Coordination Chemistry Reviews 306 (2016) 217–234

Contents lists available at ScienceDirect

Coordination Chemistry Reviews

journal homepage: www.elsevier.com/locate/ccr

Review

Hybrid polyoxometalate materials for photo(electro-) chemical applications

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Contents

ARTICLE INFO

Article history:
Received 2 April 2015
Accepted 23 June 2015
Available online 9 July 2015

ABSTRACT

Polyoxometalate (POM) based supramolecular assemblies have received significant attention over recent years because of their unique and diverse redox and photochemical behaviour and their potential value across a range of important light driven applications such as photo-driven synthesis and photocatalysis.

Abbreviations: POM, polyoxometalate; CT, charge transfer; LMCT, ligand-to-metal charge transfer; MMCT, metal-to-metal charge transfer; EPR, electron paramagnetic resonance; DSSCs, dye-sensitized solar cells; bpy, 2,2′-bipyridyl; MC, metal-centred; MLCT, metal-to-ligand charge transfer; Mebpy-py, 4-(4″-pyridinyl ethyl)-4′-methyl-2,2′-bipyridine; DMSO, dimethylsulfoxide; pzc, pyrazine-2-carboxylate; tbbpy, 4,4′-di-*tert*-butyl-2,2′-bipyridine; biH_2, biimidazole, doubly protonated; NPs, nanoparticles; ZnTPP, Zn(II) tetraphenylporphyrin; DMF, *N*,*N*-dimethylformamide; PVP, poly(4-vinyl)pyridine; ECL, electrochemiluminescence; D_{CT}, charge transfer diffusion coefficient; CAIP co-$poly_7$, poly($styrene_6$-co-p-(aminomethyl)styrene) amide linked to 2-(4-carboxyphenyl)imidazo[4,5-*f*] [1,10]phenanthroline; LBL, layer-by-layer; N_3 hemicyanine, (*E*)-1,1′-(propane-1,3-diyl) bis (4-((*E*)-2-(4-(dimethylamino) naphthalen-1-yl) vinyl) pyridinium) bromide; SCE, saturated calomel electrode; CoTAPc, cobalt tetraaminophthalocyanine; PAH, poly(allylamine hydrochloride); PSS, poly(styrenesulfonate); ITO, indium-doped tin oxide; FTO, fluorine-doped tin oxide; bpy-PO_3H_2, 4,4′-di-phosphonic acid-2,2′-bipyridine; 9-AC, 9-anthracenecarboxylate; TTF, tetrathiafulvalene; GO, graphene oxide; PDDA, poly(diallyldimethylammonium; PEDOT, poly(3,4-ethylenedioxythiophene); N719 dye, di-tetrabutylammonium cis-bis(isothiocyanato)bis(2,2′-bipyridyl-4,4′-dicarboxylato)ruthenium(II); phen, 1,10-phenanthroline; TEM, transmission electron microscopy; SP^+, spiropyran cation; PL, photoluminescence/photoluminescent; FS, fluorescein sodium salt.

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http://dx.doi.org/10.1016/j.ccr.2015.06.016

Keywords:
Polyoxometalate
Photoelectrochemistry
Photophysics
Supramolecular
Charge-transfer materials

This review explores the dominant approaches to assembly of polyoxometalates into supramolecular materials, both covalent and electrostatic, with particular focus on charge transfer materials and those capable of sensitized photoelectrocatalysis. The integration of POMs as components in devices such as dye sensitized solar cells, electrocatalytic photoanodes, sensing and waste remediation are considered.

1. Introduction

Design of effective materials for solar photo(electro)catalysis is important across diverse applications including energy generation, water purification, chemical synthesis and environmental waste remediation. Semiconductors such as TiO_2, WO_3 and ZnO have been the primary focus in the pursuit of catalytic materials for heterogeneous photocatalysis. However, the photoactive metal cluster complexes, the polyoxometalates (POMs), have been growing in significance in this field due to their synthetic versatility, well behaved redox properties including light driven redox chemistry, their low cost and low environmental impact. Polyoxometalates have been widely explored over many years across a breadth of applications ranging from catalysis through medicine and sensing [1–7]. This review focuses on the photochemical and photophysical properties of POMs, especially the Keggin and Dawson structures of Mo and W, and overviews some of the recent developments in the application of such POMs in heterogeneous photo(electro)catalysis. Assembly of POM building blocks into functioning devices has typically relied on electrostatic binding but has more recently been extended to covalent systems and the particular advantages of these two approaches is discussed, along with the photophysics of inter-species charge transfer in both systems. POM-based water oxidation catalysis using transition-metal substituted sandwich POM compounds (see Fig. 1(f)) is also briefly considered.

1.1. Polyoxometalate structures

The polyoxometalates are transition metal oxide clusters of d^0 or d^1 metal ions bridged via oxygen atoms. Literally hundreds of POM complexes have been prepared, most commonly from Mo, W, V and Nb. In many structures, the cluster framework includes a heteropolyanion comprising for example phosphorous or sulfur, e.g. in the form of tetrahedral SO_4^{2-} [8]. The structures of POMs are diverse, but the most common are the Keggin, Dawson, Lindqvist, Anderson, sandwich and Preyssler structures, which are illustrated in Fig. 1. The Keggin and Dawson structures have been most widely studied [9]. In addition, more recent covalent functionalization of traditional POM architectures has led to new classes of hybrid species [10–12].

The Dawson-type POMs are useful components in interfacial supramolecular devices due to their well-behaved redox chemistry. They are capable of undergoing multiple proton and electron transfer steps reversibly and without substantial decomposition under irradiation and/or electrochemical bias. In addition, both the Keggin and Dawson structures exhibit excellent chemical stability relative to some other POMs: for example the well-known and commercially available phosphotungstate $K_3[PW_{12}O_{40}]$ is stable towards thermal decomposition up to 580 °C [16].

The conventional Dawson structure; α-$[S_2Mo_{18}O_{62}]^{4-}$ is shown in Fig. 2(c). This species is sufficiently stable under redox conditions that both the one and two-electron reduced products have been electro-synthesized by bulk electrolysis and isolated as a stable crystalline species [17,18]. Interestingly, efforts to isolate a crystal structure of the two-electron reduced form yield a protonated form of the two-electron reduced material, i.e., the reduced forms tend to be very basic and easily protonated. The Dawson structures in their oxidized states do not typically absorb strongly in the visible spectral region. However, their reduced analogues usually have intense visible metal to metal charge transfer (MMCT) transitions and are thus deeply coloured.

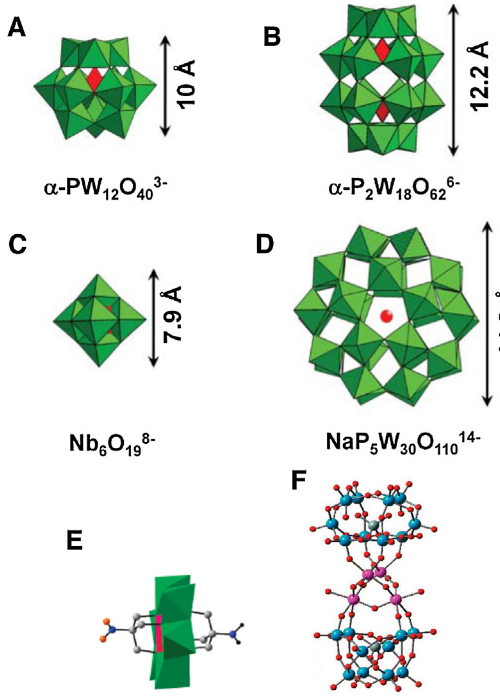

Fig. 1. Diagrams of various polyoxometalate geometric structures. (a) Keggin structure; (b) Dawson structure; (c) Lindqvist structure and (d) Preyssler structure incorporating Na^+ (red) viewed approximately down the molecular C_5 axis. Reproduced from [13] with permission of The Royal Society of Chemistry. (e) Anderson structure. Reprinted with permission from [14]. Copyright 2008, American Chemical Society. (f) The "sandwich" anion $[Ru_4(\mu\text{-}O)_4(\mu\text{-}OH)_2(H_2O)_4(\gamma\text{-}SiW_{10}O_{36})_2]^{10-}$, showing Ru(IV) centres (lilac) sandwiched between two $\{SiW_{10}O_{36}\}$ fragments. Reprinted with permission from [15]. Copyright 2008, American Chemical Society.

The Dawson polyanion exhibits a horizontal mirror plane which separates two Mo_9 clusters with the principle C_3 axis of rotation connecting the two sulfur atoms. However, there is diversity even amongst conventional Dawson and Keggin structures. For example non-conventional sulfite-containing Dawson clusters α/β-$[S_2Mo_{18}O_{60}]^{4-}$ (Fig. 2(a) and (b)) exhibit a structure which is distorted inward at the equator. This "peanut" configuration arises from the charge distribution of the encapsulated SO_3^{2-} groups, which are not isostructural with true tetrahedral ions such as PO_4^{3-} and SO_4^{2-} [19]. The structural isomers vary in the orientation of the encapsulated sulfite moieties relative to each other as viewed down the principle axis of rotation. In the α case the sulfite groups are staggered and in the β case they are eclipsed. Since the staggered conformation is thermodynamically favoured, the α isomer is the more stable. This difference is considered negligible in the case of the fully oxidized POM ions, but in their reduced forms this energy difference becomes increasingly significant, and from electron paramagnetic resonance (EPR) spectroscopic studies the