Colloidally synthesized defect-rich MoSe₂ nanosheets for superior catalytic activity

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Abstract. Transition metal dichalcogenide (TMD) nanosheets (NSs) with defect-rich and vertically aligned edges are highly advantageous for various catalytic applications. However, colloidal synthesis of defect-rich NSs with thickness variation has been a challenging task. Here, we report a colloidal synthesis of 2H-MoSe₂ NSs having a large number of defects and vertically aligned edges, where the thickness is varied by changing the amount of coordinating solvent. The Se-vacancies in these NSs have introduced defect sites which are corroborated by the presence of additional vibration modes in Raman spectra. These NSs exhibit electrocatalytic hydrogen evolution reaction performances with a low overpotential (210–225 mV) at 10 mA cm⁻² current density and a small Tafel slope (54–68 mV per decade). Moreover, these MoSe₂ NSs are also employed as counter electrodes (CEs) for the fabrication of dye sensitized solar cells *via* a cost-effective and simplified procedure. The power conversion efficiencies of $7.02 \pm 0.18\%$, comparable with Pt CE ($7.84 \pm 0.10\%$) could be routinely achieved. These results demonstrate a novel synthetic strategy to prepare layered TMDs with superior catalytic applications.

Keywords. Transition metal dichalcogenides; MoSe₂ nanosheets; hydrogen evolution reaction; dye sensitized solar cells; counter electrode.

1. Introduction

Two-dimensional (2D) layered transition metal dichalcogenides (TMDs) e.g., MoS₂, MoSe₂, WS₂, WSe₂, have made a smooth entry into the elite class of materials due to the perfect amalgamation of unique and tunable material properties such as quantum-well with a broad range of indirect to direct band gap, thickness dependent band transitions, in-plane charge carrier mobility, high specific surface area and enhanced spin-orbit coupling [1–8]. These properties have enabled TMDs for potential applications as electrocatalysts for the hydrogen evolution reaction (HER), as counter electrode (CE) in dye sensitized solar cells (DSSCs), in optoelectronic devices, transistors, spintronics, supercapacitors, photodetectors and sodium-ion batteries [9–18]. Previously, 2D MoSe₂ nanostructures have been synthesized by liquid exfoliation, mechanical exfoliation, chemical vapour deposition and solvothermal reactions [1,19–21]. All these methods have their respective limitations such as low yields, substrate assisted nanostructure synthesis, less control over thickness and lateral dimension and crystallinity. These limitations render the methods unsuitable for large-scale production for practical applications. The colloidal bottom-up syntheses

of nanostructured MoSe₂ nanosheets (NSs) have significant advantages in large-scale applications such as high yield and substrate free method. However, desired control over thickness, lateral dimensions and morphology has not been explored extensively. Recently a few reports have emerged on the synthesis of MoSe₂ NSs *via* the colloidal synthesis route [6,22–24]. Scalable amount of hierarchical ultrathin MoSe_{2-x} NSs were also reported by Zhou *et al* [6]. Sun *et al* [23] prepared MoSe₂ nanoflowers with a few layers of sheets. Jung *et al* [24] recently utilized the colloidal route for the synthesis of MoSe₂ NSs where they could vary the sheet thickness upon changing the functional group of the capping ligand. But to date, there is a lack of systematic studies for the formation of defect-laden NSs with exposed edges and thickness variation which are highly preferable for superior catalytic performances.

Similar to other TMDs, 2D MoSe₂ nanostructures consist of two types of surface sites: terraces and edges [25]. Terrace sites at basal planes are terminated with less number of dangling bonds and are electrocatalytically inert, whereas the edge sites on the side surfaces have more number of dangling bonds which are active sites for catalytic reactions [25,26]. So, it is highly desirable to increase the number

of exposed edges either by synthesizing vertically aligned NSs or introducing defects induced cracks in the NSs which boost the catalytic activity [27,28]. Although Pt is the most superior electrocatalyst for HER and an efficient CE for DSSCs, due to its low abundance and high cost, it needs to be replaced by other materials which would be helpful in large-scale applications [29–31]. Among the TMDs (MX_2 where $\text{M} = \text{Mo}, \text{W}$; $\text{X} = \text{Se}, \text{S}$) MoSe_2 is considered as a superior active electrocatalyst because both Mo and Se edges are active for H^+ binding [25]. Various groups have recently probed MoSe_2 [6], alloys of MoSe_2 with S [9], S-doped MoSe_2 [22], vertically aligned MoSe_2 [26], nanohybrid of MoSe_2 [32], ultrathin MoSe_2 NSs decorated on graphene and carbon fibre as electrocatalysts for HER [33,34]. Recently, Chen *et al* and Lee *et al* used Mo/MoSe_2 as efficient CE in DSSCs [10,11].

In the present investigation, we report the colloidal synthesis of defect-rich mono and few-layer 2H- MoSe_2 NSs having a large number of vertically exposed edges using oleylamine (OA) as the solvent as well as the coordinating ligand. Here, the solvent dilution effects play a crucial role in varying the thickness of MoSe_2 NSs. This phenomenon has not been reported till date in MoSe_2 NSs. High resolution transmission electron microscopy (HRTEM), Raman spectra and compositional analyses show a large number of vertically aligned edges along with Se vacancies in NSs, resulting in more active exposed edges that in turn justify its use as an electrocatalyst. We utilized the as-synthesized MoSe_2 NSs in electrochemical water splitting and catalysing the reduction of I_3^- to 3I^- in DSSCs. These NSs show high HER activity with low onset overpotentials (145–155 mV), a large cathodic current density of 10 mA cm^{-2} at lower overpotentials (210–225 mV) and a small Tafel slope (54–68 mV per decade). Thinner MoSe_2 NSs show better activity due to higher electrochemical surface area (ECSA), higher conductivity and lower potential losses resulting from smaller number of hopping steps of electrons required between the consecutive layers as compared to thicker sheets. Using MoSe_2 NSs as CEs in DSSCs, we obtained power conversion efficiency (PCE) of $7.02 \pm 0.18\%$ as compared to $7.84 \pm 0.10\%$ efficiency obtained from cells fabricated under identical conditions using the standard Pt electrode. In comparison with other reported studies [10,11] where MoSe_2 CEs were fabricated by DC sputtering followed by selenization at a higher temperature, our fabrication procedure of CEs using MoSe_2 is very simple without need of any sophisticated instrumental techniques and involves simply drop-casting the materials on FTO and annealing at 470°C in an inert environment.

2. Experimental

2.1 Materials

Ammonium molybdate tetrahydrate $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$, 98%, SRL), acetyl acetone ($\text{C}_5\text{H}_8\text{O}_2$, 98%, SDFCL), selenium powder (Se, 99.99%, Aldrich), OA ($\text{C}_{18}\text{H}_{35}\text{NH}_2$,

technical grade 70%, Aldrich), bulk molybdenum diselenide (MoSe_2 , 99.9%, Aldrich), 1-butanethiol ($\text{C}_4\text{H}_{10}\text{S}$, Merck, >98%), TiO_2 paste (18 NR-T paste, Dyesol), fluorine-doped tin oxide (FTO, $7\text{--}8 \Omega \text{ sq}^{-1}$, Aldrich) titanium tetrachloride (TiCl_4 , 99%, Spectrochem), ditetrabutylammonium *cis*-bis(isothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylato) ruthenium(II) (N719 dye, NMR 95%, Aldrich), acetonitrile (CH_3CN , 99.8%, Merck), *tert*-butanol $((\text{CH}_3)_3\text{COH}$, 98%, Fischer Scientific), valeronitrile ($\text{C}_5\text{H}_9\text{N}$, 99%, Spectrochem), iodine resublimed (I_2 , 99.99%, Merck), 1-butyl-3-methylimidazolium iodide (BMII, 99%, Aldrich), 4-*tert*-butylpyridine ($\text{C}_9\text{H}_{13}\text{N}$, TBP, 95%, Aldrich), guanidine thiocyanate ($\text{C}_2\text{H}_4\text{N}_4\text{S}$, GTC, 99%, CDH), dihydrogen hexachloroplatinate(IV) hexahydrate ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$, 37.5% Pt basis, Aldrich), nitric acid (HNO_3 , assay 69–70%, Fischer Scientific), hydrochloric acid (HCl , assay 35.8–38%, Fischer Scientific), ethanol ($\text{C}_2\text{H}_5\text{OH}$, absolute, Merck) and toluene ($\text{C}_6\text{H}_5\text{CH}_3$, 99%, Fischer Scientific) were used as received. Double distilled water was employed throughout the study.

2.2 Synthesis of Mo precursor material $\text{MoO}_2(\text{acac})_2$

Precursor Mo-salt i.e., $\text{MoO}_2(\text{acac})_2$ was synthesized from $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ via cleavage of the giant structure using distilled acetyl acetone [35]. In a 100 ml beaker, $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ (6 g, 5 mmol) was dissolved in 25 ml distilled water at room temperature under magnetic stirring. After complete dissolution of Mo cluster, acetyl acetone (8 ml) was added drop by drop maintaining the rate at 0.5 ml min^{-1} . The pH of the solution was adjusted to 3.5 by adding 10% HNO_3 and immediately, a greenish yellow colour product was observed. In order to complete precipitation, the stirring was continued for another 1.5 h and a greenish yellow solid was obtained by centrifugation for 5 min at 6000 rpm. After washing the solid three times with copious amount of distilled water and two times with ethanol, the sample was dried in a vacuum oven at 60°C temperature and the solid was stored in a glove box for further use.

2.3 Preparation of Se precursor

Se precursor was prepared according to the previously reported method with slight modification [36]. Se powder (0.240 g, 3 mmol) was suspended in 3.14 ml OA in a 25 ml round-bottom (RB) flask. The mixture was degassed under vacuum for 20 min and then kept under an argon (Ar) atmosphere for 15 min at room temperature under stirring. 1-Butanethiol (0.430 ml) was injected into the reaction mixture at room temperature and kept for 30 min under an inert atmosphere.

2.4 Synthesis of MoSe_2 NSs

We developed a phosphine-free synthetic method to prepare MoSe_2 NSs using a high temperature colloidal synthetic route. In a 100 ml four-neck RB, $\text{MoO}_2(\text{acac})_2$ (0.163 g, 0.5 mmol)

was dissolved in 7.5–22.5 ml OA at 160°C under continuous stirring in an Ar atmosphere. The colour of the solution became yellowish red at this temperature. Freshly prepared Se precursor (2.63 ml, 2 mmol) was swiftly injected into the Mo precursor solution and the temperature was increased to 270°C. After 4 h, the reaction mixture was cooled down to room temperature under stirring and gas flow. The mixture was precipitated out with dropwise addition of ethanol and centrifuged at 6000 rpm for 10 min to obtain a black colour solid product. The product was purified three times with addition of toluene and ethanol mixture (2:1 by volume) and redispersed in toluene and stored in a refrigerator for further applications.

2.5 Fabrication of DSSCs

FTO-coated glass substrates ($2 \times 2 \text{ cm}^2$) were cleaned by sonication with soap solution for 15 min, followed by further sonication with distilled water, acetone and ethanol consecutively. The washed FTO were dipped into a 40 mM aqueous TiCl_4 solution at 70°C for 30 min and washed thoroughly with water and ethanol. After drying, it was annealed in a muffle furnace at 500°C for 30 min. 18 NR-T transparent TiO_2 paste was deposited on the TiCl_4 -treated FTO with a thickness of 12 μm and dimension of the active area was ($0.25 \times 0.25 \text{ cm}^2$). The TiO_2 -coated FTO was annealed in a furnace through a series of increasing temperatures: 325°C for 10 min, 375°C for 15 min and 500°C for 30 min. The annealed TiO_2 electrode was again dipped into 40 mM aqueous TiCl_4 solution as described before and annealed at 500°C for 30 min. The electrode was finally immersed into a 0.5 mM N-719 dye solution in a mixture of acetonitrile and *tert*-butyl alcohol (volume ratio, 1:1) and kept in the dark for 24 h. Then the CE solution was prepared by dispersing 1 mg/10 ml MoSe_2 NS sample in toluene and 100 μl was drop cast on drilled FTO. After drying, it was annealed on a hot plate for 5 min at 80°C. The same procedure was performed thrice consecutively to achieve maximum efficiency. To remove the insulating ligands the MoSe_2 -coated FTO was annealed in a furnace at 470°C under an inert atmosphere, followed by cooling under inert conditions. For reference a Pt CE was made by drop casting 0.005 M H_2PtCl_6 solution on FTO and annealed on a hot plate at 80°C for 10 min and in a furnace at 400°C for 15 min. The CE and the prepared photoanode were then assembled together by using a 25 μm thick parafilm to form a sandwich-type configuration. Finally a conventional electrolyte containing 0.03 M I_2 , 0.6 M BMII, 0.1 M guanidine thiocyanate (GuSCN) and 0.5 M 4-*tert*-butylpyridine in acetonitrile–valeronitrile (volume ratio, 85:15) was introduced into the cell *via* the drilled holes. Finally the holes were sealed with parafilm and cover glass.

For electrochemical impedance spectra (EIS) measurements symmetrical cells were fabricated following the same procedure as DSSC but the photoanode was replaced with another CE.

2.6 Characterization

Absorbance spectra were recorded using a Perkin-Elmer Lambda 1050 spectrophotometer by dispersing material in toluene and placed in 1 cm quartz cuvettes. Powder X-ray diffraction (PXRD) studies were carried out on a Bruker D8 Advance diffractometer with Ni-filtered $\text{Cu-K}\alpha$ radiation and further analysis was carried out using JCPDS data. HRTEM images were obtained using JEOL 2100F operating at 200 kV and transmission electron microscope (TEM) imaging was performed using JEOL JEM-1400 Plus operating at 120 kV accelerating voltage. A TEM grid was prepared by drop casting diluted solution of nanocrystal in toluene and allowed to dry and kept in a desiccator for 12 h before measurement. Scanning electron microscopy (SEM) images were obtained using a Zeiss EVO 18 system. The X-ray photoelectron spectroscopy (XPS) measurements were carried out by X-ray photoelectron spectroscopy (PHI 5000 Versa Probe II, ULVAC-PHI, Inc., Japan) with an incident $\text{Al K}\alpha$ X-ray of energy $h\nu = 1486.6 \text{ eV}$. Raman analyses were performed in a Renishaw plc micro-Raman Spectrophotometer. Thermogravimetric analysis (TGA) was carried out using a Perkin-Elmer instrument. Fourier-transform infrared (FTIR) spectra were recorded using Cary 600 FTIR instrument. Elemental analyses were performed using an Agilent 7900 ICP-MS instrument and TM3000 table top microscope Hitachi with an EDX detector. Atomic force microscopy (AFM) imaging was performed in a Veeco Nanoscope-IV system.

For electrochemical HER, a three electrode assembly was used, where Pt wire was used as CE, aqueous Ag/AgCl was used as reference electrode (RE) and a glassy carbon electrode coated with sample was used as working electrode (WE). To form homogeneous catalyst ink 50 μl water, 50 μl isopropanol and 10 μl Nafion were added to a mixture of 1.5 mg MoSe_2 and 0.75 mg Valcan XC-72 powder and then vigorously sonicated for 30 min. Five microlitres of the catalyst ink was cast onto a glassy-carbon electrode. 0.5 M H_2SO_4 in MilliQ water was used as electrolyte. The linear sweep voltammetry was measured in Autolab (PGSTAT302N) by applying the potential range -0.7 to 0.2 V at scan rates of 20 mV s^{-1} . EIS measurements were carried out at selected overpotentials in a frequency range of 100,000–0.5 Hz. Tafel slopes were fit to the Tafel equation ($\eta = a + b \log j$) where η is the overpotential, b is the Tafel slope and j is the current density. To check the stability of the electrocatalyst, a chronoamperometric study was carried out at a constant potential of 0.210 V vs. RHE (corresponds to current density of 10 mA cm^{-2}) for 10 h.

Photovoltaic performances (J – V characteristic) of DSSCs were measured using a Keithley 2634B SYSTEM source meter and the illumination source was AM 1.5G solar simulator (PET PHOTO EMISSION, Model No. SS50AAA). The intensity of the simulated solar light was calibrated to 100 mW cm^{-2} using a standard silicon solar cell (NREL).

Cyclic voltammetry (CV) and EIS were carried out in a three-electrode assembly where Pt foil was used as a CE, Ag/Ag⁺ non-aqueous electrode used as a reference electrode (RHE) and MoSe₂ drop cast onto FTO-coated substrate followed by inert atmosphere annealing as WE. The electrolyte contained 10 mM LiI, 1 mM I₂ and 0.1 M LiClO₄ in acetonitrile. These spectra were measured by Autolab (PGSTAT302 N) at scan rates of 50 mV s⁻¹. EIS measurements were performed over a frequency range of 10,000–0.5 Hz with zero bias potential.

3. Results and discussion

3.1 Characterization of materials

Precursor Mo-salt i.e., MoO₂(acac)₂ was synthesized from (NH₄)₆Mo₇O₂₄·4H₂O via cleavage of the giant

structure as shown in figure 1a. All the Mo centres in (NH₄)₆Mo₇O₂₄·4H₂O exist in an octahedral environment and the oxides show different coordination modes e.g., terminal, doubly bridging and triply bridging oxide whereas in MoO₂(acac)₂, Mo is surrounded by two terminal oxide ligands, two ketonic oxygens and two oxide ions [37]. This facilitates the reaction between MoO₂(acac)₂ and Se-precursor. MoSe₂ NSs were synthesized by reacting MoO₂(acac)₂ with Se precursor at 270°C under an inert atmosphere, where OA is used as the solvent as well as the Z-type capping ligand preventing the overgrowth and aggregation of the sheets [38]. Presumably, our Se precursor reacts with the metal precursor in the form of (Se)_m(OA)_n as suggested in recent work [39]. In the presence of butanethiol, Se powder is reduced to Se²⁻ and butanethiol converted to disulphides as byproducts [40]. This anionic species makes a highly reactive soluble Se precursor (Se)_m(OA)_n at room temperature by reacting with OA [39,41].

Figure 1. (a) Syntheses of MoO₂(acac)₂ and MoSe₂ NSs. The giant structure of [Mo₇O₂₄]⁶⁻ breaks down in the presence of acetyl acetone forming MoO₂(acac)₂ which reacts with Se precursor to form MoSe₂ NSs. (b) PXRD pattern of NS_1 M and NS_6 M NSs along with bulk pattern (JCPDS #87-2419). (c) and (d) are the zoomed in part of pattern along the (002) direction for NS_1 M and NS_6 M NSs, respectively. (e) shows the absorbance spectra with thickness dependent band transition. (f) Growth along the *c*-direction gives multilayer NS in the presence of less amount of OA while restricted growth ensues along the (002) plane due to passivation of basal planes in the presence of a large amount of OA. (g) Raman spectra indicate a large number of Se vacancy defects in the NSs. Colour coding: NS_1 M red, NS_6 M green.

Previously, it was reported that Se may form Se–OA complexes in the presence of a reducing agent e.g., NaBH_4 [42]. Here, butanethiol also acts as a surfactant to lower the basal plane surface energy which causes the anisotropic growth [22]. We have synthesized MoSe_2 NSs of two thicknesses precisely; 1 and 6 monolayer (ML) by performing the reaction in 22.5 and 7.5 ml OA, respectively. From here on for the sake of brevity, the NSs obtained for different volumes of OA 7.5 and 22.5 ml are termed as NS_6 M and NS_1 M, respectively. Here NS_6 M and NS_1 M correspond to 6 ML and 1 ML MoSe_2 NSs as reflected from PXRD pattern discussed later on. The structural, optical, morphological and compositional analyses verify the formation of defect rich MoSe_2 NSs along with exposed edges.

The main aim of characterization is to ascertain the number of MLs formed in the MoSe_2 NSs. One of the ways is to utilize the PXRD data shown in figure 1b that matches well with the 2H phase (JCPDS #87-2419). Although the peaks corresponding to the extended directions should be sharper, those emanating from the confined layers would turn out to be broad as a direct consequence of the Scherrer equation [43]. In turn, the width of these broad peaks should also give us an estimate of the layer thickness. The confinement of the MoSe_2 NSs is known to be along the *c*-axis that is seen here along the (002) direction [44]. An estimate from the peak widths for NS_6 M gives a thickness of 6 MLs, whereas NS_1 M results in ML thickness. The diffraction data for the small region corresponding to the (002) reflection, the direction perpendicular to the plane of the NSs, is shown in figure 1c and d for the two cases. Due to the limited number of planes along this direction, the counts are extremely low and a large number of scans are needed to be added to see anything above the noise level. For the NS_6 M in figure 1d we can still see a peak but for the NS_1 M in figure 1c, this is hardly visible even after an average of 10 scans. The absence of a peak indicates the non-availability of a second plane along this direction that would result in diffraction and presumably what we have formed here is a single ML of MoSe_2 . More proof, which is provided below, is required before we can be completely sure of this.

It has been reported that bulk MoSe_2 exhibits excitonic peaks at 827 and 725 nm which are shifted to 790 and 693 nm in single layer MoSe_2 , marked as A and B in figure 1e [24]. For NS_6 M NSs the excitonic features appear at 816 and 723 nm; blue shifted from bulk MoSe_2 . The shift of the excitonic peaks towards higher energies i.e., the blue shifting occurs because of the combined effect of out of plane confinement of the charge carriers and interlayer coupling of the electronic states during transition [45,46]. However, for NS_1 M the excitonic peaks are observed at the wavelengths similar to the single ML case at 795 and 693 nm. We propose that the amount of coordinating solvent used, i.e., OA plays a crucial role to vary the thickness of sheets. Previously Chen *et al* [24] reported that OA strongly prefers to bind edge facets rather than basal planes producing multilayer MSe_2 ($\text{M} = \text{W}, \text{Mo}$) NSs due to growth along the (002) direction. We observed the same trend

when the amount of coordinating solvent is less. But with increasing the amount of coordinating solvent we obtained low ML NSs due to passivation of basal planes along with the edges as shown in figure 1f resulting in limiting the growth along basal planes. By varying the solvent from 7.5 ml to 22.5 ml we obtained two different thicknesses i.e., 1 and 6 ML. These materials are highly soluble in toluene due to the presence of hydrophobic long chains and showed colloidal stability even after one week (supplementary figure S1a and b). These NSs are also soluble in a diverse range of organic solvents (supplementary figure S1c and d). The colloidal stability and solubility make it suitable for thin-film-based device applications. Elemental composition and binding energy of NS_1 M NSs were examined with XPS (see supplementary figure S2). The Mo 3d survey shows that it consists of several set of peaks *viz.* doublet of Mo^{4+} peak at 229.1 and 232.4 eV corresponds to $3d_{5/2}$ and $3d_{3/2}$, respectively and a peak at 226.1 eV corresponds to S 2s that is coming from the butanethiol which is attached with the MoSe_2 NSs during reaction. The 3d scan of Se shows peaks at 54.6 and 55.3 eV corresponding to Se $3d_{5/2}$ and $3d_{3/2}$, respectively. These values suggest Mo is present in the +4 oxidation state while Se in the –2 oxidation state in MoSe_2 NSs; this is consistent with the previously reported values of MoSe_2 NSs [47,48].

Bulk MoSe_2 shows characteristic Raman peaks at 243.5 and 283.7 cm^{-1} corresponding to A_{1g} and E_{2g} modes [49,50]. With a decrease in the number of layers the A_{1g} mode shifts to lower energy whereas the E_{2g} mode shifts to higher energy due to the phenomena known as stiffening and softening, respectively [23]. In NS_6 M peaks appear at 238 and 287.31 cm^{-1} whereas these peaks are shifted to 235.73 and 290.41 cm^{-1} in NS_1 M as shown in figure 1g indicating the stiffening–softening phenomena are more pronounced in NS_1 M. This result clearly indicates that NS_1 M NSs comprise of smaller number of ML. Previously it was reported that pristine A_{1g} peaks were observed at 243.5 and 240.27 cm^{-1} for bulk and single MoSe_2 , respectively [49]. In our case, the A_{1g} peak is further shifted to a lower wave number along with a new peak at 252.46 cm^{-1} . This type of phenomena happens when there is a large number of Se vacancies in the NSs which introduce additional vibrational modes due to the disturbance of crystal symmetry. Such selenium vacancies left the fingerprint for characteristic Raman peak in the crystal which was previously observed by Samani *et al* [51]. As we see below, these defects in the surface are much needed for the catalytic applications that we are looking into.

Morphology and nature of MoSe_2 NSs were examined under a TEM. Figure 2a and b shows the ultrathin nature of NS_1 M NSs with a large quantity of standing edges which are observed as dark black lines. These types of standing edges are highly desirable for better catalytic activity as it increases the number of active edge sites [26,27]. Thermodynamically the formation of this type of standing edges are unfavourable, but the formation in the present case may be due to the strong passivation of edges by OA

Figure 2. (a, b) TEM and (c, d) HRTEM images of defect-rich NS_1 M NSs.

during the growth of NSs [9,52]. HRTEM images show interplanar spacing of 0.27 and 0.65 nm which are consistent with the (100) and (002) planes, respectively, as shown in figure 2c and d. The orientation of the (002) planes in different directions indicates the disorder in NSs which generates active edge sites making it highly useful for catalytic applications. Also due to the presence of defects there is a crack in the basal planes which causes folding in NSs. This type of folding is a common phenomenon in 2D materials [27,45]. TEM images of NS_6 M NSs (supplementary figure S3) show that sheets are stacked with each other and form multilayer NSs. The SEM images (supplementary figure S4) of NS_1 M NSs show the average lateral dimension of the NSs are 150–200 nm. The thickness of the NS_1 M NSs is 1.02 nm obtained from the AFM measurement which confirms the presence of single ML (supplementary figure S5a). Because of the presence of ligands the thickness is higher than its usual thickness of 0.70 nm. The thickness of NS_6 M NSs is 4.8 nm which corresponds to ~ 6 ML thickness (shown in supplementary figure S5b).

3.2 Thickness dependent HER activity of MoSe₂ NSs

During electrocatalytic HER, electrons from the external circuit combine with H⁺ at catalytic sites resulting in the production of molecular H₂ [53]. We chose NS_1 M and NS_6 M NSs and bulk MoSe₂ as electrocatalysts as these materials have different thickness and thus we can study the effect of thickness on the catalytic activity. Before measurements these materials were heated at 470°C under an inert Ar atmosphere to remove the insulating OA that is attached onto the surface of MoSe₂. From TGA and FTIR spectra analyses, it is confirmed that there was removal of insulating ligands at 470°C, but there was no noticeable change in thickness and crystallinity of the materials after annealing as reflected from PXRD diffractogram (supplementary figure S6). We have shown in supplementary figure S7 that the annealing step largely improves the catalytic activity because of the removal of insulating ligands.

As shown in figure 3a the polarization curves (J – V plot) of NSs exhibit a small onset potential in the range

0.14–0.15 V for the as-synthesized NSs, beyond which the cathodic current increases sharply under more negative potential. To quantify the electrocatalytic activity we compare the overpotentials required to reduce water at a current density of 10 mA cm^{−2} in table 1. NS_1 M shows superior performance compared to NS_6 M followed by bulk. The catalytic activity of the as-synthesized pure MoSe₂ NSs is better than or comparable to most of the reported values so far (table 2) [9,21,22,32,33,41,54–56]. Generally, the performance of a HER catalyst depends on active sites, high surface area as well as higher conductivity [27,57]. Raman, inductively coupled plasma mass spectrometry (ICP-MS) and energy-dispersive X-ray spectroscopy (EDS) measurements (supplementary table S1) of NSs reveal large Se vacancy related defect sites generating the active edges which are much needed for HER [6,27,58]. HRTEM images showed that there are a large number of vertically aligned edges in the NSs which make these NSs highly advantageous to show superior HER activity [26]. Also, being a 2D material having a large surface area allows more electrolyte to come in contact. This contributes towards faster kinetics in HER. Interestingly NS_1 M NSs i.e., single ML NSs seem to be more active as an electrocatalyst as compared to NS_6 M NSs and bulk which are composed of more MLs. To further understand the HER activity the linear portion of Tafel plots were fit as shown in figure 3b. Tafel slope which is an inherent property of the sample, determines the kinetics of the HER processes. Smaller Tafel slopes are more desirable as it indicates faster generation of hydrogen [22]. In NS_1 M the reduced Tafel slope value indicates faster generation of molecular H₂ in LML NSs. A similar trend for thickness dependent HER activity was also observed without annealing the samples (supplementary figure S8) though the performance is much inferior. We have investigated the mechanism for better activity of low ML NSs as compared to high ML. In 2D materials a potential barrier exists in the gap of the successive layers which drives the hopping processes [25]. On increasing the number of layers the hopping steps of electron increases as compared to low ML manifesting in a large potential required to produce H₂ as shown in figure 3c [59]. Previously, several groups reported that in TMDs the electronic properties are highly dependent on sheet thickness [3,60]. Yang *et al* [6] have shown that the electronic density of state of single layer MoSe₂ is higher as

Figure 3. Electrochemical measurements of MoSe₂ NSs for HER electrocatalysis in 0.5 M H₂SO₄: (a) polarization curves of MoSe₂ NSs, bulk MoSe₂ powder, 10% Pt powder was used for comparison. Overpotentials required to reduce water at 10 mA cm⁻² current density can be compared at the dashed line, (b) the corresponding Tafel plots of NSs. The solid black lines indicate linear fitting for the plots. (c) Hopping of electrons in the vertical direction of MoSe₂ layers. High ML NS requires more number of hopping steps as compared to low ML NS to reach the electron from external circuit to the outermost layer for catalysis. (d) EIS of MoSe₂ NSs; (e) *i*-*t* plot of NS_1 M NSs in 0.5 M H₂SO₄ at a constant current density of 10 mA cm⁻².

Table 1. Electrocatalytic performance parameters of MoSe₂ NSs.

Electrocatalyst	η at $j = 10 \text{ mA cm}^{-2}$ (mV)	Tafel slope (mV per decade)	R_{CT} (Ω)
NS_6M	225	68	118
NS_1M	210	54	86

compared to its bulk counterpart resulting in higher intrinsic conductivity as well as carrier density in single layered materials.

To investigate the charge transfer kinetics between the NSs and electrolyte, EIS spectra were recorded at an overpotential of 150 mV. In general, R_{CT} is related to the electrocatalytic kinetics and a lower value corresponds to a faster reaction rate. We observe in figure 3d that NS_1 M exhibits lower charge transfer resistance as compared to NS_6 M and much lower than bulk indicating that low ML exhibits faster HER kinetics. The corresponding equivalent circuit diagram is shown in supplementary figure S9 in Supporting Information. Previously, it has been shown theoretically that the intrinsic conductivity increases with decreasing the number of layers [6]. We hypothesize that the faster charge transfer in low ML NSs is due to the higher conductivity resulting in better performance of low ML MoSe₂ NSs. Beside these, to estimate ECSAs of our NSs, electrochemical double-layer capacitances (C_{dl}) were measured using the CV method [61]. The C_{dl} values of 1.49 and 1.23 mF cm⁻² were obtained for NS_1 M and NS_6 M NSs, respectively (details are shown in supplementary figure S10). From these values we obtained

that NS_1 M NSs has higher ECSA as compared to NS_6 M NSs [62]. So, the combined effect of thickness dependent hopping mechanism, conductivity and the larger ECSA value are contributors for better catalytic activity of NS_1 M NSs.

Recyclability is another important property for any electrocatalyst, so that the electrocatalyst can function for a long period of time making it cost-effective. To investigate the cycling stability, we performed the chronoamperometric measurements of the NS_1 M catalyst continuously for 10 h. As shown in figure 3e, after 10 h there is a small drop in the current density, attesting for the electrochemical durability. The change of current density may be due to the delamination of the catalyst from the electrode or accumulation of H₂ around the electrode surface that hinders the reaction. The NS_6 M catalyst also shows a small drop of activity loss during HER processes as shown in supplementary figure S11. To check whether there is any deformation, after recovering the electrocatalyst from electrode surface we analysed it through PXRD pattern as shown in supplementary figure S12. The same crystal structure exists, indicating no deformation of electrocatalyst during HER processes.

Table 2. A brief survey of MoSe₂ and MoSe₂-based HER electrocatalysts reported in the literature.

Reference	Electrocatalyst	η at $J = 10 \text{ mA cm}^{-2}$ (mV)	Tafel slope (mV per decade)
This work	Pure MoSe ₂ NS	210	54
[54]	2H MoSe ₂ on vertical graphene	135	184
	N-doped 2H MoSe ₂ on vertical graphene	98	49
[72]	Amorphous MoSe ₂	270	60
[55]	Pure MoSe ₂ NSs	—	110
	MoSe ₂ with 50% carbon black mix	208	62
[56]	Pure MoSe ₂	330	92
	MoSe ₂ /Cu ₃ Se ₂	130	46
[9]	Pure MoSe ₂	181 ± 1	45 ± 1
	MoSSe	164 ± 2	48 ± 2
[33]	Pure MoSe ₂ NSs	—	177
	PVP–MoSe ₂ on graphene	—	70
[32]	MoSe ₂	—	95
	MoSe ₂ –NiSe nanohybrids	210	56
[21]	Pure MoSe ₂ NSs	390	103
	MoSe ₂ /RGO hybrids	195	67
[33]	Pure MoSe ₂ NSs	—	177
	PVP–MoSe ₂ on graphene	—	70

Figure 4. (a) CV curve using MoSe₂/FTO and H₂PtCl₆/FTO as working electrodes, non-aqueous Ag/Ag⁺ as reference and Pt wire used as CE at 50 mV scan rate. (b) Nyquist plots of the symmetric cells. (c) Photovoltaic performances (J – V characteristics) of DSSCs with MoSe₂/FTO and H₂PtCl₆/FTO CEs, under simulated AM 1.5 G solar light (100 mW cm⁻²). (d) Shows the stability of cell containing MoSe₂ CE.

3.3 Use of MoSe₂ NSs as CEs in DSSCs

The CE in DSSCs acts as a catalyst that collects the electrons from the external circuit and transfers these electrons into the electrolyte to recycle the redox species. An ideal CE possesses high electrocatalytic activity for the reduction of electrolyte, high conductivity and stability under ambient conditions [63–65]. We fabricated DSSCs using MoSe₂ NSs as the CE. This type of MoSe₂ CE has two advantages: (1) high charge carrier mobility and (2) large surface area for better contact with electrolyte facilitating a fast charge transfer process. We used the LML, NS_1 M NSs for fabrication of CE, as it possesses higher conductivity as observed from the HER studies.

In order to study the electrocatalytic activity of the NSs first we performed CV measurements in a three-electrode system.

Figure 4a shows the CV profiles using MoSe₂ and H₂PtCl₆ as CEs in the same environment. From the CV profile it is seen that both CEs have curves with two pairs of anodic peaks and two cathodic peaks. The pair of peaks at lower potential Ox₁ and Re₁ is due to the oxidation and reduction of iodide/tri-iodide according to equation (1), while the other pair at Ox₂ and Re₂ is attributed to redox reaction shown in equation (2) [66]:

Here, a similar behaviour of the curves indicates the same electrochemical behaviour of both CEs towards the electrolyte. As the CEs are mainly concerned with the reduction of I₃⁻ to 3I⁻ the peaks at Ox₁ and Re₁ are more useful to

Table 3. Photovoltaic and electrochemical parameters of the DSSCs assembled with MoSe₂ and H₂PtCl₆ CEs.

CE	J_{SC} (mA cm ⁻²)	V_{OC} (volts)	FF	Efficiency (%)	R_S (Ω)	R_{CT} (Ω)	E_{PP} (mV)
H ₂ PtCl ₆	17.05	0.75	0.63	7.94	16.55	2.65	400
MoSe ₂	16.18	0.74	0.60	7.20	16.97	3.94	410

understand the existing catalytic process [67]. The peak current density and peak to peak separation (E_{PP}) value are considered as two important parameters to determine the catalytic performances of different CEs [10,68]. E_{PP} values elucidate redox reaction kinetics at the CEs [68]. Values of the cathodic and anodic peak current densities for MoSe₂ and H₂PtCl₆ at Ox 1 and Re 1 are very similar indicating that both the CEs are suitable to reduce the electrolyte. The E_{PP} value for 1 ML MoSe₂ is 410 mV and for H₂PtCl₆ is 400 mV indicating almost identical catalytic activity of the two CEs.

To further evaluate the catalytic activity of MoSe₂ NSs, EIS measurements were performed in symmetrical cell configuration with two identical CEs (CE/electrolyte/CE). From EIS measurements in figure 4b we obtained two types of resistances: R_S i.e., the ohmic series resistance of the CE and R_{CT} i.e., the charge transfer resistance at the electrolyte/electrode interface. R_S value is composed of the resistance of the CE material, the resistance of FTO and contact resistance. The slightly higher R_S value should be due to the higher resistance of MoSe₂ NS. The R_{CT} value of MoSe₂ NS-based cell is higher as compared to the Pt-based cell, which indicates that MoSe₂ has slightly smaller catalytic activity to reduce I_3^- as compared to usual Pt-based cell.

The photocurrent density–voltage (J – V) curves with MoSe₂ and H₂PtCl₆ CEs are shown in figure 4c and the photovoltaic performance parameters are tabulated in table 3 for the champion solar cell. Detailed photovoltaic parameters of four individual devices are given in supplementary table S2. In our present investigation, photoanodes were the same in all the devices, so the difference in device performance is due to the presence of different CEs. Under the same environmental conditions, the DSSC with MoSe₂ and Pt CE shows PCEs of 7.20 and 7.94%, respectively as shown in table 2. The first thing to note is that there is hardly any difference in the open-circuit voltage (V_{OC}) values, reason being these DSSCs have the same photoanode and the electrolyte. As V_{OC} is the potential difference between the Fermi energy level of metal oxide and the redox potential [69], the small difference of V_{OC} arises from the change in the redox potential of the electrolyte in the presence of different CEs. The short circuit current density (J_{SC}) of MoSe₂ CEs are comparable with Pt CEs. Generally, the photocurrent of DSSC is affected by electrical conductivity, electrocatalytic activity and electrolyte diffusion of CEs [70]. CV measurement showed that MoSe₂ NSs have high catalytic activity, much-like Pt, which is advantageous to produce high photocurrents [67]. Also, being a 2D mesoporous material, electrolyte easily diffuses

into the MoSe₂ NSs. The slightly less J_{SC} value may be due to the higher series resistance as shown in EIS measurement. In MoSe₂ we obtained 60% fill factor (FF) whereas in Pt 63% was achieved. Due to 2D structure, MoSe₂ has the ability to shuttle the electrons across the network [71], resulting in a reasonably high FF. In a few reports, where CEs have been fabricated in MoSe₂/Mo configuration i.e., in the first step Mo films were DC-sputtered on soda-lime glass followed by selenization at a high temperature, the reported FFs are even higher than those obtained using Pt CE and as high as 72% due to the good conductivity of Mo [10,11]. We fabricated CEs through a very simple way of drop-casting the materials onto FTO obtaining 60% FF, very close to that achieved with Pt. This lower FF compared to the MoSe₂/Mo devices is a result of higher R_S and R_{CT} values as observed in EIS measurement shown in figure 4b. At the time of CEs fabrication, after depositing MoSe₂ NSs on FTO, we annealed the CEs under an inert Ar atmosphere to remove the insulating ligands. Because of better contact of electrolyte and the CE, the efficiency increases from 4.27 to 7.20% and the FF improved from 43 to 60% (supplementary figure S13 and supplementary table S3). The stability of a photovoltaic device is critical for the practical application. The photovoltaic performances (I – V characteristic) of device with MoSe₂ CE were measured for 5 days under ambient conditions (supplementary figure S14), showing a drop of 20% in the PCE in ambient conditions as shown in figure 4d.

4. Conclusions

In summary, we have presented a colloidal route for the syntheses of defect-rich MoSe₂ NSs with a large number of vertically aligned edges. We have developed a synthetic route to obtain MoSe₂ NSs of two different thicknesses by varying the amount of the coordinating solvent. This needs to be worked further in order to control the thickness more precisely. These NSs show good colloidal stability and solubility in diverse range of organic solvents making them suitable for thin film-based device applications. Along with superior HER activity and stability, the present work also demonstrates the importance of thickness variation for better HER performances. MoSe₂ NSs have been employed as CEs in fabrication of DSSCs which results in PCE comparable with Pt CEs. Our fundamental findings will be of great importance to develop new kind of 2D materials for better catalytic activity as well as solar cell applications.

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