Polyoxometalates (POMs) have been used for spectrophotometric determinations of silicon and phosphorus under acidic conditions, referred to as the molybdenum yellow method and molybdenum blue method, respectively. Many POMs are redox active and exhibit fascinating but complicated voltammetric responses. These compounds can reversibly accommodate and release many electrons without exhibiting structural changes, implying that POMs can function as excellent mediators and can be applied to sensitive determination methods based on catalytic electrochemical reactions. In addition, some rare-earth-metal-incorporated POMs exhibit fluorescence, which enables sensitive determination by the enhancement and quenching of fluorescence intensities. In this review, various analytical applications of POMs are introduced, mainly focusing on papers published after 2000, except for the molybdenum yellow method and molybdenum blue method.

Keywords Polyoxometalates, electrochemistry, modified electrode, catalytic wave, spectrophotometry

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1 Introduction

Polyoxometalates (POMs) are discrete anionic inorganic clusters, which consist of addenda atoms such as molybdenum and tungsten, heteroatoms, such as phosphorus and silicon, and oxygen. The three-dimensional polymerization of addenda atoms and heteroatoms via oxygen polymerization provides a variety of structures, of which Keggin- [(X\textsubscript{12}M\textsubscript{12}O\textsubscript{40})\textsuperscript{n−}] and Wells-Dawson- [(X\textsubscript{2}M\textsubscript{18}O\textsubscript{62})\textsuperscript{n−}] type structures are found in most POMs. Since POMs exhibit fascinating chemical properties depending on their components and structures, including redox activity, strong acidity, decreased corrosivity, fluorescence and magnetism, they have been applied to a variety of research fields, such as catalysis, materials and sensors. Spectrophotometric determinations of phosphorus, silicon and arsenic are accomplished by the formation and reduction of POMs; these approaches are referred to as the molybdenum yellow method and molybdenum blue method, respectively.

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isopolytungstates. However, their components and structures are completely different from those of isopolymolybdates. Moreover, due to their slow reactions, the distribution of each isopolytungstate has not been fully confirmed as a function of pH and tungstate concentrations. A mixed molybdate(VI/V) solution was reported to generate mixed-valence isopolymolybdates with massive structures, but the solution chemistry of molybdate(VI/V) is still ambiguous. Phosphate, arsenate, silicate and germanate, which are called hetero-ions, react with molybate and/or tungstate, which are called addenda ions, under acidic conditions to form heteropolymolybdate and heteropolytungstate compounds. Similar to those of isopolyoxometalates, the formation conditions of heteropolymolybdates and heteropolytungstates are different depending on the heteroatoms. The formation of molybdophosphates is totally different from that of molybdoarsenates even though phosphorus and arsenic belong to the same group in the periodic table. It is from that of molybdophosphates even though phosphorus and arsenic belong to the same group in the periodic table. It is not noted that in acidic aqueous solutions, [PMo12O40]3–, which has been frequently used in analytical science, coexists with [PMo9O34]9–. Even if pure H3PMo12O40 is dissolved in water, it is partially converted into [PMo9O34]9–. The addition of water-miscible organic solvents leads to the selective formation of [PMo12O40]3– as well as the stabilization of [AsMo12O40]3–. Many researchers have investigated the formation of various POMs, but the formation mechanism is very complicated. Recently, direct information on the formation of POMs has been obtained by electro spray ionization mass spectrometry. Understanding the solution behavior of POMs is very important for their analytical applications.

Many POMs exhibit fascinating electrochemical properties, such as multi-electron transfer and reversible redox cycles. Generally, several one-electron transfer processes occur at each redox potential under neutral conditions, where no proton is coupled with POMs in the case of Keggin-type POMs, [XM12O40]m– and Wells-Dawson-type POMs, [X(M2O8)2]n– (Fig. 1). Comparing the same heteroatom (X)-containing POMs, the redox potentials of molybdenum-based POMs are more positive than those of tungsten-based POMs. Comparing the same addenda atom (M)-containing POMs, the redox potentials of molybdenum-based POMs are more positive than those of tungsten-based POMs. Comparing the same heteroatom (X)-containing POMs, the redox potentials of molybdenum-based POMs are more positive than those of tungsten-based POMs. Comparing the same heteroatom (X)-containing POMs, the redox potentials of molybdenum-based POMs are more positive than those of tungsten-based POMs. Comparing the same heteroatom (X)-containing POMs, the redox potentials of molybdenum-based POMs are more positive than those of tungsten-based POMs. Comparing the same heteroatom (X)-containing POMs, the redox potentials of molybdenum-based POMs are more positive than those of tungsten-based POMs. Comparing the same heteroatom (X)-containing POMs, the redox potentials of molybdenum-based POMs are more positive than those of tungsten-based POMs. Comparing the same heteroatom (X)-containing POMs, the redox potentials of molybdenum-based POMs are more positive than those of tungsten-based POMs. Comparing the same heteroatom (X)-containing POMs, the redox potentials of molybdenum-based POMs are more positive than those of tungsten-based POMs. Comparing the same heteroatom (X)-containing POMs, the redox potentials of molybdenum-based POMs are more positive than those of tungsten-based POMs. Comparing the same heteroatom (X)-containing POMs, the redox potentials of molybdenum-based POMs are more positive than those of tungsten-based POMs. Comparing the same heteroatom (X)-containing POMs, the redox potentials of molybdenum-based POMs are more positive than those of tungsten-based POMs. Comparing the same heteroatom (X)-containing POMs, the redox potentials of molybdenum-based POMs are more positive than those of tungsten-based POMs. Comparing the same heteroatom (X)-containing POMs, the redox potentials of molybdenum-based POMs are more positive than those of tungsten-based POMs. Comparing the same heteroatom (X)-containing POMs, the redox potentials of molybdenum-based POMs are more positive than those of tungsten-based POMs. Comparing the same heteroatom (X)-containing POMs, the redox potentials of molybdenum-based POMs are more positive than those of tungsten-based POMs. Comparing the same heteroatom (X)-containing POMs, the redox potentials of molybdenum-based POMs are more positive than those of tungsten-based POMs. Comparing the same heteroatom (X)-containing POMs, the redox potentials of molybdenum-based POMs are more positive than those of tungsten-based POMs. Comparing the same heteroatom (X)-containing POMs, the redox potentials of molybdenum-based POMs are more positive than those of tungsten-based POMs. Comparing the same heteroatom (X)-containing POMs, the redox potentials of molybdenum-based POMs are more positive than those of tungsten-based POMs. Comparing the same heteroatom (X)-containing POMs, the redox potentials of molybdenum-based POMs are more positive than those of tungsten-based POMs. Comparing the same heteroatom (X)-containing POMs, the redox potentials of molybdenum-based POMs are more positive than those of tungsten-based POMs. Comparing the same heteroatom (X)-containing POMs, the redox potentials of molybdenum-based POMs are more positive than those of tungsten-based POMs. Comparing the same heteroatom (X)-containing POMs, the redox potentials of molybdenum-based POMs are more positive than those of tungsten-based POMs. Comparing the same heteroatom (X)-containing POMs, the redox potentials of molybdenum-based POMs are more positive than those of tungsten-based POMs. Comparing the same heteroatom (X)-containing POMs, the redox potentials of molybdenum-based POMs are more positive than those of tungsten-based POMs.
was achieved by fluorescence enhancement of benzoic acid (BA), thiamine (TH) and 3-(4-hydroxyphenyl)propionic acid (HPPA) by ‘OH radicals generated from H2O2 under catalysis of [α-SiW12O40]4–. In the presence of BA, TH and HPPA, the determination ranges and LODs were 10 nM to 1.6 μM and 6.7 nM, 1.6 μM to 10 mM and 0.22 μM, and 10 μM to 0.25 mM and 9.6 μM, respectively.76

The decrease in absorbance due to the oxidation of molybdenum blue species upon the addition of oxidants enables the determination of NO3− and NO2− at sub ppb and ppm levels by using a flow injection system.77 The species IO3− was also determined by using a flow injection system equipped with [MoO3]3− deposited on a gold electrode with poly(dimethylammonium chloride) (PDDA) and sodium-3-mercapto-1-propanesulfonate as the working electrode of the electrochemical detector, where the same process occurs as Scheme 1.68

4 Determination of Biomolecules and Biorelated Molecules

The development of sensing techniques for biomolecules and biorelated molecules is essential for monitoring health conditions and understanding the mechanisms of the human body. Although a variety of biosensors have been developed, many issues and challenges remain to fully optimize these biosensing techniques. Additionally, (online) monitoring of amino acids requires selective and sensitive determination methods without expensive apparatuses and specialized skills. Since the amino acids: L-cysteine, L-tyrosine and L-tryptophan, as well as the nucleobases: guanine and adenine, can function as antioxidants that can reduce POMs, sensitive electrochemical determination methods have been developed by enhancing the current magnitude in the electrocatalytic waves of POMs depending on the amino acid and nucleobase concentrations (Table 2).78–83 In addition, cysteine was determined based on its ability to reduce [P2Mo18O62]6– by using a stepwise injection spectrophotometric analyzer, presenting a range of 9 μM – 0.1 mM and a LOD of 3 μM.84

Amperometric determination (0.5 – 50 μM) of the catalytic oxidation of methionine itself and peptides containing methionine separated by reverse-phase high-performance liquid chromatography (HPLC) was achieved by using an electrochemical detector with [PW11O39{Rh2(OAc)2}]5– in a sol-gel material on a carbon-based conductive composite electrode.85

A large number of glucose sensors and detection methods have been developed because monitoring glucose levels is essential for understanding the mechanism of food intake and the diagnosis of diseases such as diabetes. Glucose has been amperometrically determined with a glucose oxidase/H2O2 and POMs changes from colorless to blue upon the addition of glucose, enabling this system to be used as a spectrophotometric glucose sensor at micro-molar levels. Interestingly, POMs such as [SiW12O40]4–, [PCoW11O39]5–, [SVW11O40]3– and [SV2W10O40]4– mimic enzymes (Scheme 2). In the presence of H2O2, the use of [PV3Mo9O39]5– and lumicolin, instead of 3,3′,5,5′-tetracyano- benzidine, achieved sensitive determination of glucose due to the chemiluminescence of lumicolin.91 Flow injection analysis
| POMs | Coexisting substances | Binder substances | Base electrode | Determination range | Limit of detection | Ref. |
|------|----------------------|-------------------|----------------|---------------------|-------------------|-----|
| $\text{H}_2\text{O}_2$ | $[\text{SiMo}_6\text{O}_{18}]^{3–}$ | $[\text{Cu}((bpy)_2]^3+)$, SWCNTs | PPy | GCE | 10 – 18 nM | 1 nM | 32 |
| $[\text{SiMo}_6\text{O}_{18}]^{3–}$ | CNT, AuNPs | PEI | ITO | 1 – 98 μM | 0.052 μM | 38 |
| $[\text{SiMo}_6\text{O}_{18}]^{3–}$ | CNT, AuNPs, PEDOT | CNTs | PEDOT, Nafion | GCE | 3.4 μM – 8 μM | 0.34 μM | 60 |
| $[\text{SiMo}_6\text{O}_{18}]^{3–}$ | PPy | PEI | ITO | 0.1 – 800 nM | 1 μM | 52 |
| $[\text{SiMo}_6\text{O}_{18}]^{3–}$ | MWCNTs | PEDOT, PEI | GCE | 5 – 50 mM | 1 μM | 53 |
| $\text{NO}_2^–$ | $[\text{SiMo}_6\text{O}_{18}]^{3–}$ | CuO NPs | GO, AuNPs | PEI | 0.5 – 200 μM | 8.3 μM | 43 |
| $[\text{SiMo}_6\text{O}_{18}]^{3–}$ | CuO NPs | PEI | ITO | 0.3 – 5000 μM | 1 μM | 44 |
| $\text{ClO}_2^–$ | $[\text{SiMo}_6\text{O}_{18}]^{3–}$ | GO | PEI | ITO | 0.5 μM – 2500 μM | 0.1 μM | 51 |
| $[\text{SiMo}_6\text{O}_{18}]^{3–}$ | GO | PEI | ITO | 0.5 μM – 2500 μM | 0.1 μM | 51 |
| $\text{BrO}_3^–$ | $[\text{SiMo}_6\text{O}_{18}]^{3–}$ | CuO NPs | PEDOT, PEI | GCE | 5 – 50 mM | 1 μM | 53 |
| $[\text{SiMo}_6\text{O}_{18}]^{3–}$ | CuO NPs | PEDOT, PEI | GCE | 5 – 50 mM | 1 μM | 53 |
| $\text{IO}_3^–$ | $[\text{SiMo}_6\text{O}_{18}]^{3–}$ | CuO NPs | PEDOT, PEI | GCE | 5 – 50 mM | 1 μM | 53 |
| $[\text{SiMo}_6\text{O}_{18}]^{3–}$ | CuO NPs | PEDOT, PEI | GCE | 5 – 50 mM | 1 μM | 53 |

EMIM: 1-ethyl-3-methylimidazolium; BMIM: 1-butyl-3-methylimidazolium; OMC: ordered mesoporous carbon; TEOS: tetraethoxysilane; PPy: polypyrrole; PAu: polyaniline; PEI: poly(ethyleneimine); APS: 3-aminopropyltrimethoxysilane; SWCNTs: single-walled carbon nanotubes; MWCNTs: multiwalled carbon nanotubes; TRP: [meso-5,10,15,20-tetra(pyrildiyl)porphyrin]tetakis[bis(bipyridine)chlorido ruthenium(II)]; GO: graphene oxide; rGO: reduced graphene oxide; PVP: poly(4-vinylpyridine); PDDA: poly(diallyldimethylammonium chloride); PSS: poly(styrenesulfonate); BDD: boron-doped diamond; PG: pyrolytic graphite.
coupled with a microfluidic electrochemical sensor fabricated with Nafion-coated GOx/[P2V2W16O62]8–/polymeric ionic liquid/rGO was also used to determine glucose, with a linear range of 2 – 20 mM.92

Moreover, glucose was determined spectrophotometrically by measuring the absorbance of blue species generated by the reduction of molybdosilicate species formed in a Mo(VI)-Si(IV)-DMSO system in the presence of glucose.93,94 This

| Table 2 | Amperometric determination ranges and limits of detection of biorelated molecules with POM-modified electrodes |
|-----------------|----------------------------------------------------|------------------------------------------------|---------------------|--------------------------|-----------------|-----|-----|-----|-----|
| POMs            | Coexisting substances                               | Binder substance | Base electrode | Determination range | Limit of detection | Ref. |
| L-Cystein       | [VMo12O40]3– [BMIM]PF6                              | CPE              | 50 μM – 1 mM  | 79                      |                 |     |     |     |     |
| L-Tyrosine      | [PW12O40]3– rGO                                     | GC               | 10 pM – 10 nM | 82                      |                 |     |     |     |     |
| L-Tryptophan    | [PW12O40]3– rGO                                     | GC               | 10 pM – 10 nM | 82                      |                 |     |     |     |     |
| Guanine         | Ce[SiW12O40]4– Co(salophen)                         | MWCNT            | GC            | 0.25 – 10 nM            | 20 nM           | 78   |     |     |     |
| Adenine         | Ce[SiW12O40]4– Co(salophen)                         | MWCNT            | GC            | 0.4 – 136.0 μM          | 0.24 μM         | 83   |     |     |     |
| Dopamine        | [PW12O40]3– rGO (inkjet printing)                   | ITO              | 0.5 – 20 nM   | 96                      |                 |     |     |     |     |
| Ascorbic acid   | [PMo12O40]3– Graphene                               | GC               | 1 μM – 8 nM   | 106                     | 0.5 μM          | 106  |     |     |     |
| Uric acid       | [SiNi(H2O)W11O39]6– Prussian blue nanocubes         | PEI              | GC            | 0.75 μM – 0.41 nM      | 0.514 μM        | 107  |     |     |     |
| Acetaminophen   | [PW12O40]3– Au-Pd NPs                                | Co(II)TAP        | GC            | 1.2 μM – 1.61 μM       | 0.43 μM         | 98   |     |     |     |
| Paroxetine      | [PW12O40]3– Au-Pd NPs                                | Co(II)TAP        | GC            | 1.2 μM – 1.61 μM       | 0.43 μM         | 98   |     |     |     |
| Creatinine      | [PW12O40]3– AgNP, rGO                               | PG               | 8.0 nM – 1.0 μM | 9.0 nM                   |                 | 111  |     |     |     |
| Xanthine        | [PW12O40]3– Ferrocene, rGO                          | GC               | 50 nM – 39.8 μM | 10.1 nM                  |                 | 119  |     |     |     |
| Bilirubin       | [PW12O40]3– AuNPs, rGO                              | C4N              | GC            | 1.0 pM – 0.1 nM         | 0.1 pM           | 116  |     |     |     |
| Triclosan       | [PW12O40]3– AuNPs, rGO                              | PPy (MIT)        | GC            | 0.51 – 50 nM            | 0.15 nM          | 114  |     |     |     |
| Simazine        | [PW12O40]3– PtNP, MWCNT                              | GC               | 0.1 – 5.0 μM   | 115                     |                 |     |     |     |     |

[BMIM][PF6]: 1-n-butyl-3-methylimidazolium hexafluorophosphate; Co(salophen): N,N′-bis(salicylidene)-1,2-phenylenediaminocobalt(III); Co(II)TAP: phthalocyanatocobalt(II); PFS: poly(ferrocenyilsilane); GF: graphene flakes; PG: pencil graphite electrode; MIP: molecularly imprinted polymer.
method was also applied to the assay of α-glucosidase and its inhibitors acarbose and quercetin as well as the determination of chitin from the reaction of the glucosamine generated from hydrolysis of chitin with molybdosilicate species.95

Dopamine (Fig. S1; Supporting Information) plays a very important role in the central nervous, hormonal, renal and cardiovascular systems, but it exists in biological samples with high concentrations of other biomolecules; thus, a selective and sensitive determination method is required to monitor health conditions. Many electrochemical dopamine determination methods with POMs have been reported, as shown in Table 2.96–104 Dopamine was determined without any interference by using sequential injection analysis due to the formation of blue species generated from [P2Mo18O62]6– and [PMo12O40]3– at pH 6.0 (Table 3).129 Chlorogenic acid (Fig. S13), which is a water-soluble B vitamin, occurs in food and has been used as a dietary supplement. Since FA keeps blood cells healthy and is one of the key molecules for cell division and growth, which is of considerable biological importance, a variety of FA determination methods have been investigated. The nanomolar level of FA was determined with a [P,V,Mo,Os,Sn]4+/GO/PEI-modified GCE at pH 7.40, even in the presence of dopamine and uric acid, because the oxidation potentials of the three compounds are completely different,128 and with a [PMo,W,Os]4+/AuNP/PPy-modified gold electrode at pH 6.0 (Table 3).129 Chlorogenic acid (Fig. S14), which is a natural phenolic product that occurs in many fruits and vegetables, was detected with [PW12]4+-coated AuNPs dispersed in the holes of 3D macroporous carbon on a GCE.130 Myricetin (Fig. S15), which is a natural flavonoid and antioxidant compound that occurs in various natural foods, such as grapes and teas, was determined with P,W11/SnO2/AuNP films deposited on an ITO electrode by the LBL technique.131

In humans, acetaldehyde has a high potential for carcinogenicity, as defined by the International Agency for Research on Cancer. Hence, the highly sensitive detection of acetaldehyde in beverages is of great importance. By using [PMo10,W4]6+ on a quartz crystal, the acetaldehyde contained in cider was determined from the frequency decrease due to the interaction between acetaldehyde vapour and POM after being produced from the hydrolysis of chitin with molybdosilicate species.

### 5 Analysis Related to Food Chemistry

Many chemical components contained in food and beverages have been simultaneously analyzed using gas/liquid chromatography, mass spectrometry and capillary electrophoresis.121–127 However, some specific compounds have been electrochemically determined using POM-immobilized electrodes with high sensitivity and selectivity (Table 3). Folic acid (FA) (Fig. S13), which is a water-soluble B vitamin, occurs in food and has been used as a dietary supplement. Since FA keeps blood cells healthy and is one of the key molecules for cell division and growth, which is of considerable biological importance, a variety of FA determination methods have been investigated. The nanomolar level of FA was determined with a [P,V,Mo,Os,Sn]4+/GO/PEI-modified GCE at pH 7.40, even in the presence of dopamine and uric acid, because the oxidation potentials of the three compounds are completely different,128 and with a [PMo,W,Os]4+/AuNP/PPy-modified gold electrode at pH 6.0 (Table 3).129 Chlorogenic acid (Fig. S14), which is a natural phenolic product that occurs in many fruits and vegetables, was detected with [PW12]4+-coated AuNPs dispersed in the holes of 3D macroporous carbon on a GCE.130 Myricetin (Fig. S15), which is a natural flavonoid and antioxidant compound that occurs in various natural foods, such as grapes and teas, was determined with P,W11/SnO2/AuNP films deposited on an ITO electrode by the LBL technique.131

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solid-phase microextraction pretreatment (detection range: 0 – 24.9 mg/L; LOD: 2.0 mg/L). Based on the same process, 5-hydroxymethylfurfural (Fig. S16) in honey was detected from the frequency change of a H2[Pt2W10O40]3–/coated piezoelectric quartz crystal, with a LOD of 3.4 μg/L. Moreover, a [PW12O40]3–/rGO/Ag composite film was reported to serve as a surface-enhanced Raman scattering substrate, sensitively detecting formaldehyde, acetaldelyde, propionaldehyde and acraldehyde at low concentration levels (10 nM). A toxic mycotoxin produced by several fungal strains, such as those from the genera Penicillium, Aspergillus and Monascus, and occurs in stored grain, was determined at pH 6.0 on PtNP/[PW12O40]3–/rGO composites mounted on a GCE after passing through a molecularly imprinted PPY film. The use of metal nanoparticles and graphene composite materials with the molecular imprinting techniques have achieved high sensitivity and selectivity.

Extensive attentions have been paid to the intake of food containing antioxidants such as polyphenols and carotenoids, which are thought to support the scavenging of reactive oxygen species generated in the human body under oxidative stress. A variety of methods have been developed for the detection of individual antioxidants, estimating the total amount of polyphenol and evaluation of antioxidant capacity. Since it is quite difficult to detect all antioxidants in food and beverages, the antioxidant capacity has been commonly evaluated with the oxygen radical absorbance capacity (ORAC) method, the 2,2-diphenyl-1-picrylhydrazyl (DPPH) method and Folin – Ciocalteu (F-C) method.

Recently, with the growth of the Internet of Things (IoT) technology, extensive attentions have been paid to the development of sensitive and selective gas sensors to realize smart living. In particular, hazard monitoring is very important for human health. Long-term exposure to volatile organic compounds, even at low concentrations, increases the risk of sick building syndrome.

Titanium-substituted POMs, [PtIr5W10O40]3– and [PtIr5W20O40]3–, decorated on TiO2 nanoparticles were deposited on a fluorine-doped tin oxide (FTO) electrode, which exhibited a photocurrent response under light irradiation. The response decreased in magnitude upon the addition of acetone, which enabled the determination of acetone in the range of 10 – 50 ppm. Vanadium-disubstituted molybophosphate, [PV5Mo10O40]3–, immobilized in a zeolitic imidazolate framework (ZIF-8) ultrathin film on ZnO nanorods also exhibits a photocurrent response at 0.3 V under light irradiation. The photocurrent response was enhanced in the presence of formaldehyde. This gas sensor exhibited high sensitivity (LOD: 0.387 ppm) and high selectivity to formaldehyde in the presence of several volatile organic compounds: methanol, ethanol, acetone and toluene.

A variety of techniques have achieved high sensitivity and selectivity. Extensive attentions have been paid to the detection of individual antioxidants, estimation of the total amount of polyphenol and evaluation of antioxidant capacity. Since it is quite difficult to detect all antioxidants in food and beverages, the antioxidant capacity has been commonly evaluated with the oxygen radical absorbance capacity (ORAC) method.

**6 Gas Sensors**

Recently, with the growth of the Internet of Things (IoT) technology, extensive attentions have been paid to the development of sensitive and selective gas sensors to realize smart living. In particular, hazard monitoring is very important for human health. Long-term exposure to volatile organic compounds, even at low concentrations, increases the risk of sick building syndrome.
EuW$_{10}$/N-dodecyl-$N'$-carboxymethyl-imidazolium exhibited pH-induced fluorescence switch-on (pH 3.0) and switch-off (pH 7.2) properties (Scheme 3). The enzyme urease hydrolyses urea into ammonia and carbon dioxide, and combined with EuW$_{10}$/N-dodecyl-$N'$-carboxymethyl-imidazolium, the luminescence intensity of this hybrid material increases as urea is hydrolyzed by this enzyme. Since Cu$^{2+}$ inhibits the hydrolysis of urea by urease, it can be detected from the change in luminescence intensity (Table 4). Based on the same concept, Cu$^{2+}$ was also detected by using fluorescent particles of a EuW$_{10}$/4-ethyl-4-$'$-(trimethylaminohexyloxy) azobenzene bromide, and Cr$^{3+}$ and MnO$_4^{-}$ were detected by using EuW$_{10}$/vesicles. The vesicles formed by self-assembly of EuW$_{10}$ and different amino acids, such as arginine (Arg), lysine and histidine, enhance the luminescence compared to that with EuW$_{10}$ alone, while those with glutamic acid or aspartic acid decrease the luminescence intensity. The addition of dopamine quenches the luminescence intensity of the vesicles containing Arg, which enables the determination of dopamine.

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EuW$_{10}$/zwitterionic amphiphile 3-(1-eicosyl-3-imidazolio) propanesulfonate and poly(2-acrylamido-2-methyl-1-propanesulfonic acid) hydrogels exhibit red emission under an NH$_3$ gas atmosphere, while their emission is quenched under a HCl gas atmosphere. Upon addition of Na$_2$S, EuW$_{10}$/1,2-bis(3-hexadecylimidazolium-1-yl) ethane bromide hybrid nanoparticles exhibited decreased fluorescence intensity at 622 nm (excitation wavelength at 280 nm) and increased absorbance at 400 nm in the presence of Cu$^{2+}$, leading to rapid H$_2$S detection (in a few seconds). The composite film composed of EuW$_{10}$/polyvinylpyrrolidone/PEI/N,N'$'$-bis(δ-aminopropyl)-4,4'$'$-bipyridine bromide hydrobromide (a diaminopropyl viologen) was reported to exhibit a change in absorbance and luminescence under UV irradiation, which could be reversibly recovered depending on the relative humidity. This composite film can be used as a portable solar UV-light sensor as well as a relative humidity sensor.

The other europium-incorporated POMs have been used for fluorescent determination. In the case of [Eu(W$_{10}$O$_{36}$)]$^{3-}$, EuW$_{10}$/fluorescent determination ranges and limits of detection of food related compounds with POM-modified electrodes

| POMs                          | Analytes            | Composited materials (Coexisting substances) | Determination range | Limit of detection | Ref. |
|-------------------------------|---------------------|---------------------------------------------|---------------------|-------------------|------|
| [EuW$_{10}$O$_{36}$]$^{9-}$   | Cu$^{2+}$           | 4-Ethyl-4'$'$-(trimethylamino)hexoxy) azobenzene bromide | 50 μM - 1 mM        | 0.5 μM           | 154  |
|                               | Cu$^{2+}$           | 4-Ethyl-4'$'$-(trimethylamino)hexoxy) azobenzene bromide | 50 μM - 1 mM        | 0.5 μM           | 155  |
|                               | Cr$^{3+}$           | 0 - 5 μM                                     | 9.67 nM             | 156              |
|                               | MnO$_4^{-}$         | 0 - 10 μM                                    | 4.9 nM              | 156              |
|                               | Dopamine (Arginine) | 0 - 20 μM                                    | 3.2 μM              | 157              |
|                               | H$_2$S              | 1.2-Bis(3-hexadecylimidazolium-1-yl) ethane bromide | 1.25 - 175 μM       | 2.0 pM           | 160  |
| [Eu(SiMoW$_{10}$O$_{39}$)$_{2}$]^{13-} | AA                 | 0.1 - 0.9 mM                                 | 0.53 μM             | 162              |
|                               | NO$_2^{-}$          | 0.05 - 0.4 mM                                | 1.16 μM             | 162              |
| [Eu(PHBA)(H$_2$O)$_2$(α-PW$_{11}$O$_{39}$)]^{5-} | Cr$^{3+}$          | (p-Hydroxybenzoic acid)                      | 10 - 100 mM         | 1.423 μM         | 163  |

Table 4. Amperometric determination ranges and limits of detection of food related compounds with POM-modified electrodes.
upon the addition of AA at pH 1.0, the absorbance increased, and the fluorescence intensity decreased. On the other hand, the opposite phenomena were observed with the addition of NO$_2^-$.

The changes in absorbance and fluorescence intensities led to the determination of AA and NO$_2^-$.

The ions Cr$^{3+}$ and Ca$^{2+}$ were determined from the decrease (Cr$^{3+}$) and enhancement (Ca$^{2+}$) of the fluorescence intensity from the interactions of Eu and p-hydroxybenzoic acid (PHBA) in [Eu(PHBA)(H$_2$)O]($\alpha$-PW$_{10}$O$_{36}$)$^{13}$,163

The [PrW$_{10}$O$_{36}$]$^{10-}$, which has basically the same structure as EuW$_{10}$, also exhibits luminescence. Many artificial food coloring dyes can cause various illnesses. The development of sensitive determination methods for toxic coloring dyes is thus essential for protecting human health. Several toxic food coloring dyes, such as metanil yellow, auramine O, orange II and red 40, were determined at the nanomolar level by the fluorescence of a Na$_{10}$(PrW$_{10}$O$_{36}$)/ carbon-nano-on composite material.

Ruthenium(II) tris(bipyridine) ([Ru(bpy)$_3$]$^{2+}$), which is a photoactive compound, has been used as a mediator of photosynthesis and exhibits photoluminescence, indicating that it can be used as a sensitive photoinductor. Accordingly, 2-(dibutylamino)ethanol was detected from 6.0 nM to 8.0 mM by virtue of the electrochemical-electro luminescence properties of a [Ru(bpy)$_3$]$^{2+}$/ [PMo$_{12}$O$_{40}$]$^{3-}$/magnetic Fe$_3$O$_4$/rGO on a magnetic electrode, with a LOD of 0.4 nM.

Interestingly, this magnetic composite material could be controlled by an external magnetic field to separate it from the solution and move its position on the electrode.

### 8 Other Analytical Applications

Depending on their reduction levels, POMs can be coupled with protons, offering the potential to fabricate pH sensors. For example, [PrW$_{10}$O$_{36}$]$^{10-}$/poly(allylamine hydrochloride) (PAH) on poly(sodium 4-styrenesulfonate) (PSS) and a 3-aminopropyltriethoxysilane-treated GCE gave a Nernstian response at pH = 1 – 13.

This pH sensor could be stably used for 3 months. Similarly, Pr$_3$W$_{10}$O$_{36}$/poly(hexyl viologen) on 3-aminopropyltrimethoxysilane, poly(styrenesulfonate) and PAH-treated ITO and [Co$^{2+}$($\alpha$-PW$_{10}$O$_{36}$)]$_{12}$/poly(allylamine hydrochloride) on PSS and a 3-aminopropyltrimethoxysilane-treated GCE functioned as pH sensors at pH = 1 – 5.5 and 3 – 7, respectively.

A [Na$_2$Pr$_2$W$_{10}$O$_{36}$]$^{14-}$/PEI thin film prepared by the LBL method exhibited thermochromism, in which the film changed from colorless to blue by heating at 393 K in vacuo and from blue to colorless at 293 K under an O$_2$ atmosphere.

The trihexyl(tetracetyloxy)phosphonium salt of cis-[V$_2$W$_4$O$_{13}$]$^{+}$ was shown to exhibit solvatocromism and thermochromism, from intense orange (300 K) to bright yellow (77 K).

### 9 Concluding Remarks

Aside from the molybdenum yellow method and molybdenum blue method, polyoxometalates have been widely used for analytical applications such as speciation analysis, biosensors, gas sensors and the determination of oxidants and molecules related to food chemistry and pharmaceuticals. The combination of POMs, which work as excellent redox mediators, and metal nanoparticles and/or carbon materials such as carbon nanotubes and graphene have achieved ultrasensitive determinations at pico- and nanomolar levels. In addition, the immobilization of anionic POMs and their composite materials on the surface of electrodes with cationic polymers has led to easy determination procedures and repeatable results. Although POMs themselves exhibit less interaction and less selective reactions with specific molecules, molecular imprinting techniques enable highly selective analysis. Despite many reports on the analytical applications of POMs, only phosphorus- and silicon-containing POMs have been used in most cases. Interestingly, sulfur-containing POMs exhibit voltammetric responses at more positive potentials as well as better catalysis than the corresponding phosphorus- and silicon-containing POMs. Thus, by investigating the appropriate combinations of POMs, metal nanoparticles, polymers and electrodes, the sensitivity and selectivity could be considerably improved relative to those of reported methods, widening the analytical application range.

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### 11 Supporting Information

Supporting information includes the structure of chemical compounds detected (Figs. S1 - S20). This material is available free of charge on the Web at http://www.jacs.or.jp/analsci/.

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