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Layered transition-metal dichalcogenides (MoS_2 and WS_2) for sensing and biosensing

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ABSTRACT

Layered transition-metal dichalcogenides comprise a category of two-dimensional materials that offer exciting properties, including metallic and semi-conducting electrical capabilities, fluorescence and fast heterogeneous electron transfer. To date, these materials have mostly been employed in energy-storage and generation devices. However, in very recent times, there was a significant emerging trend in their utilization in analytical chemistry. Hence, this review aims to provide an introduction to this new trend for the analytical community.

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1. Introduction

Two-dimensional (2D) layered compounds have attracted immense interest in the past decade, exemplified by the rapid rise of graphene materials, which found their applications in sensing and biosensing [1,2]. One should note, however, that graphene itself is only the tip of the iceberg in the field of layered 2D materials [3].

In recent times, there has been a dramatic growth in research on 2D transition-metal dichalcogenides (TMDs) [4]. These materials, with the generalized formula MX_2, where M represents transition metals, such as molybdenum (Mo), tungsten (W), titanium (Ti), zirconium (Zr) or hafnium (Hf), and X represents chalcogens, such as sulfur (S), selenium (Se) or tellurium (Te) (see Fig. 1), present very interesting properties.

TMDs are layered materials of similar structure to graphite. Parallel to graphene, individual 2D layers of TMDs can be isolated by mechanical cleavage or by intercalation methods (see Fig. 2A) [5,7]. The mono-layer consists of transition-metal atoms surrounded in a sandwich structure by chalcogen atoms, which are covalently bonded to the transition-metal atoms (see Fig. 2B) [6]. However, the interactions between the individual mono-layers are of the van der Waals type.

2D TMDs are capable of offering a wide range of properties. In addition to large surface area, these materials also demonstrate a tunable band-gap, which can be achieved by changing the composition of TMDs, or by structural changes, via altering the orientations of the M and X atoms, within the 2D layer. From that, a plethora of interesting possibilities results, including the possibility of changing conductivity from metallic to semi-conducting, thereby tuning fluorescence and electrochemical performances [4].

2D TMDs have found their applications in energy generation and storage, such as electrocatalytic hydrogen evolution, lithium-ion batteries and supercapacitors [8–12]. However, the upcoming trend in

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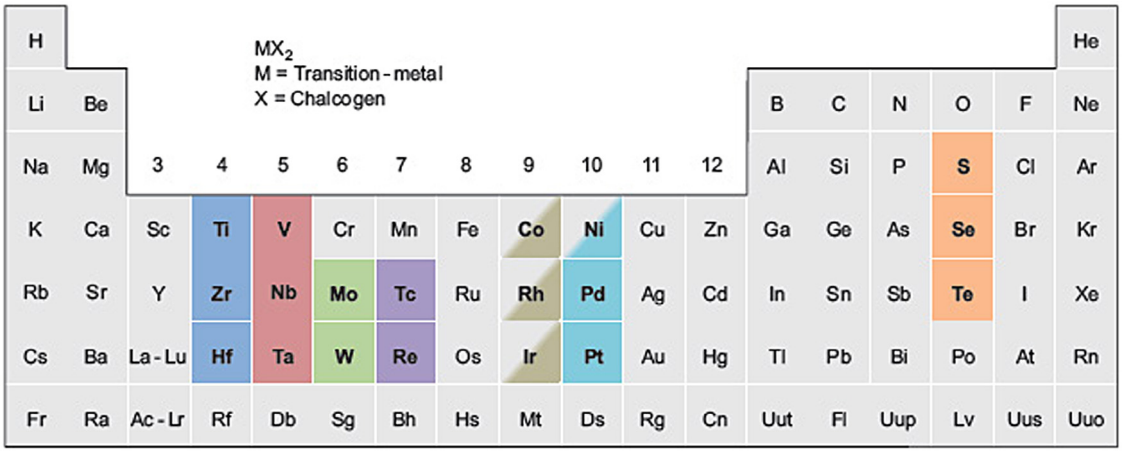

Fig. 1. Highlighted elements in the Periodic Table show those that form layered transition-metal dichalcogenides. Note that partial highlights for Co, Ni, Rh and Ir denote that only some of the dichalcogenides formed are layered. {Reproduced with permission from [4]}.

the employment of TMDs lies in sensing and biosensing devices, taking advantage of large surface area, fluorescence, electrical conductivity and fast heterogeneous electron transfer. Hence, the objective of this review is to provide an overview of the recent efforts in utilizing TMDs in this hot field.

2. Electrochemical methods

TMDs are attractive materials for electrochemical applications. It has been demonstrated that, similar to graphene, single-layer molybdenum sulfide (MoS_2) sheets can produce distinctive cyclic voltammetric peaks for a mixture of ascorbic acid, uric acid and dopamine, which is unlikely for a glassy-carbon electrode [13]. There has also been an interesting report on the electrochemical detection of nanomolar levels of hydrogen peroxide (H_2O_2) secreted by living cells using ultrasmall MoS_2 platelets (see Fig. 3A) [14].

The main electrochemical activity of MoS_2 occurs at its edge planes [17]. Hence, creating defects in MoS_2 sheets will aid the introduction of electroactive electrocatalytic sites. In view of that, MoS_2 nanosheets decorated with gold nanoparticles (AuNPs) have been utilized to facilitate the detection of dopamine in the presence of

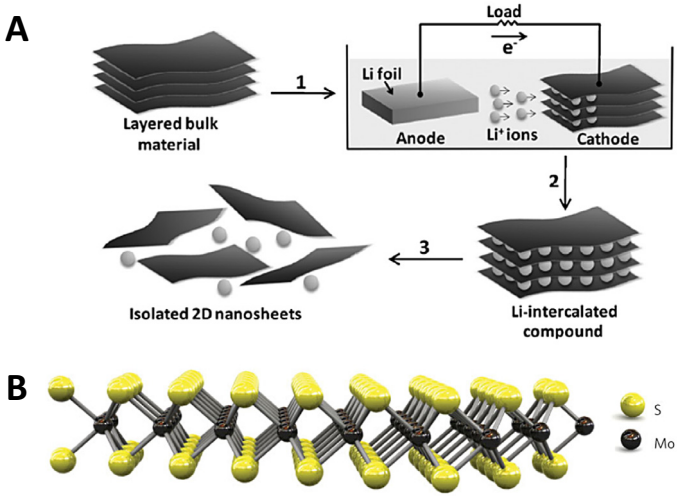

Fig. 2. (A) Preparation of single- or few-layer transition metal dichalcogenides by lithium intercalation. (B) Structure of molybdenum sulfide (MoS_2). (Reproduced with permission from [5] and [6]).

ascorbic acid [18]. Furthermore, a study performed by another group, also for the detection of dopamine, exhibited the use of an AuNP-decorated polyaniline-MoS_2 composite [19]. In another report, AuNP-decorated polymer/graphene-MoS_2 composite was employed for the analysis of eugenol [20]. Similarly, catalytic copper NP (CuNP)-decorated MoS_2 nanosheets were used for non-enzymatic electrochemical glucose detection in an alkaline environment [21] and a silver NP (AgNP)-decorated chitosan-MoS_2 composite was utilized for the electrocatalytic oxidation of tryptophan (Trp).

However, one point worthy of contemplation from the last study is that the oxidation of Trp takes place at ~0.9 V [*versus* saturated calomel electrode (SCE)], which is much later than the potential of dissolution for AgNPs [22]. The decoration of MoS_2 with metallic NPs is often justified as a technique to improve the conductivity of the composite. However, we should highlight that the metallic NPs do not serve this purpose, because, even where the metallic NPs are closely spaced, the electron-transfer process would still have to occur through the electron-tunneling effect, which is highly inefficient to carry long-range conductivity across many particles. Hence, it is more likely that the observed effects arise from the inherent electrocatalytic properties of the metallic NPs.

Apart from metallic NP-decorated TMDs, graphene-TMD composites are also gaining popularity in sensing, because graphene is capable of providing a highly porous, conductive platform, which can subsequently undergo functionalization with TMDs that serve as an electrocatalyst. The applications of such materials have been reported, with graphene-MoS_2 composite used for acetaminophen sensing [23], and graphene-tungsten sulfide (WS_2) composite utilized for the simultaneous detection of catechol, resorcinol and hydroquinone [24]. However, similar performance was shown several years ago on graphene surfaces [25] and it does not appear that MoS_2 (or WS_2 per say) offers dramatic advantage.

Systems with greater complexity have also been applied for biosensing. These systems generally involve the TMD transducer layer being functionalized with an enzymatic biorecognition layer. For example, hemoglobin was immobilized onto MoS_2 microspheres in order to detect H_2O_2 [26], while glucose oxidase was immobilized onto reduced MoS_2 sheets, with the aid of chitosan, for electrochemical detection of glucose [13]. Also, horseradish peroxidase (HRP) enzyme was immobilized onto graphene-MoS_2 composite (see Fig. 3B) for direct electrochemistry and sensing of H_2O_2 [15].

On another note, the biorecognition layer in the biosensing system can also be of a non-enzymatic nature, such as single-stranded DNA (ssDNA). To illustrate that, Huang and co-workers fabricated an AuNPs/chitosan/graphene-WS_2 composite for the covalent