Current Opinion in Colloid & Interface Science 35 (2018) 91–103

Contents lists available at ScienceDirect

Current Opinion in Colloid & Interface Science

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

Cluster polyanions and surface-covered complexes: From synergistic self-assembly to bio-functionalization

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ARTICLE INFO

Article history:
Received 17 November 2017
Received in revised form 25 January 2018
Accepted 30 January 2018
Available online 07 February 2018

Keywords:
Polyoxometalates
Electrostatic complex
Self-assembly
Synergistic interaction
Bio-function

ABSTRACT

Supramolecular self-assembly based on organic/inorganic hybrids provides a powerful strategy to construct novel nanostructured materials. Polyoxometalates acting as a type of remarkable inorganic building units have widely applied in the field of supramolecular assembly toward biorelevant materials and has attracted great interests in the fields of colloid and interface chemistry, nanomaterials and medical science. The surface of polyanionic clusters can be modified by cationic organic surfactants, biomolecules and polymers via electrostatic interaction. The formed ionic complexes not only combine chemical activity of both inorganic and organic components, but also display well-organized structures and enhanced functions. In this context, we summarized the recent progress on the self-assembly and bio-functions of polyoxometalate complexes. As an amphiphilic organic/inorganic hybrid system, the concerned complexes assembling into diverse nanoscaled structures are described, together with their smart response to external temperature, pH, optical and other factors. Furthermore, the synergistically enhanced functions involving catalysis, photochroism, luminescence, and so on, by combining polyoxometalates and surfactants/biomolecules in the complexes, are summarized on the biocompatibility and protection referring to multifunctions such as magnetic, luminescent and photo-thermal transformation properties under bio-conditions. While pointing out the possible difficulties, the encouraging aspects of polyoxometalate based complexes dealing with bio-related applications such as biological imaging contrast agents and therapeutic medicines for antivirus and antifibrillation of proteins have been outlined.

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1. Introduction

Many nanoclusters and nanoparticles with multiple surface charges display colloidal behaviors and have been used to modulate and/or support physicochemical properties of various assemblies in recent years due to their precise molecular structure, controllable surface property, and unique functions [1,2]. In comparison to those inorganic/organic nanoparticles with uncontrolled size and morphologic distribution proper, most of nanoclusters perform features of individual molecule with a bigger scale [3]. As a family of typical molecular nanoclusters, polyoxometalates (POMs) comprising of mostly early transition metal ions bridging by oxygen atoms, possess uniform cluster shapes and sizes from one to several nanometers, adjustable delocalized surface charges that can reach several tens, and stable structural architectures in a suitable pH range [4].These important characteristics make POMs perfect model particles for constructing diverse self-assemblies and understanding the interfacial behaviors of particle assemblies.

In addition to the size and morphology providing the opportunity for their own self-assembly in solutions, the multiple charges surrounding the surface of POM nanoclusters, which are derived from the condensation of oxometalates, also play a crucial role in driving themselves together and controlling self-assembled structure and morphology. For example, the giant POMs self-assemble into blackberry like hollow capsules and their counterions acting as the medium not only weaken the charge repulsion but also act as a bridging media to collect the clusters together with the aid of electrostatic neutralization by locating between the clusters with multiple negative charges [5]. More importantly, the POMs can also be regarded as comparably scaled counterions of cationic organic surfactants and even crosslinkers of polymer electrolytes/amphiphiles, yielding a new type of ionic complexes showing amphiphilicity and having the capability of self-assembly both in solution and at interfaces [6,7].

Beside the size and surface charge properties, the intrinsic functions of POMs have been managed to realize in the meantime of assembly and self-assembly. As the POMs hold multifold material properties on catalytic redox and esterification/hydrolysis, photochroism and photothermal transition, electronic and magnetic, as well as bioactivity on antivirus and antibacterial capability, the programmed functions are desirable to be incorporated in assemblies. The synergistic effect greatly recovers the functional performance of POMs in assemblies much more than those in isolated dispersion state meanwhile overcoming their

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https://doi.org/10.1016/j.cocis.2018.01.016
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own disadvantages which could not be avoided by themselves without the supports of partner components generally.

With these functions, POMs have been used to interact with organic components, polymers and biomolecules. The formed ionic complexes have been developed into a distinctive type of specific building blocks and become a necessary approach for hierarchical assemblies comprising organic and inorganic building units, which could not be achieved through a direct procedure. Considering the rapid progress and the known publications involved in this field, in this review, we only summarize the aspects on the interaction principles of POMs and organic/polymer cations, biomolecules, the typical self-assembled structures and bio-related functionalization.

2. Self-assemblies of POM clusters and their ionic complexes

The surface of POMs comprises of terminal O atoms that bind to metal ions and bridging O atoms that connect two/three metal/nonmetal ions. The main metal ions adopting octahedral coordination with O atoms usually do not expose to the external environment directly in most cases. Thus, the POM clusters have an O atom shell with delocalized negative charges though the electronic density may distribute a bit more around terminal O atoms and a typical performance of the surface feature of POMs is that when mixing POMs with organic cations, a great polarity decrease of both POM and the organic component in the formed ionic complexes occurs, which enhances the ionic interaction and leads to insoluble of the formed complexes in aqueous solution. Unless there is an additional polar group in organic molecules, the ionic combination results in a precipitation if the organic molecules do not have enough hydrophilicity. In the case that the cationic organic molecules are more hydrophobic, the ionic complexation can be conducted in two phases, the organic phase bearing cationic organic component and aqueous phase dissolving POM clusters. As a result, the POM clusters transfer into organic phase spontaneously and leave the counterions at the aqueous phase while the counterions of organic molecules get into aqueous phase and accomplish the ionic exchange. Thus, the cationic organic molecules (normally cationic surfactants) combine with POMs, forming surface-covered cluster electrostatic complexes. Oppositely, for more hydrophilic cationic organic molecules, their ionic complexation with POMs leads to a water-soluble product. Though binding intensity becomes not as strong as that in organic phase, the complexation still remains, and this property shows potentials for the combination of POMs with biomolecules in aqueous solution systems.

2.1. Interaction of POMs and amino acids

Amino acids bear both amino and carboxylic groups and display acidic, neutral, or basic property depending on the molecular structure and the number of acidic or basic groups. In a systematic investigation, Sandwich like luminescent $K_{13}[Eu(SiW_{10}MoO_{39})_2$, $K_{11}[Eu(PW_{11}O_{39})_2]$, and $K_9[EuW_{10}O_{36}]$ clusters bearing echelon negative charges are used to interact with natural amino acids (Fig. 1a) [8•]. Selective interactions between POMs and amino acids are demonstrated from the intensity change of POMs' luminescence. Higher charged number of POMs performs favorable for stronger interaction while the acidity and hydrophobicity of the amino acids take more effect for the binding that are believed from electrostatic interaction. Because of the positive feature of amino group, the electrostatic interaction mainly occurs at the site close it. When the pH of the solution is lower than the pK value of amino group, the electrostatic interaction becomes obvious. Thus, in general, POMs show much stronger interaction with basic amino acids, while in many cases the hydrogen bonding between amino group and terminal O atom supports the interactions.

2.2. Interaction of POMs with peptides and proteins

Diphenylalanine peptide, as a shortest peptide which could be extracted from Alzheimer's β-amyloid polypeptide [9], can act as a building block in the construction of versatile supramolecular structures.

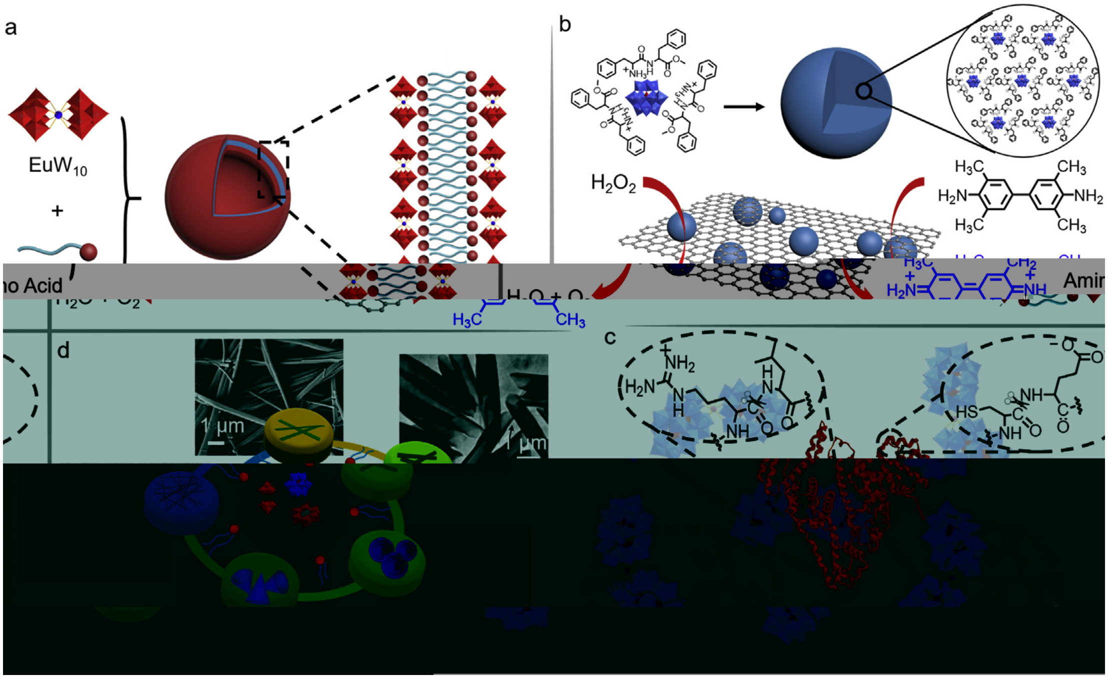

Fig. 1. Schematic illustration of (a) the vesicles formed by $Na_9(EuW_{10}O_{36})$ and amino acids [8•]. *Source: Reprinted from ref.* [8•]. *Copyright 2016 American Chemical Society*; (b) the assembly process of the peptide@POM@graphene complex and its function of peroxidase like mimics [12•]. *Source: Reprinted from ref.* [12•]. *Copyright 2015 American Chemical Society*; (c) $K_{15}H[Zr(\alpha_2\text{-}P_2W_{17}O_{61})_2]$ as an active artificial protease selectively hydrolyzing human serum albumin at four distinct positions [14]. *Source: Reprinted from ref.* [14]. *Copyright 2014 John Wiley and Sons*; (d) Alkane surfactants covered POM complex self-assembly in various morphologies: nano-cones [22], *Source: Reprinted from ref.* [22] *Copyright 2009 American Chemical Society*, nanotubes [22], nanoflowers [24].
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