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Nanohybridization of Polyoxometalate and Nanomaterials for Electrochemical Application

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초 록

Polyoxometalates (POMs)는 뛰어난 특성과 전기 화학 응용 분야에 대한 많은 잠재력을 가지고 있다. POM은 매우 잘 녹는 성질 때문에 전기화학 소자에서 POM의 잠재력을 최대한 활용하기 위해서는 다양한 기능성 재료에 POM을 고정화하는 과정이 필수이다. 본 논문에서는 우리는 최근 개발된 고정화 방법인 나노 카본 및 전도성 고분자와 같은 전도성 나노 물질에 POM을 도입하는 기술들에 대해서 논하고자 한다. Langmuir-Blodgett 기술, 층별 자기 조립 및 전기 화학 in-situ 중합을 사용하여 전도성 고분자 매트릭스 및 POM을 나노 카본으로 도입할 수 있는 다양한 고정화 전략을 소개한다. 또한 우리는 POM의 응용 분야인 물 산화용 전극 촉매, 리튬 이온 배터리, 슈퍼커패시터 및 전기화학적 바이오 센서 등의 다양한 전기 화학 응용 분야를 다룬다.

Abstract

Polyoxometalates (POMs) have outstanding properties and a great deal of potential for electrochemical applications. As POMs are highly soluble, the implementation of POMs in various functional materials is required to fully use their potential in electrochemical devices. Here, we will review the recently developed immobilization methods to incorporate POMs into conductive nanomaterials, such as nanocarbons and conducting polymers. Various immobilization strategies involve POMs entrapped in conducting polymer matrix and integration of POMs into nanocarbons using a Langmuir-Blodgett technique, a layer-by-layer self-assembly, and an electrochemical in-situ polymerization. In addition, we will review a variety of electrochemical applications including electrocatalysts for water oxidation, lithium-ion batteries, supercapacitors, and electrochemical biosensors.

Keywords: polyoxometalate, nanocarbon, electrochemistry, nanohybrid

1. Introduction

Polyoxometalates (POMs) are transition metal oxide clusters, in which heteroatoms of tungsten, molybdenum, phosphorus, silicon, or oxygen are bonded to each other in three-dimensional structure[1-3]. The unique properties of POMs in terms of structure, size, redox, chemistry, photochemistry, and charge transfer, have made them as a potential candidate of nanobuilding blocks for nanocomposites in a wide range of energy conversion and storage, electrochemical sensors, and electrochemical catalysts[4-6]. The electrochemical properties of

POMs have been extensively investigated in homogeneous and heterogeneous conditions using various electrochemical techniques of cyclic voltammetry, galvanostatic charge/discharge, and impedance[5]. Heterogeneous form of POMs are preferred for many applications in electrochemical industry because they provide better chemical and thermal stability and allow easier material recovery and recycling. Many previous reviews described the properties of POMs in homogeneous states. This review will focus on POM-based electrodes in a heterogeneous state for electrochemical applications.

The immobilization of POMs onto a conductive support or integration of POMs into conductive matrix is essentially required for fabrication of nanostructured electrode materials[1,2]. The nanocarbon materials of carbon nanotubes (CNTs), graphene, and conducting polymers have been widely used as supporting or matrix materials for immobilization of POMs[7-10]. The nanocomposites of POMs and nanocarbons provide synergistic effects of high electrocatalytic performance

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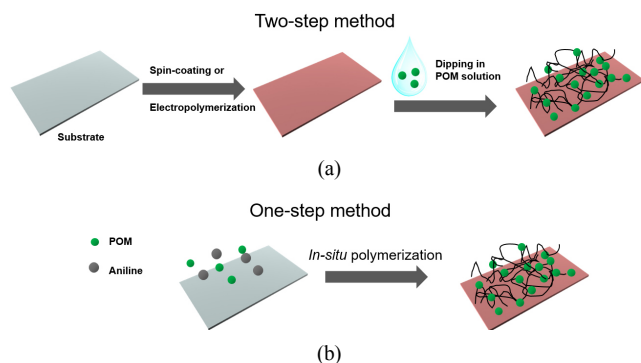 Tel: +82-33-570-6545 e-mail: bgchoi@kangwon.ac.kr

Figure 1. Scheme of preparation of POM/conducting polymer matrix through (a) two-step and (b) one-step methods.

in POMs and high electronic conductivity in nanocarbons, resulting in dramatic electrochemical performances in electrochemical devices. In most cases, the immobilization of POMs relies on non-covalent interactions with the nanocarbons. So far, various immobilization strategies have been developed, including (1) POMs entrapped in conducting polymers matrix[7,8], (2) self-organized hybrids based on POMs and cationic surfactants[11,12], (3) Langmuir-Blodgett technique[13], (4) layer-by-layer self assembly method[14,15], and (5) other approaches.

The scope of this review is to describe how to make nanohybirds of POMs and nanocarbons, including various immobilization methods. The most promising immobilization methods for fabrication of nanohybrids will provide a perspective on the capabilities and limitations of these methods. Next, we summarized a great potential of nanohybrids of POMs and nanocarbons in electrochemical applications of sensors, water splitting, supercapacitors, and batteries with highlights on the outstanding electrochemical performances of nanohybrids.

2. POM Background

The POMs are a class of metal oxide cluster anions with the general formula $(MO_x)_n$, where M is transition metals of Mo, W, V, or Nb and x = 4-7. The cluster framework includes a heteropolyanion, for example, sulfur, or phosphorous. Thus, the POMs form a huge variety of shapes, sizes, and compositions with remarkable physicochemical and other unique properties. These POMs can be generally classified into three main categories:

Heteropolyanions: These materials include two types of atoms, the heteroatom and the addenda atom. The heteroatoms are W, Mo, or V, while highest oxidation state atoms of Nb, Ta, Re, and I are addenda atoms in many heteropolyanions. Most POMs are based on the Keggin-type $[X_2M_{12}O_{40}]^{n-}$ and the Wells-Dawson-type $[X_2M_{18}O_{62}]^{n-}$ structures, in which X is the geteroatom and M is the addenda atom [3]. The Keggin-type and Wells-dawson-type POMs are redox active through multiple electron transfer, resulting in unique electrochemical performances.

Isopolyanions: Isopolyanions are the same structural framework as heteropolyanions, in which high-valent Group 5 or 6 transition metal ions are bonded to each other without the central heteroatom[6]. The representative isopolyanion is the Lindqvist anions with formula $[M_6O_{19}]^{n-}$, which are found for the full range of 4d and 5d polyanion-forming metal ions (Nb, Ta, Mo, W). Compared to the heteropolyanions, the isopolyanions are more native charge and less stable structures.

Giant polymolybdate clusters: The molybdenum blue and molybdenum brown, for example, 140 MoO_6 octahedra and 14 $MoO_6(NO)$ pentagonal bipyramids are linked[3]. These POMs create well-defined geometries by varying the number of building groups. The well-ordered structures prefer highly symmetric ring or sphere-shaped morphologies with pore structures[16].

Based on transition metals and structure, POMs can be synthesized in variety of POM forms. We will describe the common heteropolyanions of Keggin and Dawson POMs, because these POMs are generally used in electrochemical applications. The redox properties of these POMs can be easily tuned by changing their heteroatoms or addenda atoms[17,18]. The redox properties of POMs with multiple electron transfer are key factors for developing energy storage and conversion and electrochemical sensors.

3. Strategies in Preparing POM-based Nanohybrids

The POMs are highly water-soluble because of their intrinsic negative charges. Prior to their electrochemical applications, the POMs should be immobilized into conductive supports, such as, nanocarbons. In this section, we will introduce various immobilization strategies, including (1) POMs entrapped in conducting polymers matrix, (2) integration of POMs into nanocarbons using a Langmuir-Blodgett technique, a layer-by-layer self assembly, and an electrochemical in-situ polymerization.

3.1. Entrapping POMs into conducting polymer matrix

The conducting polymers (CPs) are electronically conductive and reversibly redox reactive in electrochemical electrodes and can provide a good substrate for immobilization of POMs. Various CPs have been adopted to incorporation of POMs into the CP matrix, including polypyrrole (PPy), polyaniline (PANI), polythiophene (PT) and their derivatives[7,8]. The electrostatic interaction-assisted immobilization method is applied to the fabrication of POM/CP nanohybirds (Figure 1a). First, CP film is fabricated by spin-coating or electropolymerization method. The obtained CP films were soaked in the solution containing POMs. The highly negative charged POMs are strongly interacted with cationic polymer matrix. Hence, the POMs are efficiently immobilized in the polymer matrix. For instance, Wang *et al.* reported a hybrid Langmuir film of Anderson-type POM encapsulated by three tetrabutylammonium ions using a 3,5-bis(tetradecyloxy)benzoic acid by amidation[19]. This two-step method often uses layer-by-layer (LBL) deposition by means of electrostatic attraction. As the POMs are negative charged ions, cation polymer electrolytes have been used for LBL process. A number of cation polymer electrolytes involves polyallylamine hydrochloride (PAH), polyethyleneimine (PEI), poly(sodium styrene sulfonate) (PSS), chitosan, and poly(diallyldimethylammonium
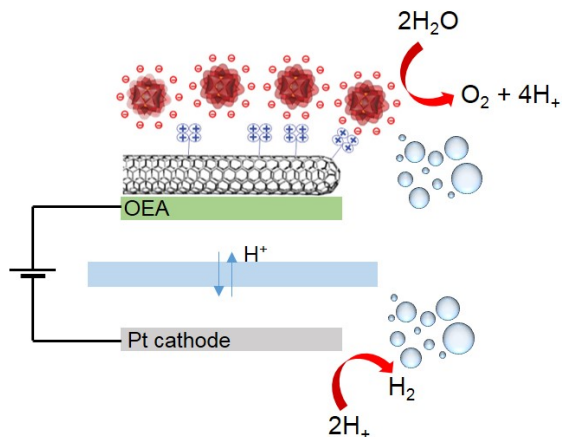
Figure 2. Schematic illustration of water splitting electrochemical cell with integrated nanostructured oxygen-evolution anode (OEA) based on the Ru$_4$-POM/MWNT (Reproduced from ref. 31 with permission of Springer Nature).

Figure 3. Schematic illustration of the CNTs-SW$_{11}$ nanocomposite as anode materials for LIBs via covalent bonding between POM and CNTs (Reproduced from ref. 25 with permission of Royal Society of Chemistry).

chloride) (PDDA)[20-23].

Another method is *in situ* immobilization of the POMs through one step process (Figure 1b). This process involves the chemical or electrochemical oxidation of CP monomers to form a poly film in the presence of POM solution. The strong acidity of POMs acidized CP monomers, such as aniline, pyrrole, and thiophene, and thus resulting in polymerization process. The final product is POM-doped CP nanohybrids or nanocomposites. The one-step method is the most promising and straightforward method for POM/CP nanohybrids. For example, Yang *et al*. reported POM-doped PANI nanopollar films using *in-situ* electrochemical polymerization[8]. They fabricated nanopillar structured polymer films by photo/soft-lithography and then coated with a thin layer of gold nanoparticles. Based on gold-coated polymer nanopillar films, the POM-doped PANI films were synthesized using a co-electrodeposition process using an amperometric technique. The electrolyte contains POMs and aniline monomers dissolved in sulfuric acid. During the electrodeposition process, the POMs were entrapped in the PANI matrix. They also developed a control method of the coating layers by means of electrodeposition time[7]. As the deposition time increases, the coating thickness increased linearly. As-synthesized POM/CP/nanopillar electrodes showed excellent electrochemical performances for pseudocapacitor and enzymeless electrochemical sensors. In addition, the use of CP matrix enabled to high mechanical resistance against to bent and twisted states. Paik *et al*. reported nanofibers of POM/PANI using a chemical polymerization procedure with the presence of ammonium persulfate oxidant. The resultant nanofibers improved electrochemical properties in lithium ion battery application[24].

3.2. Integration of POMs into nanocarbons

The nanohybrids of POMs and nanocarbons can be prepared by two main strategies of covalent and non-covalent functionalization approaches. Covalent method is based on the stable organo-functionalized POMs, including alkoxides, silanes, phosphonates, and imides. The intermolecular interactions between the POMs and organic func-
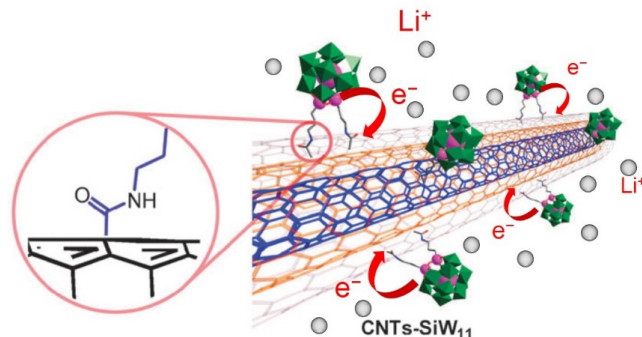
tionalization groups lead to specific cluster assembly. However, the interaction among them is often relatively weak for many electrochemical applications. Chen *et al*. reported hybridization of POMs and functionalized nanocarbons. The POM clusters are interacted with the pendant amine groups on the surface of nanocarbons[25].

Non-covalent interactions have been widely used for preparing nanohybrids of POMs and nanocarbons (*e.g.*, CNTs and graphene)[26-28]. The chemisorption of POMs and nanocarbons has been often used to fabricate nanohybrids. This method is straight forward; the POMs can directly interact with oxidized carbon surface. The oxidized carbon materials are dispersed in an aqueous or organic POM solution and agitated by stirring or ultrasonication under ambient conditions. In addition to the oxidized carbon materials, the electrostatic interactions between the negative charged POMs and positive charged nanocarbons are the most promising driving forces for hybridization. The positively charged carbons can be synthesized by covalent attachment of cations using oxidized carbons in which hydroxyl and carboxyl groups are available. In addition, van der Waals or π-π interactions can lead to functionalized nanocarbons. Wei *et al*. reported one-step electrochemical fabrication of reduced graphene oxide (RGO)/POM/CNT composites through aromatic π-π stacking and electrostatic attraction [29]. Yang *et al*. described a simple anion exchange method for preparing POM/RGO nanohybrids. The poly(1-vinyl-3-ethylimidazolium bromide) (PIL) was used as a functional group for RGO[30]. Cation-p interactions between the PIL and the RGO lead to Br⁻ anion functionalized RGO materials. The halide anions of PIL can be easily exchanged by POM anions through metathesis reaction or conversion into complex anions by Lewis acid addition. The resultant POM/PIL/RGO nanohybrids show strong intramolecular interactions.

4. Electrochemical Applications of POMs

The POMs have been widely used in electrochemical energy conversion/storage and sensing area due to their remarkable electrochemical activities. In this section, we will review a variety of electrochemical applications including electrocatalysts for water oxidation, lithium-ion batteries, supercapacitors, and electrochemical biosensors.
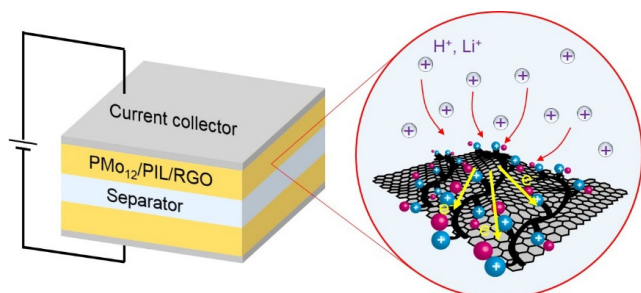
Figure 4. Schematic illustration of the symmetric supercapacitors based on the PMo_{12}/PIL/RGO nanohybrids created by exchange reaction of bromide in PIL for anionic POM (Reproduced from ref. 30 with permission of John Wiley and Sons).

Figure 5. Schematic representation of the amperometric biosensors based on PMo_{12}/PANI nanopillars PIL/RGO nanohybrids[8].

4.1. Water oxidation catalysts

Based on an unusual and tunable redox activity, the POMs can be a promising candidate for water oxidation catalysts (WOCs). Typically, water oxidation is not only limited by sluggish oxygen evolution reactions involving the four proton-electron transfer but also required an additional driving force (termed the overpotential) to drive the reactions[31]. To overcome these problems, transition metal-substituted POMs have been explored as the WOCs. Toma *et al.* prepared the Ru-substituted POMs on cationic polymer-coated MWNT (Ru_4-POM/MWNT) by self-assembly and used an anode for water splitting devices (Figure 2)[32]. The Ru_4-POM/MWNT showed an appreciable turn of frequency (TOF, 0.01 s^{-1}) of water oxidation at low overpotential of 0.35 V. Hill group also reported the Ru_4-POM/graphene as the efficient WOCs, which showed high TOF of 0.82 s^{-1} at overpotential of 0.35 V[33]. More recently, Ding *et al.* developed the Ru_4-POM/Ni foam electrodes using silane chemistry[34]. As-prepared Ru_4-POM/Ni foam provided excellent electrocatalytic activity toward oxygen evolution with overpotential at 0.55 V. Wu *et al.* synthesized the Co-substituted POMs and then assembled with a mesoporous carbon nitride (Co_4P-POM/MCN) through two-step vacuum-assisted impregnation[35]. The Co_4P-POM/MCN exhibited the TOF of 0.3 s^{-1} with applied potential at 1.4 V (vs. Ag/AgCl) and moderate overpotential up to 0.55 V.

4.2. Lithium ion batteries

The fast, reversible, and stable multi-electron redox abilities allow the POM to be new electrode materials for lithium-ion batteries (LIBs). However, there are very limited examples of the POM-based LIBs due to good solubility, low surface area, and poor electrical conductivity. Therefore, the linkage of the POMs with electrically conductive supports is highly desirable to make an efficient electrode for LIBs. Kawasaki *et al.* used the Keggin-type POM, $[PMo_{12}O_{40}]^{3-}$ (PMo_{12}), and single-wall carbon nanotubes to prepare POM/SWNT nanohybrids as a cathode by electrostatic interactions, which provided much higher capacity (320 mAh g^{-1}) than that of usual LIBs (c.a. 150 mAh g^{-1})[36]. Chen *et al.* also reported the nanocomposites based on amine-functionalized $SiW_{11}O_{39}$ attached on CNT through covalent bonding (Figure 3) [25]. It employed as an anode for LIBs and exhibited high discharge
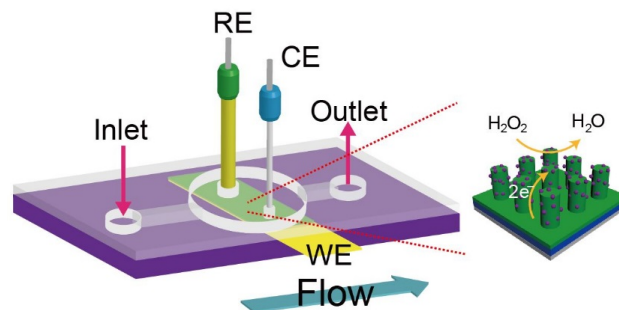
capacity of 650 mAh g^{-1} at 0.5 mA cm^{-1} and good cycle stability up to 100 cycles. Quite recently, Diao group successfully synthesized the 3D graphene aerogels embedded PANI and $[PW_{12}O_{40}]^{3-}$ (PW_{12}) nanospheres as a cathode in LIBs via hydrothermal treatment, resulting in high capacity of 285 mAh g^{-1} and remarkable cycle stability up to 1,000 cycles[37].

4.3. Supercapacitors

Besides batteries, the POMs immobilized on conducting polymers and carbonaceous materials have been employed as electrode materials for supercapacitors. In 2003, Gómez-Romero *et al.* firstly reported the electrodeposited PMo_{12}/PANI nanocomposites as electrode materials for supercapacitors[38]. The results showed that as-prepared PMo_{12}/PANI achieved areal capacitance of 195 mF cm^{-2} and energy density of 24.4 mJ cm^{-2}, and cycle stability up to 500 cycles. After this initial report, Gómez-Romero and coworkers further developed the POMs assembled with activated carbon (AC) and RGO through the simple mixing and the hydrothermal treatment, respectively[39,40]. The resulting composite materials represented outstanding long cycle stability over 10,000 cycles and excellent specific capacitance values of 245 F g^{-1} (AC-PW_{12}) and 276 F g^{-1} (HT-RGO-PMo_{12}), compared to other POM-based electrodes. A different approach to deposit POM on RGO via anion exchange reactions was recently reported by Yang *et al.* who used PILs to link PMo_{12} and RGO[30]. The PILs provided strong attachment of POM and ion transfer channels, which allow the POM/PIL/RGO to obtain high specific capacitance of 408 F g^{-1}, high energy of 56 Wh kg^{-1} and power densities of 52 kW kg^{-1}.

4.4. Electrochemical biosensors

Electrochemical biosensors contain biomolecular receptors and electrochemical transducers (denoted an electrode) that translates the biological events near electrode surface into an electrical signal. In an electrochemical point of view, the signal is depended on not only electron and mass transfer at the surface of electrode but also oxidation or reduction potential applied to electrode. In this regard, the POMs with conductive supports are an ideal candidate as electrode materials for the electrochemical biosensors due to fast multi-electron transfer, high ionic conductivity, and potential tenability. Zhang *et al.* prepared the PW_{12}/RGO electrode using layer-by-layer inject printing, which

provided the sensitive detection of dopamine[41]. Choi *et al.* developed the amperometric sensors based on PMo_{12}/PANI nanopillars (Figure 5) [8]. Compared to PMo_{12}/PANI with flat surface, the PMo_{12}/PANI nanopillars showed the improved mass transport and excellent electrocatalytic activities towards reduction of hydrogen peroxide. Laskin group used a chemical bath deposition to prepare PMo_{12}/graphene nanocomposites to detect the ascorbic acid[42]. The electrochemical studies described that the fast electron transfer kinetics and better voltage efficiency of PMo_{12}/RGO led to high sensitive and selective detection of ascorbic acid in presence of interference, such as sodium chloride, glucose, uric acid, citric acid, ethanol.

5. Conclusions and Outlook

Owing to unique properties, POMs have considered a promising nanobuilding block for fabricating nanohybrids using conductive nanomaterials of nanocarbons and conducting polymers. The nanohybrids provide highly redox reactions, multiple electron transfer, and high electrocatalytic activity. So far, various immobilization methods to incorporate POMs into conductive nanomaterials, including POMs entrapped in conducting polymer matrix and integration of POMs into nanocarbons using a Langmuir-Blodgett technique, a layer-by-layer self-assembly, and an electrochemical in-situ polymerization. A number of previous reports have described the enhancement in electrochemical performances after immobilization of POMs on conducting nanomaterials. The intermolecular interactions and the charge transfer between POMs and conductive supports are important for the optimization of nanohybrids in electrochemical applications. The covalent and non-covalent interaction strategies have been employed in design and fabrication of nanohybrids. The well-developed nanohybrids have showed a great deal of potential in electrochemical energy conversion and storage, electrocatalysts, and electrochemical biosensors. To widely use POM-based nanohybrids in many applications, future efforts should focus on new chemistries of POMs and optimization of nanohybrids.

Acknowledgement

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