AMERICAN SCIENTIFIC PUBLISHERS

Reviews in Advanced Sciences and Engineering
Vol. 4, pp. 1–16, 2014
(www.aspbs.com/rase)

Polyoxometalates in Visible-Light Photocatalysis and Solar Energy Conversion

Ahmed Al-Yasari[1,2] and John Fielden[1,*]

[1] *School of Chemistry, University of East Anglia, Norwich, NR4 7TJ, United Kingdom*
[2] *College of Pharmacy, University of Kerbala, Kerbala, Iraq*

ABSTRACT

Polyoxometalates (POMs) are an important class of anionic molecular metal oxides, boasting an enormous range of structures and properties. They are commonly based on the high oxidation states of V, Mo and W and show strong absorptions in the ultraviolet (UV) due to their O-to-metal charge transfer transitions. This feature, and the ability of many species to act as stable, multi-electron acceptors means that POMs have a well-established UV photochemistry, primarily in the oxidation of organic substrates. The last decade has witnessed increasing efforts to achieve photochemistry with POMs under visible light, through sensitization with molecular or semiconductor chromophores, or by extending the visible absorption of the POMs themselves. Notable achievements have included light driven oxidation of water, and light driven reduction of protons to H_2. In this review, we summarize these achievements and provide a perspective on a growing body of work exploiting POMs in light energy conversion.

KEYWORDS: Polyoxometalates, Photocatalysis, Artificial Photosynthesis, Excitonic Photovoltaics, Electron Transfer.

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1. INTRODUCTION

Polyoxometalates (POMs) are a large class of molecular metal oxide anions, typically based on V, Mo or W in high oxidation states.[1] They show an incredible structural diversity and an similar range of useful properties–one of the most significant being the ability of certain structural types (e.g., the Keggin, $XM_{12}O_{40}^{n-}$, and Dawson $X_2M_{18}O_{62}^{n-}$ heteropolyanions, X = B, Al, P, Si, S, As, Ge, 1st row TMs, etc.) to accept multiple electrons at potentials compatible with proton or CO_2 reduction.[1,2] Incorporation of heterometal active sites into the molybdate or tungstate frameworks (for example Mn, Fe, Co, Ru) can thereby be used to produce efficient oxidation or reduction catalysts. Several species have now shown themselves to be fast, oxidatively stable water oxidation catalysts,[3] and POMs can catalyse a wide range of other oxidations and reductions.[2] These features make POMs highly attractive for use in solar energy conversion-as electron accepting components in charge separation, as catalysts in artificial photosynthesis, as electron relays or even as stores of energy in their reduced form as "proton electron buffers."[4]

However, while POMs are powerful photo-oxidants if irradiated by UV light, and are capable of oxidizing a wide range of organic compounds,[5] the vast majority absorb little in the visible and have to be sensitized through the use of other chromophores. This review will summarize efforts made over the last decade or so to access POM photochemistry with visible light-through sensitization with chromophores, and through development of visible-light absorbing POMs-with the aim of offering a perspective that can help guide future work. As this field of scientific endeavour is relatively new and little reviewed,[6] the scope of this article is necessarily broad, encompassing the use of

*Author to whom correspondence should be addressed.
Email:
Received: 17 April 2014
Accepted: 12 May 2014