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An 18-connected wheel-shaped molybdenum(v) nickel–phosphate cluster for photoelectrochemical sensing of levofloxacin†

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An 18-connected $\{Mo_{16}Ni_{16}P_{24}\}$-based 2-D layered network was constructed for photoelectrochemical sensing of levofloxacin, and it represents the highest connection number of the $\{Mo_{16}Ni_{16}P_{24}\}$ wheel cluster to date. The detection limit is as low as 6.46 nM with a high sensitivity of 110.87 μA μM^{-1} and good practicality in a milk sample.

Polyoxometalates (POMs), renowned for their intriguing nature and distinctiveness, have aroused extensive research interest owing to their rich structural diversity and potential applications in catalysis, medical science, and materials science.[1,2] In the POM family, the highly reduced phosphomolybdates assembled by $\{Mo^{V}O_6\}$ units feature wide spectral absorption, reversible redox properties and strong electron transfer ability, making them promising photo-electrocatalytic materials in catalysis, energy conversion and environment.[3] In particular, the fully reduced wheel-shaped phosphomolybdate cluster $[(Mo^{V}_2O_4)_8(HPO_4)_{14}(PO_4)_{10}M_{16}(H_2O)_{20}]^{10-}$, abbreviated as $\{Mo_{16}M_{16}P_{24}\}$ (M = Co^{2+}, Ni^{2+}), possesses a centrosymmetric structure with overall C_{4v} symmetry and a large cluster size of *ca.* 19 Å.[4,5] Owing to the low oxidation state of Mo^{V} centers and abundant low-valence transition metal sites, the $\{Mo_{16}M_{16}P_{24}\}$ cluster exhibits high negative charge and ample surface oxygen donors with strong coordination ability, allowing them to be excellent inorganic structural units to incorporate appropriate organic moieties to construct function-oriented POM-based materials.[6]

Recently, exploring the influence of the coordination mode of wheel-shaped clusters on their structure complexity and functionality has garnered significant attention due to their fascinating architectures and wide applicability in materials science.[7] Since Sécheresse *et al.* reported the first $\{Mo_{16}Co_{16}P_{24}\}$ compound in 2001, the field of surface modification chemistry for $\{Mo_{16}Co_{16}P_{24}\}$ has progressed at a leisurely pace.[8] In 2011, Yang and co-workers reported a two-dimensional layered network constructed by 10-connected $\{Mo_{16}Co_{16}P_{24}\}$ with eight 4,4′-bipyridine linkers and two pyridine (Py) molecules.[9] In 2014, Xu *et al.* utilized Py and imidazole (Imi) as dual chemical modifiers to adorn a $\{Mo_{16}M_{16}P_{24}\}$ cluster, yielding 16-connected $\{Mo_{16}M_{16}P_{24}\}$ compounds.[10] Despite the abundance of surface oxygen and metal atoms serving as potential coordination sites, the reported highest covalent connectivity of the $\{Mo_{16}M_{16}P_{24}\}$ cluster is no more 16 (Fig. 1). Therefore, it is to be expected to achieve the higher connected $\{Mo_{16}M_{16}P_{24}\}$ cluster with structural complexity and specific functionality.

It is found that most of the high connectivity $\{Mo_{16}M_{16}P_{24}\}$ compounds reported are predominantly formed with the involvement of short N-containing ligands. Recently, our group introduced the 1,4-bis(1,2,4-triazol-1-ylmethyl)benzene (BBTZ) ligand with both suitable flexible and rigid structural features into the $\{Mo_{16}Co_{16}P_{24}\}$ synthetic system to obtain a photoelectrochemically active 3-D framework possessing a *pcu* topology, wherein the $\{Mo_{16}Co_{16}P_{24}\}$ cluster was coordinated with 12 BBTZ ligands.[11]

As the ongoing work, here the 4,4′-bis((1*H*-1,2,4-triazol-1-yl)methyl)biphenyl (btmbi) ligand, with a longer size and a

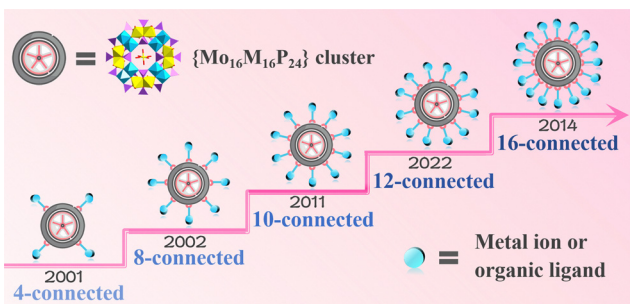

Fig. 1 Reported $\{Mo_{16}M_{16}P_{24}\}$ clusters with different connection numbers.

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Non-radical activation of peroxymonosulfate with oxygen vacancy-rich amorphous MnO_X for removing sulfamethoxazole in water

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ABSTRACT

Non-radical activation of peroxymonosulfate (PMS) is a promising technology for removing refractory organic pollutants. However, improving its efficiency is still a challenge due to its ambiguous mechanism. In this work, amorphous MnO_X was synthesized through the hydrothermal reaction between $KMnO_4$ and carbon nanopowder. The characterization results indicate that the hydrothermal temperature had little effect on the structure of the products but affected their surface composition. The sample prepared at 180 °C (MnO_X-180) had rich oxygen vacancies and exhibited high activity for sulfamethoxazole (SMX) degradation with PMS. More than 97% of SMX was removed within 30 min by 0.5 g L^{-1} of MnO_X-180 and 1 mmol L^{-1} of PMS at $pH_0 = 6.5$. Activated PMS adsorbed on catalyst surface and singlet oxygen ($^1O_2$) produced from the non-radical pathway were the active species. Surface Mn^{4+} and oxygen vacancies were found to be responsible for the generation of activated PMS and $^1O_2$, respectively. The degradation efficiency of SMX by MnO_X-180 increased with decreasing solution pH, which can be attributed to the enhanced production of activated PMS under acidic conditions. The water matrix had little effect on the performance of MnO_X-180 due to the non-radical activation mechanism, suggesting its practical application in real water treatment.

1. Introduction

Antibiotics are widely used for the treatment of diseases. Most of them cannot be effectively degraded after their discharge and have been frequently detected in wastewater [1,2]. This may cause potential harm to aquatic ecosystem and human health fackn

[3-5]. Therefore, searching for efficient technology for removing these pollutants has attracted great interest in recent years. Advanced oxidation processes (AOPs), such as photocatalysis, electrocatalysis, Fenton reaction and Fenton like reaction, can produce a large number of active radicals with strong oxidation ability [6-10]. These radicals can oxidize refractory organic pollutants into water, carbon dioxide and small organic molecules. Hence, AOPs are considered to be an efficient method for removing antibiotics in water.

In recent years, peroxymonosulfate (PMS) based AOPs have received much attention because they can effectively remove refractory organic pollutants in water [11,12]. PMS molecule has asymmetric structure (^-O_3SO-OH), and so can be readily activated into reactive species via the cleavage of O-O bond [13-15]. Various strategies have been applied to activate PMS to produce active species, such as external energy (heat, ultrasonic and ultraviolet), alkaline and transition metal-based catalyst [16-18]. Among them, PMS activation with heterogeneous catalysts has become a research hotspot due to its low energy consumption and easy operation. Among transition metal oxides, manganese oxide has been proved to be a promising catalyst for activating PMS because of its variable valence states, natural abundance on the earth, and environmental friendliness [19-23].

Up to now, various manganese oxides have been applied to activate PMS to degrade organic pollutants via different mechanisms. On one hand, sulfate radical ($SO_4^{\bullet-}$), hydroxyl radical ($^{\bullet}OH$) and superoxide radical ($O_2^{\bullet-}$) can be produced through the radical activation of PMS, which can oxidize organic pollutants through the radical pathway. On the other hand, some organic pollutants can be degraded by activated PMS on catalyst surface and/or singlet oxygen ($^1O_2$) through the non-radical pathway [24-26]. Although AOPs can produce active radicals with strong oxidation ability, the utilization rate of radicals is low due to its very short lifetime. The reactions of radicals with target pollutants can be suppressed due to the competition of common ions in water. Moreover, the reaction of halide ion and radicals might lead to the formation of some toxic halide organic intermediates. By contrast, the

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A hydrophobic artificial solid-interphase-protective layer with fast self-healable capability for stable lithium metal anodes

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Lithium (Li) metal has been considered as one of the most promising anodes for high-energy-density batteries. However, the hyperactivity of metallic Li and its dendrite growth are the major hurdles to its practical applications. Herein, a multi-functional solid-interphase-protective layer with excellent waterproof performance and fast self-healing properties was modified on the surface of Li metal to address the above issues. Under the protection of this interface, the metallic Li (denoted as P–Li) exhibited superior electrochemical stability in both Li/Li symmetric cells and full cells. Notably, even after being exposed to humid air for 3 h, the $LiFePO_4$||Li full battery with P–Li anodes still showed long-term stability with a transcendental capacity retention of ~100% after 100 cycles, revealing a significant advantage to the non-working $LiFePO_4$||Li battery with air-exposed bare Li anodes.

Li metal anode, solid interphase protective layer, stable Li plating/stripping, self-healable, hydrophobic property

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1 Introduction

To satisfy the ever-growing demand for high-energy-density devices, extensive researches on alkali metal batteries have been conducted in recent years [1–7]. Metallic lithium (Li) with the high theoretical capacity of 3,860 mA h g^{-1}, extremely low redox potential (−3.04 V *vs*. the standard hydrogen electrode), and low density (0.534 g cm^{-3}) has been considered as one of the most promising anodes for high-energy-density batteries [8–11]. Nevertheless, the practical utilization of Li metal anodes has been hindered by their high reactivity. Li metal reacts spontaneously with organic electrolytes to form a solid electrolyte interphase (SEI) layer. The native SEI layer tends to suffer from repeated rupture/regeneration during Li plating/stripping process, which usually causes low Coulombic efficiency (CE) and uneven Li deposition inducing uncontrolled dendrite growth [12–15]. Unfavorably, Li metal is also easily eroded by the trace impurities with active hydrogen atoms in batteries (*e.g.*, H_2O, organic acids, alcohols [16–18]). These side reactions can raise the irreversible capacity, the internal pressure of the battery, and even security problems [19,20].

Numerous approaches have been proposed to address the above issues, including creating current collectors with three dimensional (3D) structure [21–29], optimizing electrolyte constituents [30–32], employing gel-/solid-state electrolytes [33–36] and constructing artificial SEI layers [1,37–39]. Among these strategies, building the artificial SEI layers has been confirmed as a simple and effective method to suppress Li dendrites. Although the Li dendrites have been suppressed with the protection of the artificial SEI layers to a certain extent, it could not been avoided at present. Batteries are still in danger of being punctured by Li dendrites at any time.

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Copper-decorated covalent organic framework as a heterogeneous photocatalyst for phosphorylation of terminal alkynes†

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A layered covalent organic framework (COF) material based on an imine-linkage with high thermal and chemical stability was prepared using a deep eutectic solvent (DES) as the green medium. The as-synthesized COF materials were modified with catalytic copper. This crystalline and highly porous catalyst shows excellent photocatalytic performance in visible-light-driven coupling reactions of terminal alkynes with *H*-phosphonates at room temperature. In addition, the photocatalyst could be recovered and recycled eight times without significant loss of its reactivity.

Introduction

In organic synthesis, the carbon–phosphorus bond-forming reaction represents a valuable synthetic toolbox, which enables direct access to various organophosphorus compounds.[1] Organophosphorus moieties form the building blocks of many drugs and biomolecules and play a key role in their activities.[2] They have a wide range of applications in organic synthesis, agriculture, medicinal chemistry, materials, catalysis and coordination chemistry.[3] Among them, alkynyl phosphonate compounds, bearing reactive triple bonds and phosphoryl groups, are an important class of valuable chemicals containing carbon–phosphorus bonds, which are widely used as bioactive molecules in medicinal chemistry and as additives or flame retardants in polymer science.[4] Furthermore, they can also serve as key precursors for the synthesis of highly functional phosphorus compounds through conjugate-addition reactions, metallacycle formation, and unique cycloadditions.[5] Due to their importance, many methods have been developed for the synthesis of alkynylphosphonates from diverse organic molecules.[6] Traditional strategies for the synthesis of alkynylphosphonates mainly rely on the reaction by using toxic and moisture sensitive dialkyl or diphenyl chlorophosphates as phosphorus electrophiles with Li or Mg acetylides under hazardous reaction conditions, which usually suffer from pre-functionalization of the starting materials and poor tolerance of functional groups.[7] To address these issues, alternative methods have been developed based on the use of functionalized alkenes or alkynes, including 1,1-dibromo-1-alkenes,[8] bromoalkynes,[9] 4-aryl-2-methyl-3-butyn-2-ols,[10] arylpropiolic acids[11] and with *H*-phosphonates (Scheme 1). For technical and economic reasons, the direct synthesis of alkynyl phosphonates from readily available starting alkynes is the most attractive method. In 2009, the group of Zhao and Han first reported a copper-catalyzed oxidative coupling of alkynes with *H*-phosphonates, affording alkynylphosphonates in high yields.[12] However, secondary phosphine oxide $Ph_2P(O)H$ did not afford the oxidative coupling product under their reaction conditions. Soon after, further modifications have been made to improve the yield and efficiency of this reaction by employing various transition metals such as Ag_2CO_3,[13] $Pd(OAc)_2$,[14] $Cu/Cu_2O@Nb_2O_5$,[15] Cu_2O,[16] Cu-MnO[17] and TiO_2/Cu_2O[18] as a promoter or catalyst. Although the above oxidative cross-coupling reaction can be carried out using terminal alkynes without pre-functionalization, there are some disadvantages such as relatively stringent reaction conditions, use of excess non-recyclable catalyst and toxic solvents, carrying out the reaction at high temperature or very limited substrate scope. Therefore, from the viewpoint of green and sustainable chemistry, the development of an efficient, eco-friendly and economic approach to realize this transformation is still greatly desirable.

Solar energy, an abundant, clean, economical, and inexhaustible energy is considered to be a highly economical and environmentally friendly energy source. In the last few decades, significant advances have been made in visible-light-driven organic transformations under very mild conditions.[19]

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Green Chemistry

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Copper anchored on phosphorus g-C_3N_4 as a highly efficient photocatalyst for the synthesis of *N*-arylpyridin-2-amines†‡

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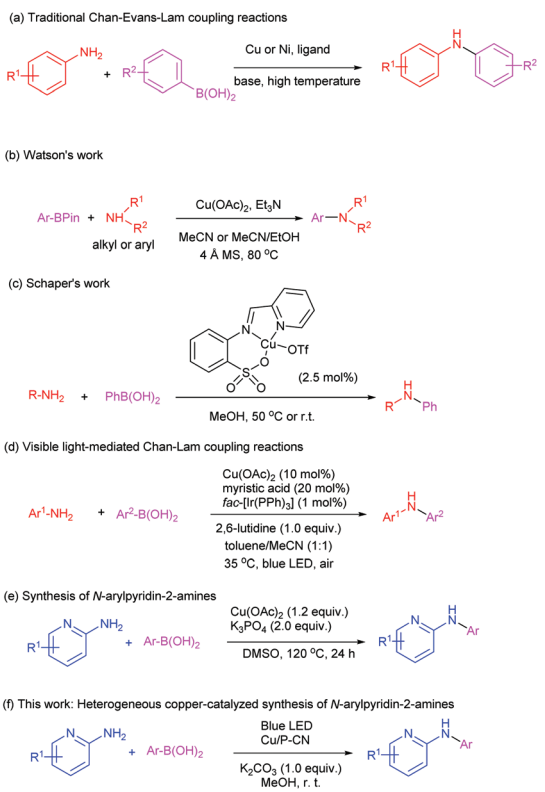
A heterogeneous photocatalyst based on copper modified phosphorus doped g-C_3N_4 (Cu/P-CN) has been prepared and characterized. This recyclable catalyst exhibited high photocatalytic activity for the synthesis of *N*-arylpyridin-2-amine derivatives by the reaction of 2-aminopyridine and aryl boronic acid at room temperature under the irradiation of blue light. Importantly, the range of substrates for this coupling reaction has been expanded to include aryl boronic acids with strong electron-withdrawing groups as viable raw materials. In addition, this heterogeneous catalyst can be used at least 6 times while maintaining its catalytic activity.

Introduction

Amines and their derivatives are core structural motifs widely found in medicinal chemistry, materials science, and catalysis. Given the preeminence of aromatic and heteroaromatic amines, a plethora of methods have been developed for the synthesis of these compounds by using various named reactions, primarily from aryl halides and boronic acids, for example, Chan–Evans–Lam (CEL) reaction,[1–4] Ullmann–Goldberg coupling,[5,6] and Buchwald–Hartwig amination.[7–9] Among them, transition metal-catalyzed Chan–Evans–Lam oxidative coupling of aryl boronic acids and nitrogen nucleophiles to synthesize secondary aromatic amines in the presence of various oxidants is one of the most important transformations, which has attracted huge attention in the past decade. Most of the methods require the use of transition metal catalysts, ligands, and/or extreme conditions (high temperature, high pressure, strong oxidants, *etc.*), which ultimately result in reduced sustainability and a limited substrate range. In particular, aryl boronic acids with electron-withdrawing substituted groups are found to be poor substrates (Scheme 1a).[10–12] In 2016, Watson developed effective reaction conditions for the Chan–Evans–Lam amination of boronic acid pinacol (BPin) esters with alkyl and arylamines. Particularly, these conditions work effectively for the coupling of alkylamines (Scheme 1b).[13] In 2018, Schaper and co-workers



Scheme 1 Previous work and present reaction design.

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Enhanced degradation of ofloxacin by persulfate activation with Mn doped CuO: Synergetic effect between adsorption and non-radical activation

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ABSTRACT

Non-radical activation of persulfate (PS) is a promising technology for removing organic pollutants in water because of the higher selectivity and stability of activated PS than radicals. Hence, the development of effective catalyst for PS non-radical activation is highly desired. In this work, a series of Mn doped CuO samples were prepared and used for removing ofloxacin with PS activation. The correlation between their surface properties and catalytic performance was studied, and the key parameter affecting pollutant degradation was explored. The result indicates that the CM3 sample (Cu:Mn = 6:1) exhibited the highest activity for ofloxacin degradation at neutral pH due to its high adsorption capacity towards ofloxacin and high activity for non-radical activation of PS, which is beneficial for their surface reaction. The large surface area and uncharged surface of CM3 at neutral pH facilitate the adsorption of ofloxacin, while its surface $\equiv Cu^{2+}$ with less electron deficiency might be responsible for the production of activated PS. Because ofloxacin was mainly degraded by the activated PS, the common ions in real water had little effect on this process. The toxicity assessment indicates that the treated ofloxacin solution was harmless. Finally, the reusability experiment demonstrates that CM3 is a stable and effective catalyst for non-radical activation of PS.

1. Introduction

In recent years, pharmaceuticals have been frequently detected in wastewater, drinking water and natural waters [1–3]. Most of them are hardly degraded by the conventional water treatment technologies and have detrimental effect on the environment and human health. Therefore, the development of highly efficient technology for removing these pollutants from water has received increasing attention. Persulfate (PS) is a strong oxidant that can be further activated into highly active species with the assistance of heat, UV irradiation, alkali, homogeneous or heterogeneous catalyst [4–10]. Therefore, PS activation processes should be efficient for removing refractory pollutants and have become a hot topic in the field of water treatment.

PS activation with heterogeneous catalysts usually requires low energy consumption and can be operated easily, thus attracting more interest among various activation processes. Up to now, numerous solid materials, including metal, metal oxides and carbonaceous materials, have been developed for PS activation [11–17]. Among them, Cu based oxides exhibited superior performance for pollutants removal due to their high activity for the generation of reactive species from PS activation. Cu_2O can readily activate PS into $\cdot SO_4^-$ via electron transfer from $\equiv Cu^+$ to PS (Eq. (1)). In addition, $\equiv Cu^{2+}$ was also found to be effective for the activation of PS into $\cdot SO_4^-$ (Eq. (2)). Besides $\cdot SO_4^-$, superoxide radical ($\cdot O_2^-$) was reported to be the dominant active species in some CuO-PS processes [18,19]. The PS molecule adhered to $\equiv Cu^{2+}$ with more electron deficiency might decompose into $\cdot O_2^-$ through the cleavage of S-O bond rather than peroxy bond. More recently, CuO was found to be an effective catalyst for PS activation through the non-radical way [20–24]. The non-radical activation is attributed to the charge transfer mediated by the catalysts. Previous studies reported that the PS solution remained stable after the addition of catalyst, while the consumption of PS was significantly accelerated by the addition of organic pollutants [20–27]. PS can be adsorbed onto CuO surface and then be activated through the outer-sphere interaction with CuO, and high solution pH might be beneficial for its non-radical activation. According to the literatures, the activated PS is relatively stable and cannot be decomposed into radicals, it has higher oxidation ability than PS and can effectively degrade refractory organic pollutants.

$$S_2O_8^{2-} + \equiv Cu^+ \rightarrow \cdot SO_4^- + SO_4^{2-} + \equiv Cu^{2+} \quad (1)$$

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Research paper

A comparative study of the removal of *o*-xylene from gas streams using mesoporous silicas and their silica supported sulfuric acids

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ABSTRACT

The three types of silica supported sulfuric acids (SSA), with the same sulfuric acid loading of 9.25 mmol g^{-1}, were prepared by a wet impregnation method from silica gel (SG), SBA-15 and MCM-41. Characterization of the prepared SSA showed that two anchoring states coexisted for sulfuric acid supported on the surface of the silicas: A physiosorbed (P)-state sulfuric acid; and a chemically bonded (C)-state sulfuric acid. Dynamic adsorption results showed that each SSA had a significant removal capacity for *o*-xylene gas in the reactive temperature regions. The ranges of the reactive regions were 120–220 °C (SSA/SG), 120–230 °C (SSA/SBA-15) and 120–250 °C (SSA/MCM-41), and this could be attributed to the sulfonation reaction between *o*-xylene and the anchored sulfuric acid. SSA/MCM-41 showed the highest theoretical breakthrough adsorption capacity ($Q_{B,\ th}$, 526.71 mg g^{-1}) compared with SSA/SBA-15 (363.54 mg g^{-1}) and SSA/SG (239.15 mg g^{-1}). $Q_{B,\ th}$ was closely associated with the amount or proportion of the C-state sulfuric acid on the surface of each SSA. Optimum breakthrough time and $Q_{B,\ th}$ was obtained by increasing the bed height and decreasing flow rate and inlet concentration. The SSA exhibited excellent recyclability and reuse performance over eight consecutive adsorption/desorption/regeneration cycles. The results suggested that the SSA, especially SSA/MCM-41, might have good potential in applications using adsorbents for the removal of BTEX pollutants.

1. Introduction

The high surface area/porous structure of silicas, such as silica gel (SG) and the mesoporous silicas SBA-15 and MCM-41, have made it the ideal choice of materials for adsorbents in separation processes (Sui et al., 2017; Hu et al., 2009; Northcott et al., 2010). They have also been used as carriers for various chemicals, such as sulfuric acid, metal/metal oxide nano-particles, dyes, drugs and organo-metallic compounds, in applications involving organic synthesis catalysis, environmental catalysis, energy conversion and drug delivery (Selvakannan et al., 2013; Smeulders et al., 2012; Wu et al., 2019; Tiozzo et al., 2013; Vallet-Regi et al., 2007; Vaz-Ramos et al., 2020; Kiatphuengporn et al., 2016; Mohan et al., 2020; Mu et al., 2008; Moroz et al., 2019). Silicas possess stable inorganic skeletons, well-developed micro/mesoporous structures, high specific surface areas, and a high density of surface silanol groups (–Si–OH) which can be used to introduce chemical functionality (Vaz-Ramos et al., 2020; Valdes et al., 2020). Sulfuric/sulfonic acid functionalized SG, SBA-15 and MCM-41 have been employed as reagents or catalysts in a wide range of chemical reactions such as condensation (Shobha et al., 2009; Zhang et al., 2010; Wu et al., 2011), benzene nitration (Simantiraki and Gidarakos, 2015), Fischer type glycosylation (Roy and Mukhopadhyay, 2017), esterification (Testa et al., 2010), cationic polymerization (Qu et al., 2015), sodium borohydride hydrolysis (Manna et al., 2015), sulfonation of aromatic compounds (Hajipour et al., 2004) and oxidation aromatic compounds (Wu et al., 2013), etc. One of the major advantages of sulfuric/sulfonic acid functionalized silica is that it can be recovered and reused repeatedly without loss of efficiency (Costa et al., 2020; Shaterian et al., 2008). Consequently, the development of novel applications for these materials has attracted considerable research interest (Costa et al., 2020; Konwar et al., 2019; Xu et al., 2015).

Recently , we demonstrated that silica supported sulfuric acid (SSA) could be used as an adsorbent for the removal *o*-xylene from gas streams (Dong et al., 2019). The SSA demonstrated a high breakthrough adsorption capacity (Q_B) for *o*-xylene in the gas stream. A novel reaction-type adsorption removal mechanism was proposed involving the sulfonation of *o*-xylene on the SSA. Thus, its removal capacity was mainly dependent on the adsorption temperature and sulfuric acid

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Ultra-trace determination of hexavalent chromium in a wide pH range triggered by heterometallic Cu-Mn centers modified reduced phosphomolybdate hybrids

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Cr(VI) detection

ABSTRACT

Ultra-trace determination of the carcinogen chromium(VI) in wide pH water environment *via* electrochemical sensing technology is of great significance, in which the key point is to develop high sensitive and selective electrocatalyst. Herein, two heterometallic centers modified reduced phosphomolybdate hybrids with formula of $[Cu^{I}(BBTZ)]_4[Mn^{II}(H_2O)_3]_2[Cu^{II}(P_4Mo^{V}_6O_{31}H_7)_2]\cdot H_3PO_4\cdot 3H_2O$ (**1**) and $Na^{I}_2(H_2BBTZ)[Na^{I}(H_2O)(BBTZ)]_2[Mn^{II}(H_2O)_2]_2[Mn^{II}(P_4Mo^{V}_6O_{31}H_6)_2]\cdot 2H_2O$ (**2**) (BBTZ = 1,4-bis(1,2,4-triazol-1-ylmethyl)benzene) were synthesized as electrocatalysts, in which the reduced phosphomolybdate $[P_4Mo^{V}_6O_{31}]^{12-}$ (abbr. $\{P_4Mo_6\}$) clusters cooperated with different kinds of heterometallic centers (Cu^{I}, Cu^{II} and Mn^{II}) achieve an efficient electrochemical detection of ultra-trace Cr(VI) in wide pH ranges of 0–5 for the first time. In electrolyte of pH = 0, hybrids **1**–**2** displayed prominent sensitivities of 111.08 $\mu A\cdot\mu M^{-1}$ and 119.87 $\mu A\cdot\mu M^{-1}$, along with ultra-low LODs towards Cr(VI) of 1.59 and 2.91 nM, respectively, which fully satisfy the WHO standards for drinking water. In the pH range of 1–5, good sensitivities and low LODs (<25 nM) are also achieved by hybrids **1**–**2**, realizing the ultra-trace Cr(VI) detection in wide pH ranges. Moreover, hybrids **1**–**2** exhibited high selectivity of 87.38 $\mu A\cdot\mu M^{-1}$ and 83.62 $\mu A\cdot\mu M^{-1}$ and low LODs of 2.03 nM for **1** and 3.5 nM for **2** in the actual water sample along with excellent anti-interference ability and electrochemical stability. The activity origin of hybrids **1**–**2** for impressive electrochemical behaviours were investigated that originated from the synergistic effect between reduced $\{P_4Mo_6\}$ cluster and heterometallic centers at the molecular level. This work firstly explored the wide-pH-response electrochemical sensors for Cr(VI) detection and proposed an important guidance for designing efficient electrochemical sensors towards the ultra-trace detection of heavy metal ions in practical environment.

1. Introduction

The rapid development of urbanization and industrialization has caused serious heavy metal pollution to the soil and groundwater system, which severely threatens human health due to the considerable biological toxicity and accumulation effect of heavy metal ions on human body [1–4]. Hexavalent chromium (VI) as a representative of the most toxic heavy metal ions has arose wide attention from researchers owing to its high poisonousness and mutagenic-carcinogenic effects on people's health [5–7], which can easily cross the cell membrane to cause lungs, liver, kidney, and skin cancer [8–10]. Therefore, the Cr(VI)-containing compounds have been listed as human carcinogen by the World Health Organization (WHO) and International Agency for Research on cancer (IARC) [11–13]. So far Cr(VI) as important industrial raw material has been widely used in leather tanning, electroplating, dye and stainless-steel industries, and importantly, its solubility in environmental waters can lead to transmit and accumulate in plants and soil, leading to irreversible damage to organisms and ecological environment[14]. To protect human health and environment, the WHO defined that the maximum permissible limit for total Cr element in drinking water and industrial water are 0.05 ppm and 0.5 ppm[15], respectively. Therefore, it is significant and necessary to establish a rapid and efficient technique for monitoring Cr(VI) content in water.

Nowadays, electrochemical sensing method has been recognized as a good analytic technique for trace Cr(VI) determination owing to its notable merits in high sensitivity, low cost, convenient operation and

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Carbon Counter Electrodes in Dye-Sensitized and Perovskite Solar Cells

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Developing highly effective and stable counter electrode (CE) materials to replace rare and expensive noble metals for dye-sensitized and perovskite solar cells (DSC and PSC) is a research hotspot. Carbon materials are identified as the most qualified noble metal-free CEs for the commercialization of the two photovoltaic devices due to their merits of low cost, excellent activity, and superior stability. Herein, carbonaceous CE materials are reviewed extensively with respect to the two devices. For DSC, a classified discussion according to the morphology is presented because electrode properties are closely related to the specific porosity or nanostructure of carbon materials. The pivotal factors influencing the catalytic behavior of carbon CEs are also discussed. For PSC, an overview of the new carbon CE materials is addressed comprehensively. Moreover, the modification techniques to improve the interfacial contact between the perovskite and carbon layers, aiming to enhance the photovoltaic performance, are also demonstrated. Finally, the development directions, main challenges, and coping approaches with respect to the carbon CE in DSC and PSC are stated.

1. Introduction

The conversion of renewable and clean solar energy into electricity with photovoltaic devices is a promising method to solve the global energy and environmental crises. The dye-sensitized solar cell (DSC) is a potential third-generation photovoltaic device, compared with traditional silicon and thin-film solar cells.[1–8] The DSC is generally composed of three parts: the photoanode (dye-sensitized mesoporous semiconductor film), electrolyte (or hole transport material), and counter electrode (CE). **Figure 1** illustrates the working principle of a DSC. Under illumination, a sensitizer molecule (S) transitions from the ground state (S) to the excited state (S*), which releases a photoelectron (e^-). The photoelectron is subsequently injected into the conduction band (CB) of the semiconductor, leaving a sensitizer hole (S^+). Then, photoelectrons in the CB are transported to the electron collector and complete the electron migration to the external load. Finally, the electrons are collected by the CE, where the oxidative state of the electrolyte (Ox) is reduced to the reductive state (Red) by the photoelectrons. At the same time, S^+ is regenerated to the ground state by Red. The working processes are often accompanied by recombination between photoelectrons and S^+ (or Ox), which is the dominant source behind efficiency loss.[9,10] The specific merits of the simple fabrication process and high tolerance to illumination angle and intensity make the DSC a potential alternative power source for portable electronic devices.[11,12] Moreover, the advantages of versatile implementation with respect to shape and color make DSC suitable for building-integrated photovoltaics (BIPV).[13] Therefore, the DSC has developed rapidly, and the power conversion efficiency (PCE) of DSC under indoor lighting (1000 lux) has exceeded 30%.[14] A high PCE under low-light intensity makes DSC a potential candidate power source for indoor electronic devices. However, under standard illumination, the PCE is lower than 15%, and this is a tough issue that needs to be resolved.[15] In the DSC system, the PCE is determined to a great extent by the photoanode, which is generally fabricated with a dye-sensitized mesoporous semiconductor film. Designing and synthesizing a highly effective sensitizer is a feasible method to enhance the PCE value. Several papers have reviewed the advancements in sensitizers.[16–18] Moreover, the semiconductor is another key part of the photoanode, and it determines the adsorption quantity of the sensitizer. Additionally, the Fermi level of the oxide semiconductor relates closely to the open-circuit voltage (V_{oc}). Commonly used semiconductors include TiO_2, SnO_2, Nb_2O_5, WO_3, etc.[19–24] The electrolyte is another decisive component, and the potential of the redox couple and the additives have a close relationship with V_{oc} as

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Preparation of paramagnetic ferroferric oxide-calcined layered double hydroxide core–shell adsorbent for selective removal of anionic pollutants

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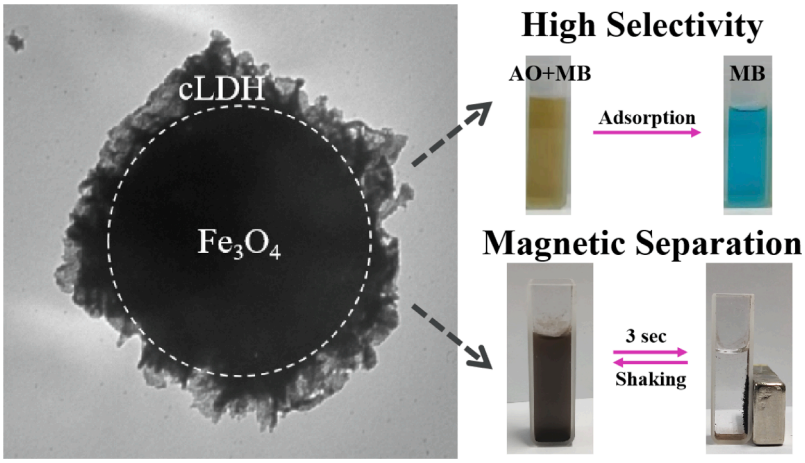
HIGHLIGHTS

- Fe_3O_4@cLDH core–shell adsorbent was prepared by the calcination of PB@LDH.
- Fe_3O_4@cLDH adsorbent exhibits high anionic dye selectivity.
- The paramagnetic Fe_3O_4@cLDH can be easily collected by a magnet.
- The adsorption capability is affected by the pH and soluble CO_2 in aqueous solution.

GRAPHICAL ABSTRACT



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ABSTRACT

Adsorption is one of the most common methods of pollution treatment. The selectivity for pollutants and recyclability of adsorbents are crucial to reduce the treatment cost. Layered double hydroxide (LDH) materials are one type of adsorbent with poor recyclability. Prussian blue (PB) is a sturdy and inexpensive metal–organic framework material that can be used as the precursor for synthesizing paramagnetic ferroferric oxide (Fe_3O_4). It is intriguing to build some reusable adsorbents with magnetic separation by integrating LDH and PB. In this work, paramagnetic Fe_3O_4-calcined LDH (Fe_3O_4@cLDH) core–shell adsorbent was designed and prepared by the calcination of PB-ZnAl layered double hydroxide (PB@LDH) core–shell precursor, which exhibits high anionic dyes selectivity in wastewater solutions. The paramagnetism and adsorption capability of Fe_3O_4@cLDH come from the Fe_3O_4 core and calcined ZnAl-LDH shell, respectively. Fe_3O_4@cLDH shows an adsorption capacity of 230 mg g^{-1} for acid orange and a high selectivity for anionic dyes in cation–anion mixed dye solutions. The regeneration process indicates that the high selectivity for anions is related to the specific hydration recovery

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