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# Shape-selective Synthesis of Sn(MoO<sub>4</sub>)<sub>2</sub> Nanomaterials for View Article Online Catalysis and Supercapacitor Applications

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#### ABSTRACT

Size and shape-selective Sn(MoO<sub>4</sub>)<sub>2</sub> nanomaterials have been synthesized for the first time using a simple hydrothermal route by the reaction of Sn(II) chloride salt with sodium molybdate in CTAB micellar media under stirring at 60 °C temperature for about three hours. Needle-like and flake-like Sn(MoO<sub>4</sub>)<sub>2</sub> nanomaterials were synthesized by optimizing CTAB to metal salt molar ratio and by controlling other reaction parameters. The eventual diameter and length of the nano needles are  $\sim 100 \pm$ 10 nm and ~ 850  $\pm$  100 nm respectively. The average diameter of the flakes is ~ 250  $\pm$  50 nm. The synthesized Sn(MoO<sub>4</sub>)<sub>2</sub> nanomaterials can be used in two potential applications, namely, catalytic reduction of nitroarenes and anodic material in electrochemical supercapacitor. From catalysis study, it was observed that  $Sn(MoO_4)_2$ nanomaterials could act as potential catalyst for the successful photochemical reduction of nitroarenes into their respective aminoarenes within a short reaction time. From supercapacitor study, it was observed that Sn(MoO<sub>4</sub>)<sub>2</sub> nanomaterials of different shapes show different specific capacitance (C<sub>s</sub>) values and the highest C<sub>s</sub> value was observed for  $Sn(MoO_4)_2$  nanomaterials having flake-like morphology. The highest C<sub>s</sub> value was observed as 109 F g<sup>-1</sup> at a scan rate of 5 mV s<sup>-1</sup> for flake-like Sn(MoO<sub>4</sub>)<sub>2</sub> nanomaterials. The capacitor shows an excellent long cycle life along with 70% retention of C<sub>s</sub> value even after 4000 consecutive times of cycling at a current density of 8 mAcm<sup>-2</sup>. Other than the application in catalysis and supercapacitor, the synthesized nanomaterials can find further application in photoluminescence, sensor and other energy related devices.

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#### Introduction

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In the past few years, synthesis of one-dimensional (1-D) nanomaterials, namely, nanoneedles, nanowires, nanoribbons, nanotubes have attracted great attention because of their distinct electronic, spectroscopic and chemical properties that appears due to their small size and higher surface to volume ratio.<sup>1-4</sup> 1-D nanomaterials of metals, metal oxides, metal sulphides and semi-conductors have been synthesized utilizing various synthetic routes. Different synthetic routes such as wet-chemical process, microwave heating, vapour-phase, template method or vapour-liquid-solid method have been employed for their synthesis. The solid and vapour phase synthesis was disadvantageous as opposed to liquid phase in terms of size and shape of particles, processes being expensive, difficulty of producing uniform shapes and requires well sophisticated instruments which makes them unsuitable for large scale industrial applications. The solution phase synthesis found advantages in terms of low reaction temperature, low cost of instruments, convenience of handling, ease of procedural control and being comparatively easy to generate uniform size and shaped particles which makes them very promising for large scale material synthesis. Size and shape controlled synthesis of different metals such as Au,<sup>5</sup> Ag,<sup>6</sup> Pd,<sup>7</sup> Pt<sup>8</sup> have been reported utilizing wetchemical process. Shape-selective ZnS<sup>9</sup> and CdS<sup>10</sup> nanomaterials with various morphologies can be synthesized by using hydrothermal route. Shape-selective cobalt-oxide nanomaterials can be synthesized utilizing a simple microwave heating process.<sup>11</sup> Careful literature survey reveals that the synthesis of mono-metallic and bi-metallic nanomaterials of noble metals has been studied extensively while the study on ternary metal oxides is scarce due to difficulties in attaining compositional and structural control of ternary and quaternary compounds. So it is very important for the synthesis of ternary metal oxide nanostructures with controlled size and shape to utilize a simple route which might be found beneficial from fundamental and technological view points. Among the different ternary metal oxides, metal tungstates and metal molybdates which have large bivalent cations (ionic radius > 0.99 Å) exist in the form of Scheelite structure where the molybdenum and tungsten atom adopts a tetrahedral coordination.<sup>12</sup> Moreover; they have found potential applications in catalysis, magnetic studies and energy related fields. When tungstates or molybdates have smaller bivalent cations (ionic radius < 0.77 Å), they belongs to Wolframite structure where tungsten or molybdenum atom adopts an overall six fold coordination.<sup>13</sup>

Most of the previous reports for synthesis of ternary metal molybdates require high temperature, harsh reaction conditions and high reaction temperature, finally, the reaction

ends up with inhomogeneous particles with undesirable morphology. So it is pessential and the second s synthesize the metal molybdate materials by altering to an easy route and simultaneously obtain desirable morphologies at nanoscale dimensions. Among the ternary metal molybdates, there are plenty of reports originates from metals like Co,<sup>14</sup> Ni,<sup>14</sup> Mn,<sup>14</sup> and Ca<sup>15</sup> but the report on tin-molybdates having formula Sn(MoO<sub>4</sub>)<sub>2</sub> is scarce. Wang et al. synthesized size and shape-controlled calcium molybdates by utilizing a simple wet-chemical route.<sup>16</sup> Xiao et al. synthesized Ni and Co molybdates using hydrothermal method.<sup>17</sup> In general Ni, or Co molybdates can be seen as the product of NiO or CoO with MoO<sub>3</sub>. Under atmospheric condition, Ni or Co molybdates exists in three basic forms. Low temperature α-AMoO<sub>4</sub>, high temperature  $\beta$ -AMoO<sub>4</sub>, or high pressure AMoO<sub>4</sub>-II where A =Ni or Co. The difference of  $\alpha$ and  $\beta$  phase is the coordination of Mo<sup>6+</sup> ions either octahedral or tetrahedral geometry. Ding et al. synthesized phase-controlled metal molybdates hydrate MMoO<sub>4</sub> nH<sub>2</sub>O (M = Co, Ni and Mn) using hydrothermal process at high temperature.<sup>14</sup> Mai et al. prepared hierarchical MnMoO<sub>4</sub>/CoMoO<sub>4</sub> hetero-structure nanowires and studied their electrochemical properties.<sup>18</sup> Rullen et al. prepared transition metal (Ni, Mn, Co) molybdates using a poly-zwitterionic matrix at high temperature.<sup>19</sup> Martos et al. prepared  $Sn_{1,x}Mo_xO_2$  mixed oxides of low crystallinity by mechanical milling of the starting elements in an air atmosphere at room temperature and studied their application in lithium batteries.<sup>20</sup> Recently, Turgut et al. prepared Mo doped SnO<sub>2</sub> thin films using spray pyrolysis route.<sup>21</sup> Martos et al. prepared cation deficient  $Mo_ySn_xO_2$  oxides as anodes for lithium ion batteries.<sup>22</sup> Lee et al. studied the lithium ion insertion in molybdenum oxide nanoparticles.<sup>23</sup> Very recently, Guo et al. studied the formation of Mo-Sn oxide cage-bell hybrid nanoparticle aggregate by solvothermal alcoholysis strategy and employ them as anode material for lithium ion batteries.<sup>24</sup> There are few other studies has been done in Mo doping on SnO<sub>2</sub> thin films.<sup>25-27</sup>

The metal molybdates or tungstates have been found potential applications in different catalytic reaction, batteries and supercapacitors as they exhibits the desirable properties of high power density, fast charging, excellent cyclic stability, small size and low mass that makes them a promising candidate for next generation power devices.<sup>14,18,19,28-30</sup> In complementary of batteries or fuel cells, supercapacitor can be used in many important applications such as power back-up, pace makers, air bags or in electrical vehicles. So it is important to study the supercapacitor property of the ternary metal molybdates at high current densities by preparing controlled morphology with large surface areas. To the best of our knowledge, there is no study, for the shape-selective formation of  $Sn(MoO_4)_2$  nanomaterial and their potential application in catalysis and electrochemical supercapacitor studies.

In this article, we demonstrated for the first time, the synthesis of size and share article Online selective Sn(MoO<sub>4</sub>)<sub>2</sub> nanomaterials using a hydrothermal route. Needle-like and flake-like  $Sn(MoO_4)_2$  nanomaterials can be synthesized by the reaction of Sn(II) chloride salt with sodium molybdate in CTAB micellar media under stirring at 60°C temperature for total three hours. The morphology of the particles can be tuned by merely optimizing CTAB to metal salt molar ratio and by controlling the other reaction parameters. The eventual diameter and lengths of the nanoneedle is~  $100 \pm 10$  nm and ~  $850 \pm 100$  nm respectively. The average diameter of the flakes is ~  $250 \pm 50$  nm. The synthesized Sn(MoO<sub>4</sub>)<sub>2</sub> nanomaterials can be used in two potential applications, such as a catalyst for the reduction of nitro arenes and as a anode material in electrochemical supercapacitor studies. From catalysis study, it was observed that  $Sn(MoO_4)_2$  nanomaterials could be a potential catalyst since for the very first time here we have used it for the successful photochemical reduction of nitroarenes into their respective amino arenes within a short reaction time. From supercapacitor study, it was observed Sn(MoO<sub>4</sub>)<sub>2</sub> nanomaterials of different shapes show different specific capacitance  $(C_s)$  values and the highest  $C_s$  value was observed by  $Sn(MoO_4)_2$  nanomaterials having flakelike morphology. The highest C<sub>s</sub> value was observed as 109 F  $g^{-1}$  at a scan rate of 5 mV s<sup>-1</sup> for flake-like Sn(MoO<sub>4</sub>)<sub>2</sub> nanomaterials. The supercapacitor shows an excellent long cycle life along with 70% retention of Cs value even after 4000 consecutive times of cycling at a current density of 8 mAcm<sup>-2</sup>. The proposed synthesis process is simple with no need of any sophisticated instruments and can be completed in a short time scale. Other than catalysis and super capacitor application, the material can be further applicable in different realms, namely, photoluminescence, sensors and other energy related applications.

#### **Experimental Section**

#### **Reagents and Instruments.**

Chemicals used in this present work were analytical reagent (AR) grade. The tin (II) chloride (SnCl<sub>2</sub>), sodium molybdate (Na<sub>2</sub>MoO<sub>4</sub>), Cetyl trimethyl ammonium bromide (CTAB, 99%) were obtained from Sigma-Aldrich and used as received. Different nitro arenes, namely, 4-Nitrophenol (4-NP), 4-Nitrostyrene (4-NS), 4-Nitroaniline (4-NA) and 2-Nitrophenol (2-NP) were procured from Sigma-Aldrich and used as received. Super P carbon, carbon black, polyvinylidene fluoride (PVDF), N-methyl-2-pyrrolidinone (NMP) and potassium hydroxide were procured from Sigma-Aldrich and used without any further purification. Nickel foam was purchased from Sigma-Aldrich. De-ionized (DI) water was used for the entire synthesis and application purposes. The shape-selective  $Sn(MoO_4)_2$ 

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nanomaterials were characterized by using several spectroscopic and microscopic techniques of the specification of the supporting Information (SI) section.

#### Size and shape controlled synthesis of Sn(MoO<sub>4</sub>)<sub>2</sub> nanomaterials.

Needle-like and flake-like  $Sn(MoO_4)_2$  nanomaterials has been synthesized by the reaction of Sn(II) chloride with sodium molybdate in CTAB micellar media under continuous stirring for ~ 3 hours at 60 °C. In a typical synthesis, 60 ml of 0.1 M sodium molybdate was mixed with 0.434 g of CTAB and stirred for 30 minutes. Then 60 ml of Sn(II) chloride (ethanolic solution) was added drop wise within 120 minutes while stirring at 60 °C. The solution color was initially light brown then dark brown and finally blackish brown at the end of the reaction. Then the solution was placed in an autoclave vessel and heated for 10 hrs at  $120^{\circ}$ C. After that it was allowed to cool at room temperature, washed and then centrifuged at 5000 rpm using water-ethanol mixture for 3-4 times to remove excess CTAB and other byproducts. Then the solid mass was dried at 80 °C. Finally, the solid mass was calcinated at different temperature of 200 °C, 300 °C, 400 °C, 500 °C and 600 °C respectively. At high CTAB concentration the synthesized products mainly form particles of needle-like morphology. Now by changing the concentration of CTAB to metal salt, other morphologies were also prepared. The concentration of all the reagents, time of reaction, particle size and shape are summarized in Table 1. The schematic formation of  $Sn(MoO_4)_2$  nanomaterials by hydrothermal route is shown in Scheme 1.

#### Preparation of sample for catalysis study.

Photochemical catalysis of nitroarenes into their corresponding aminoarenes using  $Sn(MoO_4)_2$  nanomaterials as catalyst was done. For a typical catalysis reaction, 10 ml of  $10^{-3}$  M nitro arene (4-NP, 4-NS, 4-NA and 4-NBA) in acetonitrile was taken in a clean 15 ml glass vial and 50 mg of  $Sn(MoO_4)_2$  catalyst was added into it. The mixture was kept in front of UV light and irradiated. The successive reduction of nitroarenes was monitored by change in color and reduction of absorption peak in UV-Vis spectrum. The kinetics of photochemical reduction was monitored using UV-Vis spectrophotometer for every 10 min of UV irradiation.

Fabrication of electrodes for electrochemical supercapacitor study.

The electrochemical studies including cyclic voltammetry (CV), galvonostatic charge actice online discharge and electrochemical impedance spectroscopy (EIS) were done at room temperature in 3 (M) KOH solution using an electrochemical work station CHI 6034C. The EIS measured at an ac voltage of 5 mV amplitude in the frequency range 0.1Hz to 100 KHz at open circuit potential. The electrochemical cell had three electrode configurations which consist of platinum foil as counter electrode, Ag/AgCl as reference electrode and a working electrode. The CV tests were done in the potential window 0-0.65 V at different scan rates varying from 5-125 mVs<sup>-1</sup>. The GCD measurements were measured at different current densities from 0.8 mAcm<sup>-2</sup> to 5 mAcm<sup>-2</sup>. The working electrode was prepared by mixing an electroactive material, carbon black, polyvinylidonedifluride (PVDF), with a ratio of 80:10:10. A small quantity of N-methyl-2-pyrrolidine (NMP) was added to prepare slurry and pressed on nickel foam and dried in vacuum for 12 hrs at 100 °C the loading of mass of electroactive material is 2-3 mg. The specific capacitances calculated from CV and GCD curves according to the following equations.<sup>31</sup>

$$C = \frac{\int I(V)dV}{vm\Delta V} \qquad (1)$$

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$$C = \frac{I\Delta t}{m\Delta V} \qquad \dots \dots \dots \dots (2)$$

Where I (A) is the current density used for charge-discharge,  $\Delta t$  is the time elapsed for the discharge cycle. m (g) is the weight of the active electrode material,  $\Delta V$  is the potential window and V is the scan rate (Vs<sup>-1</sup>).

#### Preparation of sample for various other characterizations.

The shape-selective  $Sn(MoO_4)_2$  nanomaterials were characterized using UV-Vis, TEM, FE-SEM, EDS, XRD, XPS, Raman, thermal analysis, and FT-IR studies. For UV-Vis study a liquid solution was made by sonicating the solid  $Sn(MoO_4)_2$  powder for 20 min with DI water. The samples for TEM analysis was prepared by placing a drop of the diluted  $Sn(MoO_4)_2$  NPs solution onto a carbon coated Cu grid followed by slow evaporation of solvent at ambient conditions. For EDS, XRD, XPS, Laser Raman, and FT-IR analysis, the prepared powder samples (after being annealed at 600 °C) were directly used for the measurements. For FE-SEM analysis, the samples were prepared in a similar way as

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discussed before on glass slides but only a single layer deposition was done. For TGA/DTAticle Online analysis, the as synthesized  $Sn(MoO_4)_2$  nanopowders are used for the measurement. The preparation procedure for catalysis study and the fabrication of electrodes for supercapacitor study is already described in the main text.

#### **Results and Discussion**

#### UV-Vis study.

Figure 1 shows the UV-Vis absorption spectra of the different solution mixture for the formation of shape-selective Sn(MoO<sub>4</sub>)<sub>2</sub> nanomaterials. Figure 1-A shows the UV-Vis absorption spectrum where all the spectra are taken in aqueous solution while 1-B shows the transmittance spectrum of only Sn(MoO<sub>4</sub>)<sub>2</sub> nanomaterials for two different morphology. In Figure 1-A, curve a shows the absorption spectrum of only aqueous CTAB solution which has no specific band at higher wavelength region. Curve b, Figure 1-A shows the absorption band of the ethanolic SnCl<sub>2</sub> solution which shows prominent absorption peak at 206 nm which appears due to ligand to metal charge transfer (LMCT).<sup>32</sup> Curve c, Figure 1-A shows the absorption band of only aqueous Na<sub>2</sub>MoO<sub>4</sub> solution which shows two peaks one at a wavelength of 207 nm and the other with small hump at 229 nm. These peaks appear due to LMCT as well as d-d transition.<sup>33</sup> Curve d, Figure 1-A shows the absorption spectrum of a mixture of CTAB and Na<sub>2</sub>MoO<sub>4</sub> where we can see that both the original peaks of Na<sub>2</sub>MoO<sub>4</sub> alone have been shifted which indicates the interaction or absorption of  $MoO_4^{-2}$  ions to CTAB. Now the peaks are appeared at a position of 198 nm and 230 nm respectively. Curve e, Figure 1-A shows the absorption spectrum of the mixture of CTAB, Na<sub>2</sub>MoO<sub>4</sub> and SnCl<sub>2</sub> solution where the original peaks of both Na<sub>2</sub>MoO<sub>4</sub> and SnCl<sub>2</sub> either disappeared or shifted with change in intensity indicating their interaction among them. In this case, two small humps appeared at a wavelength of 200 nm and 233 nm respectively. Now after heating the solution mixture to 60°C for ~2 hr, the solution color changed to pale or dark brown indicating the formation of Sn(MoO<sub>4</sub>)<sub>2</sub>nanomaterials. Curve f and curve g in Figure 1-A show the UV-Vis absorption band of Sn(MoO<sub>4</sub>)<sub>2</sub> nanomaterials having needle-like and flake-like morphology which show strong peak at 209 nm and a small hump at 232 nm for needle-like whereas a strong peak at 207 nm and a small hump at 230 nm appear for flake-like morphology respectively. The absorption spectrum of Sn(MoO<sub>4</sub>)<sub>2</sub> nanomaterials in solution phase has not been reported before so we are unable to compare our result with reported values. Figure 1-B shows the optical transmittance spectra of the solid Sn(MoO<sub>4</sub>)<sub>2</sub> sample for

two different morphology where curve a indicates the spectrum of needle-like morphology and curve b indicates for flake-like morphology. Here the curve is plotted as  $(\alpha E_p)^2$  versus  $E_p$  (eV) and the corresponding slope calculated from the Tauc plot which gives the band gap energy of the materials. The observed band gap of the synthesized Sn(MoO<sub>4</sub>)<sub>2</sub> nanomaterials having needle-like morphology is 3.43 eV and for flake-like morphology is 3.33eV respectively. The band gap value is found to be high in case of needle-like morphology whereas it is less in the case of flake-like morphology. In general, the band gap energy decreases with increase in particles diameter<sup>32</sup> and in our present case also we can see the diameter of the flakes are much more compared to needles, so the band gap energy is more in case of needles compared to flakes. Turgut et al. observed similar type of transmission spectrum for Mo doped SnO<sub>2</sub>thin films for their calculation of band gap energy using Tauc plots for various concentration of Mo doping in SnO<sub>2</sub> nanomaterials.<sup>21</sup>

# Field emission scanning electron microscopy (FE-SEM) and Transmission electron microscopy (TEM) analyses.

Size and morphology of the shape-selective  $Sn(MoO_4)_2$  nanomaterials are measured using field emission scanning electron microscopy (FE-SEM) and transmission electron microscopy (TEM) analyses as seen in Figure 2. In Figure 2, image A-C show the FE-SEM images of Sn(MoO<sub>4</sub>)<sub>2</sub> nanomaterials having needle-like morphology at different magnification where image D shows the high resolution TEM image of the same particles. The average diameter and the length of the needle-like particles is calculated from FE-SEM images are ~  $100 \pm 10$  nm and ~  $850 \pm 100$  nm respectively. From HR-TEM image in Figure 2-D, the lattice fringes are visible and the average distance between two lattice planes is~0.312 nm. The inset of Figure 2-D shows the corresponding selected area electron diffraction (SAED) pattern which reveals that the particles are crystalline in nature. Here we did not observe any separate individual spots rather we got ring type pattern which is due to contribution of so many particles. A similar type of SAED pattern was observed earlier in our study on NiWO<sub>4</sub> or ZnWO<sub>4</sub> nanomaterials on DNA scaffold.<sup>29,30</sup> Figure 2, image E-G show the low and high magnified FE-SEM images of the Sn(MoO<sub>4</sub>)<sub>2</sub>nanomaterials having flakelike morphology. Figure 2, E and F show the low magnified images whereas Figure 2, G shows the corresponding high magnified image. The average diameter and length of the flakes are  $\sim 250 \pm 50$  nm and  $1200 \pm 100$  nm respectively. Figure 2, image H shows the high resolution TEM image of the same flake-like particles where the lattice fringes are visible and

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the average distance between two lattice planes is ~0.316 nm and 0.27 nm for two differenticle online crystal planes. The inset of Figure 2-H shows the corresponding SAED pattern which speaks that the particles are crystalline in nature. Here also we did not observe any separate individual spots rather we got ring type pattern like before. Both in FE-SEM and TEM analyses, we can see that the particles are not fully mono-dispersed rather they are closer to each other which might be due to presence of a little quantity of surfactant associated with them as we are unable to remove by repeated centrifugation. So from the above analysis we can confirm that size and shape-selective  $Sn(MoO_4)_2nanomaterials$  can be synthesized by controlling the reaction parameters during the synthesis.

#### EDS analysis.

Figure 3 shows the energy dispersive X-ray spectroscopic (EDS) analysis of  $Sn(MoO_4)_2$  nanomaterials after annealed the sample at 600 °C. We tested both the needle-like and flake-like morphology in EDS and both gave exactly similar types of EDS spectrum which is quite expected as both were prepared in exactly the same way and the only difference is in their morphology. As representative we put here the EDS spectrum for needle-like morphology which consists of different peaks originated from the elements of Sn, Mo, O, Br, C, and N. The high intense Sn, Mo, and O peak is from the synthesized  $Sn(MoO_4)_2$  nanomaterials whereas a low intense Br peak came probably from the CTAB used as a capping agent for the stabilization of the synthesized  $Sn(MoO_4)_2$  nanomaterials. Similarly a low intense N peak is also appeared which came from the CTAB and a high intense C peak which came from the CTAB or from the black carbon tape used while fabricating the sample for FE-SEM and EDS analyses. So by analyzing the EDS spectrum we can say that  $Sn(MoO_4)_2$  nanomaterials are formed and is stabilized via the CTAB surfactant.

#### X-ray diffraction (XRD) analysis.

X-ray diffraction pattern of the  $Sn(MoO_4)_2$  nanomaterials are illustrated in Figure 4. As discussed in the Scheme 1 and experimental section, to get the crystalline morphology of the sample, we have annealed the sample at different temperatures ranging between 200-600 °C. Figure 4A shows the XRD pattern of the  $Sn(MoO_4)_2$  nanomaterials at different annealing temperature where a, b, c, d are the XRD plot of as-synthesized samples which are annealed at 200 °C, 300 °C, 400 °C and 500 °C respectively. We can see that with increase in annealing temperature the intensity of the different peaks and crystallinity is also increasing. At 100°C and 200 °C, the XRD peaks are shown as fully amorphous in nature while at 500

°C, the peaks show some crystalline nature. Figure 4B shows the XRD pattern<sub>0.1</sub>9% the from the Sn(MoO<sub>4</sub>)<sub>2</sub> nanomaterials where the sample was annealed at 600 °C, where we observed fully crystalline peaks. In Figure 4B, curve a indicates the XRD pattern for needle-like morphology while curve b indicates for flake-like morphology. In both the cases in curve a and b, the diffraction peaks originated from (020), (110), (040), (021), (130), (101), (111), (041), (060), (150), (200), (061), (002), (211), (112), (042), (171), (081), (152), (0100), (0101) planes respectively. All the diffraction peaks are matches with joint committee for powder diffraction standard (JCPDS) data file number 00-036-1240.<sup>34,35</sup> The reference peak for JCPDS card number 036-1240 is also assigned with the same Figure 4B for comparison.<sup>34</sup> A similar type of XRD pattern was observed by Safonov et al. earlier.<sup>35</sup> As there is no direct report of Sn(MoO<sub>4</sub>)<sub>2</sub> nanomaterials we compared our XRD pattern with either Mo doped SnO<sub>2</sub> or Sn-Mo based composite oxides like Mo<sub>y</sub>Sn<sub>x</sub>O<sub>2</sub> or Sn<sub>1-x</sub>Mo<sub>x</sub> O<sub>2</sub> where some of the peaks are matches with our result.<sup>20,22</sup> Moreover, from the XRD analysis we have not observed any other peaks at lower 20 region which indicates the absence of any impurity with our synthesized Sn(MoO<sub>4</sub>)<sub>2</sub> nanomaterials samples.

#### **XPS** analysis.

Figure 5 depicts the X-ray photoelectron spectroscopy (XPS) analysis of  $Sn(MoO_4)_2$ nanomaterials. As a representative we have used needle-shaped  $Sn(MoO_4)_2$  nanomaterials for the detailed XPS analysis since the other morphology such as flake-like shape also gave similar results. Figure 5A shows the XPS survey spectrum which consists of various characteristic peaks originated from Sn (3p) at 719.2 eV, O (1s) at 530.4 eV, Sn (3d) at 492.8 eV, Mo (3p) at 421.7 eV, C (1s) at 286.8 eV, Mo (3d) at 237.7 eV and Sn(4d) at 25.9 eV respectively. Figure 5B shows high resolution XPS scan of Sn (3d) where  $Sn^{2+} 3d_{3/2}$  and  $Sn^{2+}$  $3d_{5/2}$  peaks are appeared at a binding energy of 492.3 eV and 486.4 eV respectively. The Sn<sup>4+</sup>  $3d_{3/2}$  and  $Sn^{4+}$   $3d_{5/2}$  peaks are appeared at a binding energy of 494.7 eV and 487.03 eV respectively. Figure 5C shows the high resolution XPS scan for Mo (3d) peaks where Mo<sup>6+</sup>  $3d_{3/2}$  and Mo<sup>6+</sup> 3d <sub>5/2</sub> peaks are appeared at a binding energy of 236.05 eV and 232.8 eV respectively. All the high resolution peaks are fitted with peak sum and background spectra. Figure 5D shows the high resolution scan for Mo (3p) peaks where Mo  $3p_{1/2}$  and Mo  $3p_{3/2}$ peaks are appeared at a binding energy of 405.9 eV and 399.3 eV respectively. In the same spectrum N (1s) peak is also plotted which came at a binding energy of 397.8 eV. Figure 5E shows the high resolution XPS spectrum for O (1s) which appeared at a binding energy of

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530.6 eV. Figure 5F shows the high resolution XPS spectrum of C (1s) which appeared  $^{\text{Mat}Adjicle Online}_{66T00208K}$  expected binding energy of 285.09 eV. As there is no report on the XPS spectra of Sn(MoO<sub>4</sub>)<sub>2</sub> nanomaterials, we compared our result with Mo doped SnO<sub>2</sub>, Sn doped MoO<sub>3</sub>, SnO<sub>2</sub> or MoO<sub>3</sub> nanomaterials where the high resolution scan of Sn or Mo are matching nicely.<sup>20,36-38</sup>

#### Thermal stability analysis of Sn(MoO<sub>4</sub>)<sub>2</sub> nanomaterials.

Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) of assynthesized  $Sn(MoO_4)_2$  nanomaterials were carried out to investigate the thermal stability of the synthesized material at prolonged temperature ranges. The as-synthesized solid Sn(MoO<sub>4</sub>)<sub>2</sub> sample was taken and heated up to 1000 °C in air at a rate of 10 °C/minute. As before, here also we are plotting the thermal analysis curves by taking needle-like  $Sn(MoO_4)_2$ nanomaterials since other morphology (flake-like) also gave almost similar types of results. In Figure 6, curve A indicates the TGA curve and curve B indicates the DTA curve. From TGA curve we can see that the weight loss started around 100 °C and continued upto 240 °C. This weight loss is mainly due to loss of water molecule form within the sample. After 240 °C to 523 °C, there is a steep weight loss observed which might be due to removal of excess surfactant CTAB and the decomposition of the parent material. After 523 °C, the curve is straight and there is no further weight loss is observed as seen in curve A. for TGA analysis, we have started with 2.97 mg of sample and after heating up to 1000 °C, the amount of sample remaining is 1.83 mg. So the % of weight loss for the process is 38.38%. From the DTA curve, two strong exothermic peaks observed with one located at a broad temperature range 314 °C to 406 °C and another at 488 °C. The desorption peak near 100 °C is corresponding to endothermic peak and is generally attributed to the evolution of reversibly bound water molecules. The desorption takes place in between 100 °C to 300 °C where a small endotherm appeared at 240 °C which might be due to evolution of water molecule from the integral part of the Sn(MoO<sub>4</sub>)<sub>2</sub> crystal associated with water molecule. So the weight loss from TGA curve and the endothermic peaks below 300 °C in DTA curve is mainly due to evolution of water molecule reversibly bound to the hydrated crystal phases of the Sn(MoO<sub>4</sub>)<sub>2</sub> nanomaterials. Two well noticeable exothermic peaks observed from the DTA curve centred at 350 °C and 488 °C correspond to crystal phase transformation from the hydrate phase to crystalline phase. A similar type of phase transformation takes place for NiMoO<sub>4</sub>. nH<sub>2</sub>O and CoMoO<sub>4</sub>. nH<sub>2</sub>O at 340 °C and 440 °C respectively.<sup>17</sup> Another previous

#### **BET Analysis.**

The BET analysis was done to know the pore volume and the surface area of the synthesized shape-selective  $Sn(MoO_4)_2$  nanomaterials. We measured the surface area of the both morphologies (needle-like and flake-like  $Sn(MoO_4)_2$  nanomaterials) with the BET technique which was carried out at liquid nitrogen atmosphere. The Bruner-Emmer-Teller (BET) surface area for two different morphologies was observed as 6.046 m<sup>2</sup>gm<sup>-1</sup> (for needle-like) morphology and 7.218 m<sup>2</sup>gm<sup>-1</sup> (for flake-like) morphology. The corresponding pore volumes are 0.016 cc/g and 0.014 cc/g respectively. Barrett-Joyner-Halenda (BJH) analysis indicates the presence of pores with mesoporous structure along with a pore size distribution of 1.5-5 nm. Such a pore size distribution is favourable to improve the electrochemical behaviour of the flake-like  $Sn(MoO_4)_2$  nanomaterials (pore size 3.2 nm) and needle-like  $Sn(MoO_4)_2$  nanomaterials (pore size 4.8 nm) electrodes due to the unhindered diffusion and free access of electrolyte ions into the electrode matrix. With these two different morphologies, we studied their application in catalysis for the reduction of nitroarenes to amino arenes and as electrode material in electrochemical supercapacitor studies.

#### FT-IR analysis.

Figure 7 depicts the FT-IR spectral analysis of only CTAB and CTAB bound  $Sn(MoO_4)_2$  nanomaterials. A comparison of the FT-IR spectra of the pure CTAB and CTAB bound  $Sn(MoO_4)_2$  nanomaterials not only supports the presence of CTAB on the nanomaterials surface but also reveals the nature of interaction taking place between them. It was reported earlier that FT-IR spectrum of CTAB bound metal NPs strongly depends on particles size and shapes. Here in our present study, we used the needle-like  $Sn(MoO_4)_2$  nanomaterials for FT-IR analysis but other morphology is also tested and gives similar types of FT-IR spectrum (not shown here). In case of only CTAB sample (curve A), a small peak at 3649 cm<sup>-1</sup> is observed probably for –OH stretching originated from water molecule or absorbed moisture during FT-IR analysis. Another small peak observed at 3339 cm<sup>-1</sup> is due to

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N-H vibration of CTAB molecule. The N-H stretching vibration generally comes in the range of the 3330-3450 cm<sup>-1</sup>. Three other strong and sharp intense peaks are observed for only CTAB sample at 3015 cm<sup>-1</sup>, 2921 cm<sup>-1</sup> and 2849 cm<sup>-1</sup> is probably due to -C-H stretching and antistretching vibration in -CH2 group of CTAB molecule. But in case of CTAB bound  $Sn(MoO_4)_2$  sample (curve B), a broad peak observed at 3346 cm<sup>-1</sup> which shifted a bit compared to only CTAB is due to interaction of CTAB head group with the nanomaterials. The 3015 cm<sup>-1</sup> peak for only CTAB is not observed in case of CTAB bound Sn(MoO<sub>4</sub>)<sub>2</sub> sample although other two peaks 2921 cm<sup>-1</sup> and 2849 cm<sup>-1</sup> are observed in the same wavenumber region in case of CTAB-Sn(MoO<sub>4</sub>)<sub>2</sub> nanomaterials. In case of only CTAB sample there are two other small and sharp intense peaks appeared at 1400 cm<sup>-1</sup> and 1472 cm<sup>-1</sup> <sup>1</sup> which corresponds to the –C-N stretching and –OH bending mode of water molecule around the bound head group. These peaks are not at all visible in case of CTAB bound  $Sn(MoO_4)_2$ nanomaterials which clearly denotes the probable interaction among them. In case of CTAB bound Sn(MoO<sub>4</sub>)<sub>2</sub> sample, there are four intense peaks are observed at 1248 cm<sup>-1</sup>, 1392 cm<sup>-1</sup>, 1602 cm<sup>-1</sup> and 1072 cm<sup>-1</sup> which might be due to -OH bending mode of vibration, -CH<sub>2</sub> scissoring mode of vibration and -C-N stretching mode of vibration. At the lower wavenumber region below 1000 cm<sup>-1</sup>, three peaks appeared at 959 cm<sup>-1</sup>, 908 cm<sup>-1</sup> and 728  $cm^{-1}$  which are assigned to the stretching vibration of tertiary amine [RN(Me)<sub>3</sub><sup>+</sup>], -CH<sub>2</sub> rocking which are either not appeared or totally shifted in case of CTAB bound  $Sn(MoO_4)_2$ nanomaterials. Four very high and strong intense peaks are appeared in case of CTAB bound  $Sn(MoO_4)_2$  nanomaterials at lower wavenumber region at 613 cm<sup>-1</sup>, 721 cm<sup>-1</sup>, 895 cm<sup>-1</sup> and 952 cm<sup>-1</sup> respectively. The bands at 952 cm<sup>-1</sup> and 895 cm<sup>-1</sup> are attributed for the presence of Mo and are assigned to Mo-O stretching modes. Krasovec et al. reported earlier that the peak at 940 cm<sup>-1</sup> is due to Mo-O stretching with a prevalent double-bond character (Mo-O) which provides indirect evidence for the cation vacancy content of the lattice. The band at 895 cm<sup>-1</sup> is due to bridging Mo-O-Mo and Sn-O-Mo modes with randomly distributed Mo and Sn ions in octahedral connecting chains. The peak at 613 cm<sup>-1</sup> and 721 cm<sup>-1</sup> might be related to Sn-O stretching mode in Sn(MoO<sub>4</sub>)<sub>2</sub> nanomaterials. A similar type of vibration mode of Sn or Mo was reported by Wang et al. and Martos et al. earlier.<sup>16,20,22</sup> The specific FT-IR band of CTAB reported before and the bands observed in our study with corresponding band assignments are given in online SI section as Table S-1. So from the above FT-IR analysis, it is confirmed that Sn(MoO<sub>4</sub>)<sub>2</sub> nanomaterials are formed and stabilized by the CTAB molecule.

Mechanism for the formation of shape-selective Sn(MoO<sub>4</sub>)<sub>2</sub> nanomaterials.

The shape-selective  $Sn(MoO_4)_2$  nanomaterials are formed by the reaction  $9f_1Na_2Na_3$ and SnCl<sub>2</sub> in presence of CTAB under heating at 60°C for stirring and 120 °C for hydrothermal. Then we transferred the reaction mixture into autoclave and heated at 120 °C for 10 h. In our proposed reaction, the presence of CTAB is highly essential not only for the formation of desired shapes but also for the stabilization of the particles after their formation. We have seen that in our proposed reaction, in absence of CTAB and keeping all other reaction parameters fixed, Sn(MoO<sub>4</sub>)<sub>2</sub> nanomaterials are formed but with no specific shape and they have aggregated together due to absence of specific stabilizer. In our synthesis we have measured the pH of the different solution mixtures and the results are as follows: the pH of only CTAB solution (0.1M) is 5.66, pH of Na<sub>2</sub>MoO<sub>4</sub> is 7.69, pH of ethanolic SnCl<sub>2</sub> solution is 1.05, pH of a mixture of CTAB and Na<sub>2</sub>MoO<sub>4</sub> is 7.57, pH of a mixture of CTAB, Na<sub>2</sub>MoO<sub>4</sub> and SnCl<sub>2</sub> is 6.71 and the pH of Sn(MoO<sub>4</sub>)<sub>2</sub> nanomaterials for two different morphologies are 4.34 (needle-like) and 4.13 (flake-like) respectively. In our reaction,  $Na_2MoO_4$  is used as a Mo precursor which is soluble in water and having melting point 687 °C and fairly soluble (84 g/100 ml) in water. Initially, Na<sub>2</sub>MoO<sub>4</sub> reacts with cationic CTAB molecule and formed a complex. Then the complex reacts with ethanolic SnCl<sub>2</sub> solution and generate Sn(MoO<sub>4</sub>)<sub>2</sub> capped by CTAB molecule. The probable chemical reaction takes place is:

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So in the reaction, once  $Sn(MoO_4)_2$  are formed they grow on the CTAB surfactant and generate the shape-selective  $Sn(MoO_4)_2$ nanomaterials. From FT-IR analysis, we are

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confirmed that CTAB is bound with the nanomaterials surface and mainly the head group of the bound with the nanomaterials surface and mainly the head group of the bound of th the charged CTAB molecule help for the stabilization of the particles. In our earlier study, we have seen that the phosphate group of DNA molecule binds with the nanomaterials surface for their stabilization and successful generation of TiO<sub>2</sub> nanomaterials on DNA scaffold.<sup>39</sup> Similar types of binding and stabilization activity of DNA for mixed metal oxide nanomaterials like NiWO<sub>4</sub>, ZnWO<sub>4</sub> was reported recently.<sup>29,30</sup> So in our present reaction, we presume that initially  $MoQ_4^{-2}$  ions are electrostatically attached with the CTA<sup>+</sup> ions and forms a  $(MoO_4)(CTA)_2$  complex. The formation of this complex was proven by the shift of the absorption band of CTAB-Na<sub>2</sub>MoO<sub>4</sub> mixture compared to only CTAB. Now we prepared ethanolic solution of Sn(II) chloride to avoid unwanted hydrolysis in aqueous medium. Sn (II) chloride reacts with CH<sub>3</sub>-CH<sub>2</sub>-OH and formed Sn(O-CH<sub>2</sub>-CH<sub>3</sub>)<sub>4</sub>. Now, Sn(O-CH<sub>2</sub>-CH<sub>3</sub>)<sub>4</sub> is added slowly within 120 minutes with the previously formed (MoO<sub>4</sub>)(CTA)<sub>2</sub> complex under continuous stirring and generate the dark brown color Sn(MoO<sub>4</sub>)<sub>2</sub> nanomaterials. The solution color was initially light brown, then it darken and finally dark brown after completion of the reaction. In the reaction, once Sn(II) chloride is added, it generates  $Sn(MoO_4)_2$  nuclei and same time growth of the small  $Sn(MoO_4)_2$  nuclei is also started at the same time. The small  $Sn(MoO_4)_2$  nuclei subsequently grow and forms  $Sn(MoO_4)_2$  atoms and finally so many  $Sn(MoO_4)_2$  atoms aggregate together to form crystalline  $Sn(MoO_4)_2$ particles. The surfactant CTAB molecule is present in the solution and adsorbs onto the surface of these crystalline particles and slows down the growth rate of different crystal facets. From Scheme 2 we can see that when concentration of CTAB is high ~ 0.1 M, it generates Sn(MoO<sub>4</sub>)<sub>2</sub> nanomaterials having needle-like morphology while concentration of CTAB is less  $\sim 10^{-4}$  M, the process generate flake-like morphology. At a moderate CTAB concentration we have seen that process generates particles with no specific morphology (not shown here) rather they are mixture of needles and flakes together. The formation of specific shaped particles depend upon two important factors, one is the faceting tendency of the stabilizing agent and other is the rate of supply of metal (0) to the different crystallographic planes.<sup>40</sup> In our study, at a high CTAB concentration  $\sim 10^{-1}$  M, the CTAB molecule itself formed needle-shaped or worm-shaped polygonal micellar template. Murphy group reported before that high CTAB concentration results in needle-shaped micellar template and once particles grow on that template, they generate the same morphology.<sup>41-42</sup> So in our present case, higher CTAB concentration generate the needle-like morphology where we also believed that the Sn(MoO<sub>4</sub>)<sub>2</sub> have grown along the needle-shaped micellar template and

generate the needle-like Sn(MoO<sub>4</sub>)<sub>2</sub> nanomaterials. Now at low CTAB concentrations<sup>39</sup>/therrozorest initially formed Sn(MoO<sub>4</sub>)<sub>2</sub> nuclei are grow more freely as there is no restriction of their growth and finally they formed bigger sized Sn(MoO<sub>4</sub>)<sub>2</sub> flake-like nanomaterials although the detailed growth mechanism of the flake-like morphology is not fully understood yet and further study with change in solution concentration is necessary which will be focused in near future. After the formation of two different morphologies, the particles are well capped or stabilized by the CTAB molecule and remained stable for at least six months without any change in particle morphology. CTAB not only acts as a stabilizer but also kinetically control the growth rates of the various crystal faces by interacting with these faces through adsorption and desorption.<sup>43</sup> Now taking two different morphologies of Sn(MoO<sub>4</sub>)<sub>2</sub> nanomaterial, we have studied their application for the catalysis reaction for the reduction of aromatic nitroarenes in presence of UV-light and as an anode material in electrochemical supercapacitor studies as discussed below.

# Catalytic application for the photochemical reduction of the nitroarenes using $Sn(MoO_4)_2$ nanomaterials as catalyst.

The catalytic activity of non-noble Sn(MoO<sub>4</sub>)<sub>2</sub> nanomaterials were examined for some nitroarenes reduction in the presence of UV light without any reducing agents. Nitroarenes reduction in the presence of noble zero valent metal NPs are well documented. In recent years, the catalytic activity of various noble and non-noble metal NPs, namely, Au, Ag, Cu, Pd and Pt in different chemical and physical environments such as dendrimers encapsulated, polyelectrolytes supported, biological cells assisted, and so on have been explored in depth.<sup>44</sup> Besides, the catalytic activity of noble metal/metal oxide composites and metal hydroxides such as Au/ZrO<sub>2</sub>,<sup>45</sup> Pt/RGO,<sup>46</sup> β-FeO(OH),<sup>47</sup> and Ag/TiO<sub>2</sub><sup>48</sup> is also being studied intensively for the same. Though many reports for the reduction of nitroarenes are frequently found in literature, most of them employed noble metal catalysts in addition with the strong reducing agents such as borohydride. These methods cannot be made for practical large scale utilization. Moreover, the recyclability is very low in these cases due to leaching of catalysts under vigorous conditions. Hence, it is highly desired to find an alternate and greener method for the reduction of nitroarenes. There are very few reports for the reduction of nitroarenes through photocatalytic reaction. Among them, Au/ZrO<sub>2</sub>reported by Zhu et al.,<sup>45</sup> Pt/RGO reported by Nie et al.<sup>46</sup> and the work of Tada et al.<sup>47</sup> are significant ones. However, there is a report by Lauwiner et al.<sup>48</sup> for the reduction of aromatic nitro compounds by iron oxide hydroxide catalyst. Apart from this, there is no report for the reduction of nitroarenes by

photochemical methods. In our catalysis study, we pose the successful photochemical methods are a catalysis study, we pose the successful photochemical methods are as a catalysis of some nitroarenes into their respective aminoarene compounds using the synthesized  $Sn(MoO_4)_2$ nanomaterial as a catalyst for the first time. We have checked the catalytic activities of flake-like  $Sn(MoO_4)_2$  and needle-like  $Sn(MoO_4)_2$  nanomaterials for photochemical reduction of nitroarenes. Among these two, flake-like  $Sn(MoO_4)_2$  showing high rate constant compared to needle-like  $Sn(MoO_4)_2$  which is due to having slightly higher surface area as observed from BET analysis. It is important to note that we kept all the catalysis data here taking needle-like  $Sn(MoO_4)_2$  nanomaterial as catalyst and the catalysis datas taking flake-like morphology was placed in online SI part as Figure S-1 and S-2 respectively. The overall reaction scheme for nitroarene reduction reaction is given below.

$$6H^+ + 6e^-$$

 $Sn(MoO_4)_2$ ,  $hv(\lambda = 365nm)$ 

CH<sub>3</sub>CN

In the absence of catalyst the reduction reaction was occurs but at very slower rate which is not shown here. In presence of the catalyst, we successfully reduced the nitroarenes into aminoarenes at faster rate. Nitroarenes are easily dissolved in acetonitrile rather than water and acetonitrile content ~ 1% of water which is the hydrogen source for the reduction reaction. The reaction kinetics of nitroarenes catalytic reduction can be easily followed through UV-Vis spectrophotometry (Figure 8, A-D). In the case of 4-NP (Figure 8, A), the decrease in intensity value of peak at 306 nm and the increase is intensity at 224 nm were confirmed the formation of 4-AP from 4-NP via photochemical reduction. When we keep the solution for a longer time in UV irradiation, a significant decrease in the intensity at 306 nm is observed around 100 min. Similarly, we have reduced 4-NS (Figure 8, B) and 4-NA (Figure 8, C) using the same reaction conditions. In case of 4-NS, the absorption band at 310nm is gradually decreasing with increasing time of UV irradiation which denotes reduction of 4-NS and formation of 4-AS (4-aminostyrene) which is in accordance with the gradual increase in absorbance value at 225 nm. In case of 4-NA, the absorption band at 363

 $2H_2O$ 

+

nm is gradually decreasing with increasing time of UV irradiation, indicating  $4.NA^{WW}_{CCDTOO208K}$  reduced and formed 4-aminoaniline where the new peak at 229 nm is gradually increasing. For 4-nitro benzaldehyde there is almost no or very slow reduction that takes place even after 240 min (Figure 8, D). It was noticed that under these reaction conditions, [catalyst] = 50mg/10mL, concentration of  $4-NP=10^{-3}$  M in acetonitrile and UV irradiation time ~ 100 min, the yield of 4-AP was ~55%. The final concentration of all other nitroarenes including 4-NP was used  $1.13 \times 10^{-2}$  M for their respective reduction reaction. The kinetics of 4-NP, 4-NS and 4-NA reduction has been studied by monitoring the absorbance change under varying the time of UV irradiation as seen in Figure 9, A-C respectively. All the kinetic parameters are calculated from theoretical formulae and can be obtained from Beer-lambert's law,

 $A = Slope \times Concentration + Intercept$  .....(1)

 $C_u = A_u$ -Intercept /Slope .....(2)

According to the Beer-lambert's law, the theoretical conc. value can be found from equation (2) and it is used for calculating various kinetic parameters like, conversion, selectivity, turn over frequency, turn over number and rate law studies. All the above catalysis datas taking both needle-like and flake-like morphologies are tabulated in Table 2. The higher yield found in our studies were 78% for 4-NS and 55% for 4-NP with rate constant values like  $19.7 \times 10^{-3} \text{ sec}^{-1}$  (4-NS) and  $3 \times 10^{-3} \text{ sec}^{-1}$  (4-NP). The order of the reaction has been found from calibration curve which follows  $1^{\text{st}}$  order reaction for all nitroarene compounds at the same reaction conditions. Yield can be found from following equation,

Yield = Conversion × Selectivity / 100 .....(3)

Similarly, TON and TOF of the products are calculated according to literature. We have checked the various substituted nitroarenes for photochemical reduction reaction catalyzed by our  $Sn(MoO_4)_2$  nanomaterials such as 4-NP, 4-NS, 4-NA and 2-NP. In the case of 4-NP, the peak at 306 nm (due to 4-NP) was not shifted to 400 nm is due to the radical mechanism instead of quinoid mechanism using UV irradiation. Similarly, we also tried the reduction of 4-nitrobenzaldehyde under the same condition however, it is not effected even after 4 h of irradiation. Hence, we conclude that the activating groups like, NH<sub>2</sub>, OH and moderately activating group like  $-CH=CH_2$  at *para* position were responsible for the reduction of nitroarene into aminoarenes. Ramalingam et al. studied the reduction of 4-NP using NaBH<sub>4</sub>

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while the reaction is carried out in aqueous medium in presence of  $Ag@SiO_{210}NB@WagecleODIME catalyst.<sup>49</sup> In this case, the intermediate of the reaction is 4-nitrophenolate anion as monitored by UV-Vis spectrometry with the peak shifting from 306 nm to 400 nm. Gloria et al.<sup>50</sup> reported the same 4-NP reduction using Fe<sub>x</sub>Nb<sub>x</sub>Ti<sub>1-2x</sub>O<sub>2-x/2</sub> (<math>x = 0.01$ ) nanocluster as catalyst where they carried out the reaction using both NaBH<sub>4</sub> and UV irradiation. They studied the reaction both in presence and in absence of a UV irradiation. In presence of UV irradiation, the reaction is completed in 80 min but the same in absence of UV irradiation takes longer time. In both the above cases the clear mechanism is not given.<sup>49,50</sup> In our case, we also studied the same 4-NP reaction in presence of UV irradiation but in absence of any NaBH<sub>4</sub>, so we believed there is no nitrophenolate anion formed while performing the reaction. We concluded that our reduction reaction is happening from nitrophenol itself as shown in Figure 8 where we have not seen any shift in the absorption peak from 306 nm to 400 nm due to phenolate anion. The proposed reaction mechanism happening in our case is as follows:

So as a result of homolytic cleavage of water, nascent hydrogen atoms are produced which is the actual reductant that converts nitro group into amino group in our study. The reasons for the better catalytic activity of  $Sn(MoO_4)_2$ mono-metallic oxides towards nitroarenes reduction is the presence of dual metal oxide that provides the better catalytic path for reduction reaction compared to single metals. The robustness of our catalyst was further analysed by conducting the same reaction repeatedly for 7 consecutive times with same catalyst by heating the catalyst every time up to 300 °C to remove the residues of previous reaction. It was found that up to 3-4 cycles the catalytic behaviour did not decrease much although in the following cycles the time taken by the catalyst slowly increased cycle to cycle which might be due to deactivation or surface poisoning of the catalyst.

Electrochemical supercapacitor application of shape-selective Sn(MoO<sub>4</sub>)<sub>2</sub>nanomaterials.

In recent years, the depletion of traditional energy resources as well as the desire defined to obtain the energy reduce high CO<sub>2</sub> emissions associated with their use has led to significant interest in developing sustainable and clean energy products<sup>51-54</sup> such as electricity produced from windor solar-based technologies. Supercapacitors, as a new class of energy storage devices, are now attracting intensive attention<sup>52</sup> because of their ability to store energy comparable to certain types of batteries, but with the advantage of delivering the stored energy much more rapidly than batteries.<sup>54</sup> ECs fill a gap between batteries and conventional capacitors in power and energy density values. It has advantages like high power density, extended cycle life and wide assortment of applications.<sup>53,55,56</sup> However, the energy density of most of the commercial symmetric supercapacitors based on activated carbon (AC) is lower than in batteries.<sup>55</sup> Recently, metal molybdate (MMoO<sub>4</sub>, M = metal) based electrodes have attained remarkable interest in Li-ion batteries and supercapacitors due to their stable crystal structure and redox behaviour due to their accomplishable oxidation states and high electronic conductivity. Moreover, they offer many advantages such as low cost, abundant resources and eco-friendly in nature.

The electrochemical impedance spectroscopy (EIS) analysis was done to understand about the conductive performance of as-prepared electrodes. Figure 10a illustrates the EIS results and from the results it could be observed that both of the plots are exhibiting the semicircle arc at the high-frequency region followed by a straight line in the low frequency region. The interfacial charge-transfer resistance  $(R_{ct})$  occurring at the electrode/electrolyte interface and double layer capacitance  $(C_{dl})$  is can be obtained from the semi-circle arc at the highfrequency region.<sup>55</sup> The electrodes exhibits a negligible semicircle, suggesting a low charge transfer resistance and low interfacial resistance between current collector and electroactive material. In the low frequency region, the straight line of the slope of 45° represents the diffusive resistance (Warburg impedance) of the electrolyte ions in electro-active materials.<sup>57</sup> Both the electrodes were exhibiting the similar feature with a slope of 45°, indicating the more electrolyte ions diffusion to the electro-active materials. These results suggest that the better conductivity and capacitive behaviour of the as-fabricated electrode materials. Figure 10b illustrates the CV curves of the Sn(MoO<sub>4</sub>)<sub>2</sub> nanostructures with flake-like and needle-like morphologies at a scan rate of 5 mVs<sup>-1</sup>, in the voltage window 0 to 0.65 V. A pair of strong redox peaks in the CV curves is observed for both the Flake-like and Needle-like Sn(MoO<sub>4</sub>)<sub>2</sub> nanostructures indicating the fast redox reaction in Sn(MoO<sub>4</sub>)<sub>2</sub> nanostructures. The measured capacitance is mainly governed by faradaic redox mechanism, and the reaction is based on the reversible redox of  $Sn^{+2}$  to  $Sn^{+4}$ .<sup>58</sup> Here the pseudocapacitance behavior comes mainly

from the faradic redox reaction of Sn and the role of Mo is to enhance the electric and the role of Mo is to enhance the electric and the role of Mo is to enhance the electric and the role of Mo is to enhance the electric and the role of Mo is to enhance the electric and the role of Mo is to enhance the electric and the role of Mo is to enhance the electric and the role of Mo is to enhance the electric and the role of Mo is to enhance the electric and the role of Mo is to enhance the electric and the role of Mo is to enhance the electric and th conductivity of the Sn(MoO<sub>4</sub>)<sub>2</sub> materials. The redox behavior of Mo has no contribution to the measured capacitance. This is in good accordance with the Pourbiax diagram of Mo and previous reports.<sup>59</sup> When we compared flake-like with needle-like Sn(MoO<sub>4</sub>)<sub>2</sub> nanostructures, it showed an increase in current intensity which indicates that flake-like nanostructure has higher specific capacitance. From equation (1), we calculated the specific capacitance values of both flake-like and needle-like Sn(MoO<sub>4</sub>)<sub>2</sub> nanostructures which were 109 Fg<sup>-1</sup> and 96 Fg<sup>-1</sup> <sup>1</sup>at 5 mVs<sup>-1</sup> respectively. The enhanced specific capacitance of flake-like Sn(MoO<sub>4</sub>)<sub>2</sub> electrode is ascribed to their higher specific surface area which provides more number of electroactive sites for charge storage. The kinetic irreversibility in the redox process due to polarization and ohmic resistance was evident by the shift observed in the cathodic and anodic peaks while changing the scan rate from 5 to 125 mV s<sup>-1</sup> (Figure 10c and 10d) for the both flake-like and needle-like Sn(MoO<sub>4</sub>)<sub>2</sub> nanostructures at various scan rates. It could be seen that the shape of the anodic and cathodic curves of both electrodes are similar for all scan rates which indicates the good reversibility of the electrodes. Further, with the scan rate increasing, the position of the anodic and cathodic peaks is also shifted to higher and lower potentials, respectively. This phenomenon indicates that the ionic diffusion rate is not fast enough to keep pace with electronic neutralization in the redox reaction.<sup>60</sup> For comparison, the GCD curves of both both flake-like and needle-like Sn(MoO<sub>4</sub>)<sub>2</sub> nanostructures at current density of 0.8 mAcm<sup>-2</sup> are shown in Figure 11a. The voltage plateau observed from the GCD curves further confirms the pseudocapacitive nature and found good agreement with the CV peaks. Based on equation (2) the specific capacitance of two different Sn(MoO<sub>4</sub>)<sub>2</sub> electrodes was calculated to be 30 and 36F g<sup>-1</sup> for needle-like and flake-like morphology respectively at a current density of 0.8 mA cm<sup>-2</sup>. We have checked the robustness of our device at highcurrent densities such as 1, 2, 3, 4 and 5 mAcm<sup>-2</sup> and observed that the specific capacitance values are 22.9, 20, 17.3, 13.5 and 12.8 Fg<sup>-1</sup> respectively. We have compared our specific capacitance value from charge discharge curves with previous reports. As there are no reports for the supercapacitor study on Sn(MoO<sub>4</sub>)<sub>2</sub>, we compared our present result with other similar materials as summarized in Table 3.<sup>28, 30, 58,61</sup>

It can be seen that the specific capacitance of both electrodes decreases with the increase in current density. This may be due to some active material in surface becoming inaccessible for charge storage at higher current density<sup>62</sup> (Figure 11b). Long-term cyclic stability is an important parameter required for the practical applications of a supercapacitor. An endurance test based on  $Sn(MoO_4)_2$  nanostructures (flake-like and needle-like) was

conducted by GCD at 8 mAcm<sup>-2</sup> current density as shown in Figure  $11c_{DO}$  The Correct Processing measurements were repeated for 4000 cycles to test the cyclic performance of flake-like and needle-like Sn(MoO<sub>4</sub>)<sub>2</sub> electrodes which indicates a retention of ~70 % and ~ 65 % specific capacitance after 4000 cycles respectively. This clearly implies the better cycling ability of the as-prepared flake-like Sn(MoO<sub>4</sub>)<sub>2</sub> electrode than needle-like Sn(MoO<sub>4</sub>)<sub>2</sub> electrode which is due to flake-like Sn(MoO<sub>4</sub>)<sub>2</sub> having slightly higher surface area than needle-like Sn(MoO<sub>4</sub>)<sub>2</sub>. In order to get further understanding into the rate capability, electrochemical impedance spectroscopy was performed with flake-like Sn(MoO<sub>4</sub>)<sub>2</sub> electrode before and after as depicted in Figure 11d for 4000<sup>th</sup> cycles. There is not much increase in R<sub>ct</sub> value (before cycling 21.68  $\Omega$  and after cycling 28.52  $\Omega$ ) as observed which indicates the better electrochemical behaviour of our working electrode.

#### Conclusion

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In summary, we developed a new route for the synthesis of shape-selective  $Sn(MoO_4)_2$  nanomaterials by highly facile and scalable hydrothermal method.  $Sn(MoO_4)_2$  can be formed by the reaction of sodium molybdate with Sn(II)chloride in presence of CTAB molecule. Two different morphology of needle-like and flake-like are formed by changing the surfactant to metal salt molar ratio and by tuning the other reaction parameters. The eventual diameter and length of the nano-needle is ~ 100  $\pm$  10 nm and ~ 850  $\pm$  100 nm respectively whereas the average diameters of the flakes is ~  $250 \pm 50$  nm. With these two different morphologies, we studied their application for catalysis reaction and in electrochemical supercapacitor studies. Catalysis study was done for the photochemical reduction of aromatic nitroarenes to aminoarenes using Sn(MoO<sub>4</sub>)<sub>2</sub> nanomaterials as catalyst for the first time. We have tested with 4-6 different nitroarenes and the catalysis reaction was found superior in case of flake-like  $Sn(MoO_4)_2$  compared to needle-like  $Sn(MoO_4)_2$ nanomaterials. From electrochemical supercapacitor study, it was observed that  $Sn(MoO_4)_2$ nanomaterials of different shapes show different C<sub>s</sub> values and the highest C<sub>s</sub> value was observed by Sn(MoO<sub>4</sub>)<sub>2</sub> nanomaterials having flake-like morphology. The highest C<sub>s</sub> value was observed as 109 F g<sup>-1</sup> at a scan rate of 5 mV s<sup>-1</sup> for flake-like  $Sn(MoO_4)_2$  nanomaterials. Moreover, the capacitor shows an excellent long cycle life along with 70% retention of  $C_{\rm s}$ value even after 4000 consecutive times of cycling at a current density of 8 mAcm<sup>-2</sup>. The present synthesis process is simple, reproducible and does not need any sophisticated instruments for the synthesis. In future, the present process can be further extended for the

formation of other different morphologies and their potential application in photo-catal View Article Online fuel cells and lithium ion batteries.

**Supporting Information (SI) Available:** The details about instrumental techniques for characterizations and the figures related to catalysis study taking flake-like morphology are provided. The data's related to FT-IR analysis is provided in Table S-1. This material is available free of charge via the Internet at <u>http://pubs.rsc.org</u>.

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#### **Figure Captions:**

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**Figure 1.** (A) UV-Visible absorption spectra of the different solution mixtures for the formation of shape-selective  $Sn(MoO_4)_2$  nanomaterials. Curve (a) shows the absorption band of only aqueous CTAB solution; curve (b) shows the absorption band of aqueous  $SnCl_2$  solution; curve (c) shows the absorption band of aqueous  $Na_2MoO_4$  solution; curve (d) shows the absorption band of mixture of CTAB and  $Na_2MoO_4$  solution; curve (e) shows the absorption spectra of the mixture of CTAB,  $Na_2MoO_4$  and  $SnCl_2$  solution; curve (f) and curve (g) shows the absorption band of  $Sn(MoO_4)_2$  nanomaterials having needle-like and flake-like

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**Figure 2.** Field emission scanning electron microscopy (FE-SEM) and transmission electron microscopy (TEM) analysis of shape-selective  $Sn(MoO_4)_2$  nanomaterials. Image A-C shows the FE-SEM image of  $Sn(MoO_4)_2$  nanomaterial having needle-like morphology at different magnification whereas image D shows the HR-TEM image of the same particles. The inset of D shows the corresponding selected area electron diffraction (SAED) pattern. Image E-G shows the low and high magnified FE-SEM image of the  $Sn(MoO_4)_2$  nanomaterials having flake-like morphology. Image H shows the HR-TEM image of the same flake-like particles and the inset of H shows the corresponding SAED pattern.

**Figure 3.** The energy dispersive X-ray spectroscopic (EDS) analysis of  $Sn(MoO_4)_2$  nanomaterials after being annealed the sample at 600 °C.

**Figure 4.** The X-ray diffraction (XRD) pattern of the shape-selective  $Sn(MoO_4)_2$  nanomaterials. (A) XRD pattern of the  $Sn(MoO_4)_2$  nanomaterials at different annealing temperature where a, b, c, d are the as-synthesized sample annealed at 200 °C, 300 °C, 400 °C and 500 °C respectively. (B) shows the XRD pattern of the  $Sn(MoO_4)_2$  nanomaterials while the sample was annealed at 600 °C where curve a indicates the XRD pattern for needle-like morphology and curve b indicates for flake-like morphology.

**Figure 5.** X-ray photoelectron spectroscopic (XPS) analysis of shape-selective  $SnMoO_4$  nanomaterials. Figure 4 (A) shows the survey spectrum; (B) shows the high resolution scan for Sn 3d; (C) shows the high resolution scan for Mo 3d peaks; (D) shows the high resolution scan for Mo (3p) peaks; (E) shows the high resolution scan for O 1s and (F) shows the high resolution scan for C 1s XPS spectrum respectively.

**Figure 6.** Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) of assynthesized  $Sn(MoO_4)_2$  nanomaterials where curve A indicates the TGA curve and curve B indicates the DTA curve.

**Figure 7.** The Fourier-transform infrared (FT-IR) spectra of only CTAB (curve a) and CTAB bound  $Sn(MoO_4)_2$  nanomaterials.

**Figure 8.** The successive decrease in absorbance value for the reduction of nitroarenes of the successive decrease in absorbance value for the reduction of nitroarenes of the successive decrease in absorbance value for the reduction of nitroarenes of the successive decrease in absorbance value for the reduction of nitroarenes of the successive decrease in absorbance value for the reduction of nitroarenes of the successive decrease in absorbance value for the reduction of nitroarenes of the successive decrease of the successive decrease in absorbance value for the reduction of nitroarenes of the successive decrease of the successive d

**Figure 9.** In (conc.) versus time (min) plot for the determination of rate constant for catalytic reduction of nitroarenes using  $Sn(MoO_4)_2$  nanomaterials as catalyst for 4-NP (Figure 9-A), 4-NS (Figure 9-B), 4-NA (Figure 9-C) respectively.

**Figure 10.** (a) Electrochemical impedance spectroscopy (EIS) (b) cyclic voltammogram (CV) curves of needle-like and flake-like  $Sn(MoO_4)_2$  electrodes. (c) CV curves of flake-like  $Sn(MoO_4)_2$  electrodes at various scan rates. (d) CV curves of needle-like  $Sn(MoO_4)_2$  electrodes at various scan rates.

**Figure 11.** (a) Galvanostatic charge/discharge (GCD) curves of needle-like and flake-like  $Sn(MoO_4)_2$  electrodes. (b) GCD curves of flake-like  $Sn(MoO_4)_2$  electrodes at various current densities. (c) cyclic performance of flake-like and needle-like  $Sn(MoO_4)_2$  electrodes at 8 mA cm<sup>-2</sup> for 4000 cycles. (d) Electrochemical impedance spectroscopy after 4000 cycles for flake-like  $Sn(MoO_4)_2$  electrode.

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**Table 1:** The detailed final concentrations of all the reaction parameters, time of reaction, particles size, shape etc. are summarized.

**Table 2:** The data related to catalysis comparison among four different nitroarenes taking two different morphology of  $Sn(MoO_4)_2$  nanomaterials.

**Table 3:** The comparison of specific capacitance values from GCD curve for our synthesized  $Sn(MoO_4)_2$  nanomaterials with other similar materials.

Scheme 1. The schematic presentation of the overall preparation process for the formation of shape-selective  $Sn(MoO_4)_2$  nanomaterials.

Scheme 2. The formation mechanism of shape-selective  $Sn(MoO_4)_2$  nanomaterials.



Figure 1, A-B

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Figure 3





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Figure 5, A-C



Figure 5, D-F

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Figure 6



Figure 7

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Figure 9, A-C

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Figure 11, a-d

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#### Table 1

Set	Final	Final conc.	Final	Heating	Reaction	Average particles	Shape of	
No.	conc. of	of sodium	conc. of	Temp.	time	size, D = Diameter,	the	D
	СТАВ	Molybdate	Sn(II)	(°C)	(min)	L = Length	particles	
	( <b>M</b> )	solution	solution					S
		( <b>M</b> )	<b>(M)</b>					
						$D = 100 \pm 10 \text{ nm}$	Needle-	a l
1	0.01	0.05	0.05	60	155	and L ~ $850 \pm 100$	like	Z
						nm		
						$D \sim 250 \pm 50 \text{ nm and}$		<b>6</b>
2	0.0001	0.05	0.05	60	155	$L=1.2\pm100~\mu m$	Flake-like	b
								0
								5
								A
								S
				Table 2				
				i ubic 2				Ë
								5

#### Table 2

S. No	Reactan t name	UV- irradiation Time (min)		Conversion (%)		Selectivity (%)		Yield (%)		TON		TOF (h <sup>-1</sup> )		Rate constant (k)	
		F	Ν	F	N	F	N	F	Ν	F	N	F	N	F	N
1.	4-NP	40	100	45	54	100	100	45	54	21	25	32	15	$8.4 \times 10^{-3}$	3 ×10 <sup>-3</sup>
2.	4-NS	90	120	50	78	100	100	50	78	56	56	37	28	$7.5  imes 10^{-3}$	19.7 × 103
3.	4-NA	50	70	46	23	100	100	46	23	7	3	9	3	$12 \times 10^{-3}$	3.6 ×10 <sup>-3</sup>
4.	4-NBA	180	240												

Abbreviation: In this Table, 'F' stands for Flake-like and 'N' stands for Needle-like  $Sn(MoO_4)_2$  nanomaterials.

Table 3
---------

S.No	Name of the Material	Morphology	Specific capacitance	Current Density	Reference no.
1	MnMoO <sub>4</sub> /CoMoO <sub>4</sub>	Nanowire	187 Fg <sup>-1</sup>	1 Ag <sup>-1</sup>	57
2	MnWO <sub>4</sub> /DNA	Nanowires	34 Fg <sup>-1</sup>	0.5 mAcm <sup>-2</sup>	28
3	ZnWO <sub>4</sub> /DNA	Nano-chains	39 Fg <sup>-1</sup>	0.2 mAcm <sup>-2</sup>	30
4	CoMoO <sub>4</sub> /MWCNT	Nano Composites	170 Fg <sup>-1</sup>	0.1 Ag <sup>-1</sup>	59
5	Sn(MoO <sub>4</sub> ) <sub>2</sub>	Nano-flakes	36 Fg <sup>-1</sup>	0.8 mAcm <sup>-2</sup>	Present work

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Scheme 1



## **Table of Contents**

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### Shape-selective Synthesis of Sn(MoO<sub>4</sub>)<sub>2</sub> Nanomaterials for

**Catalysis and Supercapacitor Applications** 



#### ABSTRACT

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Size and shape-selective  $Sn(MoO_4)_2$  nanomaterials have been synthesized for the first time using a simple hydrothermal route by the reaction of Sn(II) chloride salt with sodium molybdate in CTAB micellar media under stirring at 60 °C temperature for total three hours. Needle-like and flake-like  $Sn(MoO_4)_2$  nanomaterials were synthesized and can be used in two potential applications, such as in photo-catalytic reduction of nitro arenes and as anodic material in electrochemical supercapacitor applications.