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ORIGINAL ARTICLE

Future Perspectives of MXenes-Based Nanocomposites for Solar Cell Applications

Imran Khan[1], Mohd. Amil Usmani[2] and Anis Ahmad[3]
[1]Department of Physics, Gandhi Faiz-E-Aam College Shahjahanpur - 242001 (M.J.P. Rohilkhand University Bareilly), India
[2]Department of Chemistry, Gandhi Faiz-E-Aam College Shahjahanpur - 242001 (M.J.P. Rohilkhand University Bareilly), India
[3]School of Basic Sciences (Physics), Galgotias University, Greater Noida - 203201, India
Email: imranphy05@gmail.com

ABSTRACT

The MXene family of materials among 2D nanomaterials has shown considerable promise in enhancing solar cell performance because of their remarkable surface-enhanced characteristics. In addition, their outstanding features, including high electrical conductivity, Young's modulus, and distinctive shape, make them very advantageous for composite synthesis. In contrast, its excellent chemical stability, electronic conductivity, tunable band gaps, and ion intercalation make it a promising contender for various applications. Photovoltaic devices, which turn sunlight into electricity, are an exciting new area of research for sustainable power. Finally, we identify new perspectives for adjusting the performance of MXene for various nanocomposites by controlling the composition of the two-dimensional transition metal MXene phase. This article reviews the progress made so far in using MXenes materials in the building blocks of perovskite solarcells such as electrodes, hole transport layer (HTL), electron transport layer (ETL) and perovskitephotoactive layer. So the versatile MXenes nanocomposite may provide a new route for the rational design and development of advanced sensing technology for complex environmental application.

Key words: *Nano composites, MXenes, Conductivity, Dielectrics, Metals*

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INTRODUCTION

MXenes in energy storage batteries have wide chemical and structural variety. For this reason, MXenes can help to define the most promising candidates for energy-storage applications. The ions penetrate between the MXenes that's why the bonds between M and X are broken easily. The surface terminations are one particular factor than can affect the performance, for example, oxygen terminations deemed most favorable, whereas hydroxyls and fluorine result in lower capacity as well as impeded Li-ion transport. MXenes can provide a range of working potentials, which makes some of them suitable as anodes and some of them suitable as cathodes. This is in agreement with the remarkably high-rate performance experimentally observed for several MXenes. Application of MXenes materials in perovskite solar cells (PSCs) has attracted considerableattention owing to their supreme electrical conductivity, excellent carrier mobility, adjustable surfacefunctional groups, excellent transparency and superior mechanical properties. MXenes are derivatives of the three-dimensional MAX phases as the parent structure and have the general formula $M_{n+1}AX_n$. [1]. M represents members from early transition metal families like scandium, titanium, vanadium, chromium, zirconium, niobium, molybdenum, hafnium, tantalum, and tungsten (Sc, Ti, V, Cr, Zr, Nb, Mo, Hf, Ta, W, respectively), A indicates an element from either group 13 or group 14, and X can be either carbon or nitrogen. Here n is an integer ranging from 1 to 3.MAX phase is a unique structure in which closely packed multilayers are present which are composed of alternating layers of M and A. M-X bonds are strong compared to weak M-A bonds. MXenes are found to be superior to their parent MAX phases in terms of electronic, magnetic, optical, and electrochemical properties. [3]. The vast majority of MXenes known to date have been produced by selectively etching Al from Al containing MAX phases. [4] During the etching process, the MXenes surface acquires terminating functional groups, which is why they are commonly designated as $M_{n+1}X_nT_x$, where T_x represents surface terminating groups such as -O, -OH, and/or –F [5-6]. In an era where electronics devices are occupying smaller spaces, compact energy storage devices like supercapacitors are needed to catch up with this trend. MXene has already made rapid progress in enhancing the volumetric capacitance compared to its predecessor graphene. But it can be further improved by optimizing both physical and chemical aspects.Most of the research group of this field showing the interest in developing new methods to fabricate this highly conductive, flexible and lightweight material due to their unique nano-fibrous structure and large surface area with high porosity. [7-9]. In 2011, Gogotsi et al. investigated transition-metal nitrides, or carbides (MXenes), as star materials from MAX phases, which are layered compounds similar to graphite with monoatomic A-element layers sandwiched between metallic electrically conductive and stiff MX-blocks. The new compound was called MXenes because the A element had been removed from the MAX phase and its structure was similar to graphene [10]. Till date different defects using additive, interface, and compositional engineering for perovskite solar cell has been published [11, 12]. To understand the benefits of energy conservation, author discusses the used of MXenes in perovskite solar cells, the ion transport speed increases when the crystalline size extended [13]. From last two-decade silicon (Si)-based solar cells dominate the industry with power conversion efficiencies (PCEs) with high production cost [14–16]. Now a day with a less expensive alternate quantum dot solar cells (QDSCs), perovskite solar cells (PSCs), organic solar cells (OSCs) and dye-sensitized solar cells (DSSCs) are used on some large scale industries [17]. Guo et al. achieved a 12% increase in efficiency by adding MXenes to the perovskite precursor [18]. Agresti et al. later demonstrated that MXenes could boost PSC PCE by 26% and reduce hysteresis when used as a dopant or interlayer. According to these conclusions, MXenes have the potential to serve as dopants in PSCs [19-20]. In order to better understand the physics and chemistry behind them, MXenes-based materials for solar cell applications are categorized into various roles, including as electrodes, additives in perovskite solar cells, electron/hole transport layers, and MXenes-silicon based heterojunction solar cells [21-22]. The solar cell properties of functional nanomaterials, such as 2D materials like MXenes, are far superior to those of traditional materials. Energy conversion efficiency has been measured at 26.5%, three times greater than carbon nanotube silicon photovoltaic cells. Photovoltaics research has focused on 2D layered nanomaterials because of their unique properties. The complex roles that MXenes play in solar cell designs have been the biggest obstacle to their widespread use [23].

On the behalf of unusual property combination, the MAX phases show promise for a wide range of uses in high temperature structural applications, protective coatings, sensors, electrical contacts, micro-electro-mechanical systems, and many more. In 2011, it was demonstrated that A layers can be selectively etched from the MAX phases [24], to form a new type of 2D material, named MXenes to emphasize the relation to the MAX phases and the parallel with graphene. Due to the development of various architectures, chemical compositions, manufacturing protocols, advances in materials, and phase stabilization techniques, efficiencies have increased dramatically since the first report on all-solid-state PSCs in 2012, from 9.7% in 2012 to 25.5% percent in 2021 [25–28]. MXenes have rapidly become established as a novel class of 2D materials with remarkable possibilities for composition variations and property tuning. For future research the more efforts on MXenes in solar cell application have to be discussed.

PEROVSKITE-BASED SOLAR CELLS

Since PVSK solar cells have such good light-harvesting qualities, they have developed rapidly in recent years, and numerous milestones have been attained in this sector, such as a high PCE of up to 23.2%, stability for more than a thousand hours, and so on. However, in order to meet its potential PCE limits (30–33%), a number of complex difficulties, such as the higher crystal size and fewer grain boundaries, must be handled. Two-dimensional MXene ($Ti_3C_2T_x$) was initially suggested as an additive in PVSK solar cells by Guo et al. in their paper [12, 25–28]. Inserting a Ti_3C_2-MXene has an energy level that is higher than the carbon electrode, which lowers PVSK's conduction and valence band, thereby decreasing the pace at which the photocurrent is transferred and accelerating the transfer of the hole. By inserting a thin layer of Ti_3C_2-MXene, it is possible to passivate the PVSK flake surface and create a direct conducting channel between Ti_3C_2-MXene and $CsPbBr_3$, which speeds up carrier transport to the carbon electrode. Recently, 2D Ruddlesden–Popper PVSK solar cells have been suggested as a way to improve the long-term stability of operation. Jin et al. [29] demonstrated perovskite solar cells with Ti_3C_2TX MXene-doped PVSK flakes, which increased the devices current density. In addition, MXene-$MAPbBr_3$ heterojunction is formed using the in situ solution growth method [30, 31].

FABRICATION OF MXENE COMPOSITE

To fabricate Ti_3C_2Tx MXene nanosheets, it was added to 30 mL solution of 9 M HCl that contained 3 g of LiF and the solution was stirred at 400C for 36 h. After-that, the product was washed and centrifuged with deionized water until the pH of the decantate reached 7. On the other hand, we shall synthesize the MXenes by using vapor deposition, sintering and thin film synthesis technique. For this, we have taken the transition metal carbides (like Ti_2C, Ti_3C_2, Nb_4C_3, etc. from (Alfa Aesar, A Johnson Matthey Company USA and Sigma-Aldrich). Grinding and mixing of micro and nano powder separately carried out in a mortar for 30 minutes to achieve homogeneity. Pellets (diameter~1.00cm and thickness for Micro~0.08 cm and for Nano~.03cm) of these powders were made by the hydraulic press by uniformly applying the pressure of 100 MPa, which results in fully isotropic material properties. The micro powder pellets were sintered at high temperature for 2 hrs to achieve strength and pellets of nano powder were not sintered just to avoid grain growth and agglomeration. PACG-M hydrogel was fabricated by thermally-induced polymerization methods in which hyper branch edpolysiloxane with dual groups (vinyl and epoxy) (HSi) used as cross-linker [29-32]. To prepare the polymer composites, the dried MXene was dispersed in propanol for 20 min and the coPA was subsequently added to obtain a 10 wt. % solution. The concentration of MXene was varied from 0.5 to 5 wt. % with respect to the concentration of coPA. The composite films were prepared by film casting using different techniques. The prepared films were dried for 24 h at room temperature and subsequently in a vacuum oven at 600C for 4 h to remove any remaining solvent.

Synthesis

Fabrication routes of MXenes are primarily focused on the removal of the more reactive "A" atoms from Mn+1Xn layers without any structural alterations. This feature is attributed to the relative weakness of M-A bonds compared to the M-X bonds, which is a stronger metallic covalent bonds. MAX phases are tightly wired to each other by strong van der Waals interaction, whichcomplicates exfoliation more than similar 2D materials like Graphene, Phosphorene, etc. Literature suggests that around twenty MXenes are successfully produced to date from more than 70 types of MAX phases. [33] According to *Ghidiu et al* [34] Ti_3C_2Tx MXene was synthesized by etching Al from the Ti_3AlC_2 phase.

Concentrated hydrochloric acid was diluted with DI water to obtain solution. This dispersed solution was stirred for 5 min using magnetic stirrer at room temperature. Ti_3AlC_2 MAX phase powder was slowly added to the HCl + LiF solution to prevent overheating as the reaction is exothermic. The reaction mixture was stirred at 40°C for about 45 h. The slurry product was centrifuged and washed with DI water to remove the unreacted hydrofluoric acid and water-soluble salts. This washing process was repeated until the pH of the filtrate reached a value of about 5. The reaction product was collected from centrifuge tubes and was extracted as Ti_3C_2Tx MXene clay [34-35].

Structural study and microscopic measurements

As we know that the quality of MXenes depends on the crystallinity and grain size of the precursor MAXphase, which are strongly affectedby crystal growthconditions. So to understand the behavior with the confirmation of successful preparation of MXenes and the phase structure of a crystal we have to study the structural properties of materials. So XRD will be used to verify the crystallinity and the structure of these as grown nanostructures. The data of in the crystalline state will be fitted using FULLPROF code for Rietveld refinement. The detailed microscopic studies like surface morphology and fracture toughness and the size of crystals in the samples will be carried out using Scanning Electron Microscope (SEM).

Electrical transport measurements

The conductivity of MXenes can be modified via altering their composition, morphology, terminations and many other factors. For instance, the surface functions may significantly alter the electronic band structures of MXene, leading to a change of the free carrier density and the effective mass.Investigations on the temperature dependence of conductivity, the effect of impurities on activation energy, the effect of annealing on conduction and the effect of high electric field on conduction mechanism is a subject of great importance because the results of such studies provide ways to control conductivity effectively. Temperature, grain boundaries, doping as well as elemental component and ionic intercalation can also affect the electrical conductivity in MXenes [36-37]. Density of localized states in the mobility gap controls many physical properties of amorphous semiconductors. The determination of density of states near the Fermi level N (EF) has been an important issue in these materials. One of the direct methods for the determination of N (EF) involves the measurement of space charge limited conduction (SCLC) which can be easily observed in low conductivity semiconducting materials. The electrical transport properties of these nanostructures materials will be studied in the temperature range from room temperature to 500K. We shall use ohmic method to measure I-V characteristics at different temperature and R-T characteristics to explain the transport mechanism. *Halim et al* [38] reported that the electrical properties, which confirm the metallic-like nature of the MXenes with resistivity, ρ, values in the range from 0.37 to 0.45 μΩ and it increase linearly with increasing the temperature furthermore, ρ increases with decreasing film thickness. The resistivity values of the Ti_3C_2Tx films are systematically higher than those produced by HF etching. For instance, 28 nm nominally thick Ti_3C_2Tx films have ρ values of 2.3 μΩ.

Dielectric properties measurements

To decrease the dielectric loss of MXene composite films, the surface of MXene was coated with SiO_2. For that a specially designed metallic sample holder is used for DC as well as AC measurements. The sample holder consists of two parts; the upper part contains two steel electrodes passes through Teflon feed, between which the samples were mounted via a screw arrangements. The lower part contains a heating element in the bottom to heat the sample. For both DC and AC measurements, the vacuum of the order 10^{-3} Torr maintained inside the sample holder. The temperature was measured by mounting a k-type Chromel-Alumel thermocouple near the sample. A Keithley picoammeter (model 6485) was used to measure the currents between temperatures from room temperature to 500K. For dielectric properties, the capacitance C and dissipation factor D is measured by using Wayne Kerr 4300 LCR meter (frequency range 20 Hz-1 MHz with 0.1% basic accuracy).

MXENE-REINFORCED NANOCOMPOSITES

Combining MXenes with polymers, ceramics, metals, and nanoparticles yields composites with improved performance. Their exceptional optical, electrical, structural, mechanical, and thermal qualities result from their one-of-a-kind chemical and physical properties. Many other nanomaterials, including graphene derivatives, metal oxides, metals, and polymer monomers, have been successfully merged with MXene to create MXene-based hybrid nanocomposites, which improve upon the characteristics and practicality of pure MXene. Effective types for preparing MXene composites are as follows.

MXene-Metals/Ceramics Composite

MXenes are often employed to reinforce polymeric materials, but they can also be utilized to reinforce metallic or ceramic materials [67-69]. Reinforcement agents like graphene and CNTs have previously been tried in metals. On the other hand, metal matrix com- posites have faced significant difficulties due to agglomeration and poor wettability [70]. Pure MXene has been successfully combined with a wide range of nanomaterials, includinggraphene derivatives, metal oxides, and metals, to create Mxene-based hybrid nanocomposites [39].

MXene-Polymer Composite

Using MXenes, polymer-based composites get a significant advantage in mechanical performance [39, 71, 72]. MXenes offer a wide range of applications as composite components because of their unique chemistry [16, 73, 74]. MXenes could greatly affect how spherulites grow and how polymeric materials crystallize [75, 76]. Since the MXene sheets have a high aspect ratio and the -OH termination groups provide hydrogen-bonding in- teractions, the $Ti_3C_2T_x$ was found to significantly alter the glass transition temperature (Tg), and the mechanical strength increased by 23 percent, from 104.6 MPa for pure Nafion to 128.4 MPa for the composite sample [77]. Polymeric molecules respond better to MXene functional groups than to Graphene's. These functional groups include the $-O_2$,–OH, and –F. Graphene devoid of surface terminations is often insufficient for composite production [78]. Due to its hydrophilic nature, MXene sheets have excellent wettability with a broad range of materials. It makes it easy to disperse and spread the sheets in various liquids [79]. Currently, MXenes have been employed in several types of polymeric matrices, including polyurethane (PU) [71, 80], polyacrylic acid (PAA) [81], polylactic acid (PLA) [16], poly-vinyl alcohol (PVA) [82], nylon-6 [83], chitosan [84], and polyvinylidene fluoride (PVDF) [35] etc.

CONCLUSIONS

Two-dimensional transition metal (MXene) contributed to the enhancement of solar cell manufacture by increasing the efficiency of produced energy and solar cells' durability. MXene-based nanocomposites offer incredibly promising possibilities as a future for this remarkably fast-growing subject of nanotechnology and may be further investigated in many fields of science and technology. Substantial work is necessary to characterize and improve the characteristics of MXene-based nanocomposites, resulting in materials with superior desirable features. Even though many Mxene-polymer composites are synthesized, understanding how the microstructural characteristics of MXene-metal or ceramic composites influence their physical properties is still in its early stages. More research is required on how varying the concentration of a surface passivating functional group affects its properties. While several MXenes are readily accessible, $Ti_3C_2T_x$ is now the most popular MXene used in solar cell fabrication. This paper reviews the recent progress in MXene-reinforced composites ranging from polymer-based materials to ceramic–or metal– matrix nanocomposites. We summarized the comprehensive studies on using MXene-based nanocomposites in solar cells and collated nearly all the results in the literature, as it has only been four years since MXene's initial application in a solar cell was proven.

FUTURE PERSPECTIVES

Here we reported the successful preparation and characterization of electrically conductive, highly transparent and flexible MXene nanosheets. In recent years, the increasing demand for higher performance of integrated circuits has been met by scaling down various device components, including on chip interconnects. However, as the use of conventional metals, such as copper, in miniaturized interconnects becomes increasingly challenging, there is a growing interest in alternative interconnect materials with high electrical conductivity and breakdown current density. A variety of MXene structures make them promising candidates for many applications. Energy storage has been the first and most studied application of MXenes. However, there are potentially other applications in which MXenes can outperform other materials. MXenes in energy storage batteries have wide chemical and structural variety. For this reason, MXenes can help to define the most promising candidates for energy-storage applications. Because the ions penetrate between the MXenes so the bonds between M and X are broken easily. MXenes worth as a reliable electrode for electrochemical energy storage devices has been proven by tackling various obstacles and this trend is expected to continue in the future. Most of the demonstrations of batteries using MXene have been done in coin-cells, naturally, because the primary focus is on characterizing the electrochemical properties of the active material. MXenes provide a conductive matrix that accommodates expansion and contraction of particles while maintaining structural and electrical connectivity. Other applications have also been studied such as water purification, reinforcement for composites, electro catalysts and catalysts in the chemical industry, lubricants, photo catalysts, and bio- and gas sensors. Therefore, we are hopeful that MXene will realize its true potential by bringing 2D materials to the industrial-scale application.

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