NANOSHEETS AND LAYERED HYBRIDS OF LAYERED CHALCOGENIDES AND OXIDES THROUGH LARGE SCALE CHEMICAL EXFOLIATION

A SYNOPSIS

Layered solids are a class of solids consisting of 2D (two-dimensional) macromolecular layers stacked to form 3D (three-dimensional) structures. In layered solids, bonding among the atoms in the same plane are strong (covalent or ionic), while bonding among the adjacent layers are weak (van der Waals force of attraction). Based on the layer charge, layered solids can be grouped into neutral, anionic and cationic layered solids. Transition metal dichalcogenides (TMDS), MO$_3$ (M=Mo, W), and graphite are a few examples of neutral layered solids. Anionic layered solids such as LDHs (layered double hydroxides) and hydroxy salts have positively charged layers and interchangeable anions in the layers to restore charge neutrality. On the other hand, cationic layered solids such as smectite clays consist of negatively charged layers with charge neutralizing cations in the interlayer.

One of the important properties of layered solids is their ability to swell when exposed to solvents. When a layered solid is dispersed in a suitable solvent, the solvent molecules enter the interlayer region diminishing the layer-to-layer interaction leading to swelling. As the swelling enhances, the layered solid loses the layer registry and the layers fall apart to give a colloidal dispersion of solvated monolayers. This phenomenon is known as exfoliation or delamination. Layered materials are exfoliated to monolayer colloidal nanosheets by suitable intercalation of surfactants ions or reactive ions/atoms such as Li$^+$. Exfoliation of layered materials into colloidal 2D nanosheets is important as the resulting nanosheets display interesting physical and chemical properties due to their anisotropy and nanoscale dimensions. Another interesting feature of exfoliated nanosheets is that a variety of nanostructures can be synthesized using 2D nanosheets as building blocks. Exfoliation has been exploited as a route to functional nanomaterials and assemblies for a wide range of applications.

In this thesis, we have studied the exfoliation behavior of reactive ion/molecule and surfactant intercalated MS$_2$ (M = Mo, W), layered titanate and birnessite in water; in polar organic solvents such as alcohols, alkane thiols and dimethylsulfoxide (DMSO); and in nonpolar solvents such as toluene and n-hexane. We have optimized the conditions of exfoliation and restacking behavior. In addition, we have prepared layered hybrids comprising of two
different layers having similar structures such as MS\(_2\) (M = Mo, W). A functional nanohybrid, MoS\(_2\)–rGO in the form of flexible paper was prepared and its application in electrochemical charge storage, photocatalysis and catalysis was explored.

The thesis will have five chapters with chapters 2 and 3 having subsections as described below.

**Chapter 1 General Introduction**

This chapter provides a brief overview of the structures, classification and properties of layered solids. Various methods of exfoliation and applications of exfoliation of layered solids in general and layered sulfides and oxides in particular are highlighted. The chemistry and applications of materials of our interest – layered sulfides such as MoS\(_2\), WS\(_2\) and their hybrids; layered oxides such as birnessite-type manganese oxide, and titanates have been discussed in detail.

**Chapter 2 Delamination of layered sulfides**

In this chapter we describe our work on the delamination of layered transition metal disulfides such as MoS\(_2\) and WS\(_2\) in water and organic solvents. This chapter is subdivided into three sections—A, B, and C.

**Section A: Two-dimensional nanosheets and layered hybrids of MoS\(_2\) and WS\(_2\) through exfoliation of ammoniated MS\(_2\) (M = Mo, W).**

We discuss the exfoliation of ammoniated MS\(_2\) (M = Mo,W) in water and in a variety of polar organic solvents in this section. Ammoniated MS\(_2\) have been synthesized by reacting Li\(_x\)MS\(_2\) with a saturated solution of ammonium chloride. While, largely neutral NH\(_3\) is present in the interlayer of ammoniated MoS\(_2\), equal amounts of NH\(_3\) and NH\(_4^+\) ions are present in the tungsten analog. The ammoniated MS\(_2\) exfoliate readily in a variety of polar solvents with exfoliation being best in water. Ammoniated WS\(_2\) forms a more stable colloidal dispersion compared to the Mo analog because the ammonium ions do not deintercalate easily from the layers even on exfoliation. The dispersions are comprised of large nanosheets of MS\(_2\) with lateral dimensions in the order of micrometers. The layers could be restacked from the colloidal dispersions by evaporating the solvent. While the colloidal dispersions of ammoniated MoS\(_2\) yield NH\(_3\)-free MoS\(_2\) on restacking, the dispersions of ammoniated WS\(_2\) yield WS\(_2\) intercalated with NH\(_4^+\) ions.
Co-stacking of MoS₂ and WS₂ nanosheets from a mixture of both the colloidal dispersions results in MoS₂–WS₂ hybrids in which the MoS₂ and WS₂ nanosheets are randomly stacked. Photoluminescence measurements of MS₂ nanosheets and MoS₂–WS₂ hybrids indicate phase stability and existence of direct bandgap.

Section B: Scalable large nanosheets of MS₂ (M = Mo, W) through exfoliation in organic solvents.

In this section, we describe the exfoliation of n-alkylamine intercalated MS₂ (M = Mo, W) in organic solvents. Various alkylamine intercalated MS₂ (M = Mo, W) have been prepared by reacting Li₅MS₂ with aqueous solutions of the amines. The amine intercalated MS₂ exfoliate readily in alcohols. While the shorter amine intercalated MS₂ exfoliate better in lower alcohols the longer amine intercalated MS₂ exfoliate better in higher alcohols. The longer amine intercalated MS₂ exfoliate well even in a nonpolar solvent, toluene. Up to 9 millimoles of MS₂ per liter could be dispersed through exfoliation in organic solvents. The dispersions are quite stable and comprise 2D-nanosheets of MS₂. Hybrids of MoS₂ and WS₂ could be prepared by evaporating the solvent from a mixture of colloidal dispersions of amine intercalated MoS₂ and WS₂. The hybrid exhibits features of a heterostructure in its photoluminescence spectrum.

Section C: Chemical unzipping of WS₂ nanotubes.

In this section, we present our work on the chemical exfoliation of WS₂ nanotubes to give nanoribbons. WS₂ nanoribbons have been synthesized by chemical unzipping of WS₂ nanotubes. Lithium atoms are intercalated in WS₂ nanotubes by a solvothermal reaction with n-butyllithium in hexane. The lithiated WS₂ nanotubes are then reacted with various solvents; water, ethanol, and long chain thiols. While the tubes break into pieces when treated with water and ethanol, they unzip through longitudinal cutting along the axes to yield nanoribbons when treated with long chain thiols, 1-octanethiol and 1-dodecanethiol. The slow diffusion of the long chain thiols reduces the aggression of the reaction, leading to controlled opening of the tubes.
Chapter 3 Exfoliation of layered oxides

This chapter describes the exfoliation of layered oxides of our interest – birnessite type manganese oxide and layered titanate $K_2Ti_4O_9$. This chapter is subdivided into two sections—A and B.

Section A: Delamination and reassembly of layered birnessite-type manganese oxide in organic solvents.

This section deals with the exfoliation of birnessite type–manganese oxide in organic solvents. The interlayer potassium ions of birnessite were exchanged with a series of short chain to long chain $n$–alkylamines to form amine–birnessites. These amine–birnessites exfoliate readily in organic alcohols such as ethanol, 1–butanol, 1–hexanol, and 1–octanol to give colloidal dispersion of $\text{MnO}_2$ nanosheets. The extent of exfoliation increases with the chain length of the intercalated $n$–alkylamine.

Section B: Preparation of titanate nanosheets and nanoribbons by exfoliation of amine intercalated titanates.

In this section, we demonstrate the preparation of titanate nanosheets and nanoribbons by exfoliation of amine intercalated titanates. Amine intercalated titanates have been synthesized by direct exchange of potassium ions of $K_2Ti_4O_9$ by alkyl ammonium ions of various alkyl chain lengths. These intercalated solids exfoliate well in alcohols of different alkyl chain lengths and non-polar solvents such as toluene and hexane to yield colloidal dispersions of titanate nanosheets. The longer the alkyl chain of the intercalated amine the better the exfoliation of the intercalated titanate in long chain alcohols and non-polar solvents. While non-uniform rectangular nanosheets were obtained when aggressive sonication was employed for exfoliating the solids, nanoribbons were obtained when the exfoliation was carried out by gently stirring the solids in the solvent.
Chapter 4 Multifunctional MoS$_2$–rGO hybrid wafers by a simple exfoliation–costacking method.

In this chapter, we show the usefulness of delamination–restacking method as a route to functional layered hybrids that show potential in energy storage and catalysis/photocatalysis. MoS$_2$–graphene oxide (GO) hybrids of different compositions were prepared in the form of a few micron thick flexible papers by a simple ambient condition evaporation of a mixture of colloidal dispersions of ammoniated MoS$_2$ and GO. These on thermal reduction at 400 °C convert to MoS$_2$–reduced graphene oxide (rGO) hybrids retaining the macroscopic paper-like structure. These hybrids show good electrochemical performance as supercapacitor electrode materials (the hybrid with equal mass percentages of MoS$_2$ and rGO exhibits a specific capacitance of 124 Fg$^{-1}$ at a scan rate of 100 mVs$^{-1}$) act as efficient photocatalysts for organic dye degradation and catalyse the reduction of nitrocompounds by sodium borohydride almost as good as 1T–MoS$_2$.

Chapter 5: Conclusions

This chapter summarizes the overall results of this work. In addition, the scope for future prospects is discussed.