocatalysis · oxynitrides ·
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water splitting

The search for means to supply a sufficient amount of clean energy is a most daunting challenge and has recently become more urgent owing to the world's growing energy demands, the rapid depletion of fossil fuels, and serious environmental concerns.[1] For a long time, sunlight, as the ultimate source of energy, has been considered as an ideal alternative energy resource that can be captured, converted, and stored in a renewable manner. To the best of our knowledge, approximately 120000 terawatts per year (TW/Y) of solar irradiation hit the Earth's solid surface, far exceeding the world's current power consumption (13 TW/Y) and the growing energy needs, which have been extrapolated to be not more than 30 TW/Y in 2050 even in the most aggressive energy demand scenarios.[1a,c] In this regard, the sun is a compelling solution to our need for abundant sources of clean energy in the future. However, the rather low energy density (1000 $\mathrm{W\,m^{-2}}$) and the inherent day–night and sun–cloud cycles of solar radiation render the harvest and conversion of sunlight in a robust, cost-efficient fashion a significant challenge.[1]

As a molecular fuel, solar hydrogen produced from photocatalytic water splitting has long been regarded as a clean, infinite, and the lightest chemical fuel, which would be available for use as a sustainable reactant in fuel cells and as a raw material for the generation of chemicals.[1d] Since the discovery of the Honda–Fujishima effect in 1972,[2] countless experiments have been conducted to establish stable photocatalytic powder systems, which were mostly based on metal oxides and (oxy)nitrides, to stoichiometrically split water into H_2 and O_2.[3] Indeed, significant advances in overall water splitting have been achieved over the past 40 years. For example, the best reported photocatalytic quantum yield of overall water splitting is 57% under ultraviolet-light irradiation at 270 nm with a $NiO/La{:}NaTaO_3$ catalyst,[4a] whereas for visible-light photocatalysts, the highest laboratory quantum yield of 6.3% was achieved at 420.5 nm for a two-photon-excitation (Z-type) system based on Pt/WO_3-$Pt/ZrO/TaON$.[4b] However, photocatalysts that simultaneously meet the basic requirements of a high quantum efficiency and a high sunlight utilization efficiency still have not been reported, which seriously hinders the practical application of photocatalysis for solar energy conversion.[3]

To achieve the goal of 10% energy-conversion efficiency to set the stage for the large-scale economic production of solar hydrogen, photocatalysts for overall water splitting must be responsive to long-wavelength visible light with sufficient quantum efficiencies, as nearly half of the sun's energy arriving on the Earth's surface has wavelengths between 400 nm and 800 nm in the visible region (Figure 1a).[1,3] On the other side, the overall water-splitting reaction is thermodynamically an uphill reaction with a large positive change in Gibbs free energy of $\Delta G^0 = 238\ \mathrm{kJ\,mol^{-1}}$ (Figure 1b). This means that a large energy input (2 electrons with 1.23 V each) is required to accomplish the overall splitting of one H_2O molecule, even without considering the kinetic barriers for water oxidation and reduction.[3b] Experimentally, to overcome the activation barriers for surface chemical reactions that evolve H_2 and O_2, large overpotentials (ca. 0.4–0.8 V) are always needed, and a larger energy input than what would be expected considering only thermodynamic aspects is thus required.[1] Hence, a photocatalyst with a band gap as narrow as 1.8–2 eV, which corresponds to an absorption edge of 600–700 nm, would be desirable, from the viewpoints of both solar energy harvesting and the surface kinetics of the water splitting reaction.[3] If a quantum efficiency of 30% could be realized at 600 nm, solar-to-hydrogen (STH) energy conversion efficiencies of up to 5% could be achieved.[3] This is considered to be a good starting point for practical applications because this approach is scalable and based on a renewable energy resource.

Recently, numerous efforts have been devoted to the development of 600 nm photocatalysts, and some d^0 transition-metal oxynitrides and nitrides with band-gap energies of 1.8–2.1 eV have been shown to be promising candidates for overall water splitting.[3] Although most of these catalysts possess band structures that are thermodynamically favorable for water splitting, and some of them can even generate both H_2 and O_2 individually from water under band-gap irradiation

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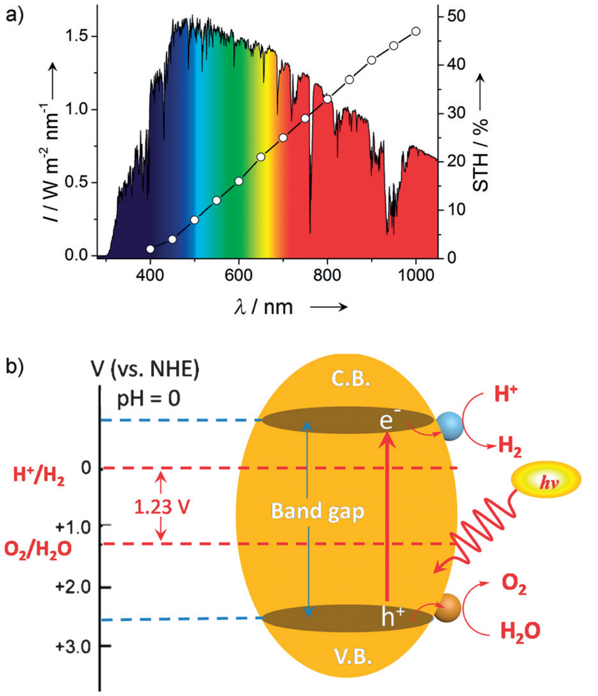

Figure 1. a) Solar spectrum (AM 1.5G) and theoretical maximum STH conversion efficiencies (with 100% solar absorption and 100% quantum efficiency) for the water-splitting reaction. b) Basic principles of overall water splitting on a heterogeneous photocatalyst. C.B. = conduction band, V.B. = valence band.

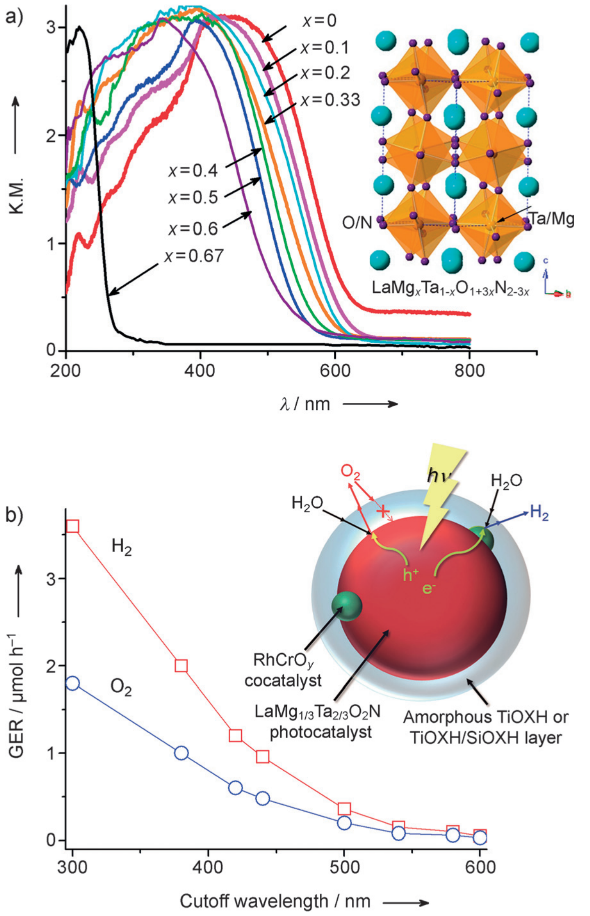

Figure 2. a) UV/Vis diffuse reflectance spectra and crystal structure (inset) of the LaMg$_x$Ta$_{1-x}$O$_{1+3x}$N$_{2-3x}$ photocatalyst. b) The dependence of the H_2 and O_2 evolution rate from pure water on the cutoff wavelength of incident light in the presence of a TiOX/SiOXH/RhCrO$_y$/LaMg$_{1/3}$Ta$_{2/3}$O$_2$N photocatalyst. The inset shows the reaction mechanism for water splitting on a surface-coated photocatalyst. GER = gas evolution rate, K.M. = Kubelka–Munk function.

in the presence of suitable sacrificial agents, all attempts to achieve overall water splitting with such compounds have failed thus far.[3] It is very likely that the surface defects, the reduced redox potentials, the backward reaction, and the lower stability of the materials all together account for this failure. Therefore, more attention should be paid to conducting photocatalyst preparation and system processing in harmony.

As part of their studies on achieving solar hydrogen production by photocatalytic water splitting, Domen and coworkers were the first to demonstrate that H_2O molecules can be stoichiometrically splitted into H_2 and O_2 under irradiation with orange light ($\lambda = 600$ nm).[5] To achieve overall water splitting with a 600 nm photocatalyst, they have developed two effective strategies for the design of a new tantalum-based oxynitride photocatalyst.

The first strategy involved the adjustment of the electronic structure, in particular of the band-gap energy and position, for water splitting (Figure 2a). A series of perovskite-type oxynitrides, LaMg$_x$Ta$_{1-x}$O$_{1+3x}$N$_{2-3x}$ ($x = 0$–$2/3$), with well-defined crystal structures were synthesized by the controlled mixing of $(1-3/2x)$ LaTaON$_2$ and $3/2x$ LaMg$_{2/3}$Ta$_{1/3}$O$_3$. The similar lattice constants of the precursors enabled the formation of uniform solid solutions with tunable band structures. UV/Vis diffuse reflectance spectra show that the wavelength of the absorption edge of LaMg$_x$Ta$_{1-x}$O$_{1+3x}$N$_{2-3x}$ is blue-shifted from 640 to 525 nm when the molar ratio of Mg^{2+} in the solid solution is increased from $x = 0$ to 0.6 (Figure 2a). The increase in band-gap energy was mainly attributed to the shift in the level of the valence-band maximum as a result of the change in O and N content and should be at least advantageous for O_2 evolution. The LaMg$_{1/3}$Ta$_{2/3}$O$_2$N solid solution ($x = 1/3$) with a band-gap energy of 2.08 eV was identified as the most suitable one for overall water splitting.

This solid-solution photocatalyst was then subjected to the second strategy, which makes use of surface engineering to improve the redox properties of the surface and to stabilize the solid solution against photocorrosion. First, a Rh/Cr mixed oxide (RhCrO$_y$) with unique properties to suppress the backward reaction was added as a H_2 evolution cocatalyst (Figure 2b, inset). Then, a double coating of amorphous oxyhydroxides MO$_{2-m}$(OH)$_{2m}\cdot x$H$_2$O (first M = Si, then M = Ti, denoted as SiOXH and TiOXH) was uniformly deposited on the surface of RhCrO$_y$/LaMg$_{1/3}$Ta$_{2/3}$O$_2$N to inhibit O_2 reduction and to protect the oxynitride from self-oxidation to release N_2. The simultaneous evolution of H_2 and O_2 in a molar ratio of nearly 2:1 with such a LaMg$_{1/3}$Ta$_{2/3}$O$_2$N oxynitride sample showed that these surface modifications effectively controlled the reaction kinetics. The onset wavelength of overall water splitting was determined to be approximately 600 nm, which is in good agreement with the band-gap energy of $LaMg_{1/3}Ta_{2/3}O_2N$ (Figure 2 b). This finding further suggests that photocatalytic water splitting is driven by band-gap excitation, and that a low-energy photon can be used to induce water splitting.

However, the quantum efficiency of overall water splitting was low (ca. 0.03 %), and only a moderate rate of simultaneous evolution of H_2 and O_2 was achieved on the $LaMg_{1/3}Ta_{2/3}O_2N$ oxynitride under 600 nm irradiation. This first report of overall water splitting with a 600 nm photocatalyst is nevertheless encouraging and expected to be an important milestone for solar hydrogen production. We believe that this result represents a new starting point for artificial photosynthesis because scientists can further refine these materials with minimal defects and optimize the reaction kinetics to achieve high-efficiency solar energy conversion, as has been already been demonstrated with the GaN:ZnO photocatalysts developed by the same group.[6] Although our own work focuses on stable heterogeneous photocatalysts based on graphitic carbon nitride polymers,[7] this work gives us great inspiration, in particular considering the high flexibility and compatibility of the strategies developed here, which should also be useful for the fabrication of polymer-based photocatalytic systems for overall water splitting.

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