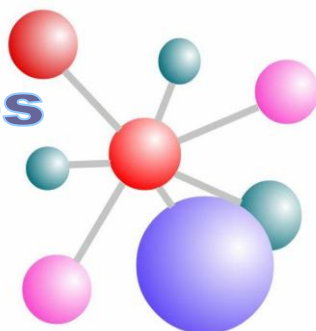


Inglês



Ciências Exatas e da Terra

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9	Você dispõe de, no máximo, três horas, para responder as 5 questões que constituem a Prova.
10	Antes de retirar-se definitivamente da sala, devolva ao Fiscal este Caderno.

Assinatura do Candidato: _____

As questões de 01 a 05, cujas respostas deverão ser redigidas EM PORTUGUÊS, referem-se ao texto abaixo.

The Emerging Technology of Solar Fuels

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The production of transportation fuels from sunlight, at costs that will be competitive with petroleum-based fuels in a future carbon-constrained economy, is one of the most important and daunting challenges facing chemists today. The use of carbon-based fuels, following current trends, will double the current level of atmospheric CO₂ in this century, possibly leading to disastrous environmental and economic consequences. The usable capacity of solar power is estimated to be 600 TW, an order of magnitude larger than the projected energy needs of the entire world in 2050, and most of the solar spectrum is delivered at energies that (thermodynamically) can drive water splitting or CO₂ reduction. Transforming the world's energy economy boils down to technological problems that are largely chemical: how to design molecules and materials that efficiently absorb light and separate charge and then drive uphill redox reactions at low overpotential.

How hard can this problem be? Very hard because electron-hole recombination, fuel-oxidant recombination, and unwanted side reactions are energetically favorable and fast relative to fuel-forming and water oxidation reactions. To put it into perspective, solar water splitting has been actively researched since 1972, when Fujishima and Honda first demonstrated it in an UV light-driven photoelectrochemical cell. The first example of photocatalytic water splitting with visible light did not come for another 29 years. Almost a decade later, the best photocatalytic water splitting systems still use only the blue edge of the visible spectrum, and their efficiency is quite low, but important advances have been made in controlling the catalytic reactions.

To realize carbon-containing solar fuels, it is necessary to react CO₂ catalytically with solar hydrogen or to reduce it directly. The Perspective by Grills and Fujita explains why the photocatalytic reduction of CO₂ to CO and other carbon-containing compounds has been a more difficult problem than water splitting. They describe progress in designing molecular donor-acceptor systems that combine the functions of light-induced charge separation and two-electron, two-proton reduction of CO₂ to CO. A bottleneck in the catalytic cycle of CO₂ reduction is the displacement of a polar solvent molecule in the coordination sphere of a transition metal, such as Re, with a weakly coordinating CO₂ molecule. Grills and Fujita show that supercritical CO₂ and biphasic CO₂/ionic liquid systems are effective media for increasing the turnover rate in these systems.

An interesting way around this problem and also the ubiquitous problem of the poor utilization of red and near-infrared light in artificial photosynthesis is to split the functions of light-induced charge separation and catalysis into low- and high-temperature stages. This approach has a number of important advantages. The high quantum efficiency of charge separation in excitonic or p-n junction solar cells can be exploited, and decomposition pathways associated with semiconductor-liquid junctions are eliminated. The need for noble metal catalysts and the TOF problem are greatly relaxed by increasing the temperature of catalytic cycles by hundreds of degrees. Licht has recently shown in a proof-of-concept system that this approach could result in very efficient solar fuel generation. The short-wavelength part of the solar spectrum is directed to an efficient multijunction photovoltaic cell. The long-wavelength part of the spectrum, along with waste heat from the solar cell, is concentrated to heat a molten carbonate electrolyte for electrolysis of CO₂, which is powered by the electrical output of the solar cell.

Fonte: *J. Phys. Chem. Lett.*, **2010**, 1 (18), pp 2738–2739

Questão 1

Explique o que, de acordo com o texto, tem sido um dos maiores desafios para os químicos nos dias atuais?

Espaço para Resposta

Questão 2

Quais são os problemas tecnológicos de natureza química, mencionados no texto, cuja solução poderá transformar economicamente o sistema de energia mundial? Por que é difícil resolvê-los?

Espaço para Resposta

Questão 3

Segundo o texto, o que Fujishima e Honda vêm pesquisando desde 1972 e quais têm sido os desdobramentos da pesquisa?

Espaço para Resposta



Questão 4

Descreva a perspectiva de Grills e Fujita.

Espaço para Resposta

