Fast Sonochemical Exfoliation of Hematene type Sheets and Flakes from Hematite Nanoarchitectures Shows Enhanced Photocurrent Density

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Abstract

This report demonstrates a sonochemical exfoliation strategy to form a hematene nanosheet and flakes from hematite nanopowder and thin film. The optical properties of obtained hematene sheets and flakes show unusual features that differ from that of a pristine Hematite film, which allows it to further apply for photoelectrochemical functionality enhancement. Here, we found that the ultrasonicated Hematite film with Hematene flakes shows enhanced photocurrent density than the pristine Hematite film. The increased light absorption property of the Hematene flakes due to the scattering effect helps in achieving it. The exfoliation process is further confirmed by the X-ray diffraction of the Hematene sheet where (104) plane Bragg peak is split up after the ultrasonication process. It is corroborated with a qualitative predictive mechanism for the fast exfoliation of nanosheets and flakes. Here, surface energies and hydroxylation of crystal facets are proposed to be the factor responsible for the quick exfoliation process.

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1.   Introduction

The emergence of 2D materials by exfoliation techniques finds paramount importance in the current development of new semiconductors. In this regard, both graphene and metal chalcogenides are studied and applied broadly. The first scotch tape-based exfoliation of 2D materials from carbon-based allotrope Graphite leads to the discovery of Graphene, and it pushes a new regime of materials research into tremendous applications, primarily for semiconductor devices and quantum physics study [1]. Next, the liquid-based exfoliation of layered materials provides high surface area results in enhanced optical and electrochemical properties, and it is possible to exfoliate them into nanosheets due to the weak out-of-plane bonding [2]. The chemical exfoliation of metal carbides forms 2D transition metal carbide layers known as Mxene, and it finds various applications from electromagnetic shielding to energy conversion and storage application [3]. Other 2D materials such as phosphorene, transition metal chalcogenides are also well studied for their diverse application [4 - 8]. Besides these, recently, interest rises to develop 2D metallene nanomaterials such as silicene, antimonene, germanene, stanene [9]. Within this category, the single layer of PdTe made by electrostatic doping shows polar metal characteristics and proven by first-principle calculations [10]. These materials are Van der Waals solids due to the force existing in between the interlayers in bulk material, as observed in the case of Graphene [11].

Metal oxides based 2D materials still need further research to decipher their role in various applications. Several metal oxides, such as TiO_2, WO_3, ZnO and Co_3O_4, have been rigorously studied and converted to their two-Dimensional forms in the form of layered double hydroxide and shows many different electrochemical properties [12]. A recent candidate of 2D copper (II) oxide nanosheet [13] is prepared by the surface Sulphur functionalization, which shows semiconductor-conductor transition. Besides these, Iron oxides and their analogues also possess widespread applications in the diverse fields of catalysis [14], magnetic storage media [15], gas sensing,

45 Lithium-ion batteries [16] and other biological applications [17]. Hematite (α-Fe_2O_3), an n-type

46 semiconductor, possesses excellent stability and an appropriate bandgap, making it well known for

47 solar water splitting photosynthesis application [18].   However, iron oxide-based 2D materials

48 such as layered double hydroxide, which is generally not photoactive, are used in electrocatalytic

49 hydrogen production due to the high surface area, low overpotential and fast water oxidation

50 kinetics. It shows a higher catalytic turnover process for the oxygen evolution reaction [19]. The

51 photoactive 2D exfoliated layers of the Hematite semiconductor has not been explored. With the

52 discovery of the ultrasonication method, various nanostructured materials with reasonable control

53 over size, morphology and crystallographic structure can be formed. Cavitation and Nebulization

54 are primary physical phenomena associated with the ultrasonic synthesis of nanomaterials [20].

55 Applying it for the exfoliation of the 2D single layer from metal oxides into sheets and flakes [21]

56 is an exciting area of materials development. Balan et al. reported a sonochemical route for the

57 exfoliation of 2D Hematite from geological Iron Ore, called *Hematene*. The Hematene layer forms

58 by breaking covalent bonds between the Fe-O layers of Hematite crystal by the ultrasonication

59 process [22]. They used the sheet-like layer for the TiO_2 photoelectrode sensitization to measure

60 the photocurrent density with an application toward water-splitting mediated hydrogen evolution.

61 The Hematene obtained also shows ferromagnetic order, while Hematite usually shows

62 antiferromagnetic behaviour. Hematene is a non-Van der waal material, and it shows exotic

63 magnetic properties with a magnetic moment of $4\mu_B$ per atom according to a recent DFT study

64 followed by its surface functionalization on Stanene converts Hematene into ferrimagnets [23].

65 Hematene, as a non-van der Waal 2D material, is also chemically stable in the ambient conditions

66 due to its oxygen passivation [24], and next, Hematene based heterostructure (Hematene / $BaTiO_3$)

67 is also developed to tune the magnetic properties [25]. Not only magnetism but Hematene also find

68 suitable application in the biomedical sector and associated energy research with the development

of it for the combined application of glucose sensing and electrocatalytic action followed by the development of a biofuel cell operated by the glucose [26]. For the oxygen evolution electrocatalysis study, recently defect enriched Hematene has a current density of 10 mA/cm^2 at 0.250 V overpotential [27]. The energy storage outlook of this material is also recently taken into consideration and is published elsewhere [28].

Hematene sheets are applied for solar water splitting reactions. However, the direct application of Hematene flakes on a pristine hematite photoanode for photoelectrochemical functionality enhancement is not carried out so far. The motivation of the current study is the ultrasonic treatment of Hematite film to get Hematene sheets and flakes and to understand its effect on photocurrent density enhancement to fill this gap. The next question is whether a short sonochemical period is enough to make such kinds of nanosheets? As the usual exfoliation time in the studies mentioned above, geological ores are long as the Fe-O strong bonding will not efficiently allow the exfoliation process [22]. However, exfoliation of Hematene from Hematite nanoparticle and their thin film can be an additional advantage concerning surface energies of different crystalline facts within different morphological variants of iron oxide [29]. Hence, the development of a fast exfoliation method is another motivation of the current study.

2. Methods

2.1. Materials

All chemicals used in the current study have been procured from commercial sources and possessed 97-99% purity. Ferric (III) Chloride hexahydrate (FeCl$_3$.6H$_2$O) and Urea (NH$_2$CONH$_2$) was purchased from Sigma-Aldrich. Absolute Ethanol used for washing the ochre yellow precipitate was of analytical grade and was obtained from Changshu (C.S.), while distilled water was distilled in our laboratory. For the deposition of Hematite, FTO glass slides were obtained from Ants Ceramic Limited, Mumbai, India.

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2.1.1. Synthesis of Hematite nanoparticle and thin film:

A synthetic protocol similar to previously reported literature has been employed to synthesize the Hematite thin film using water as a solvent [30, 51]. Here, 1 g of Ferric Chloride Hexahydrate and 2.2 g of Urea were mixed with distilled water in a round bottom flask and was stirred at 80° C. The resultant mixture forms an ochre yellow colour solution after 6 hours of the reaction. The solution was then centrifuged and washed with Ethanol. The residue obtained was dried at 70°C. Later, this mass was calcinated in the air at 500°C for 3 hours to get a reddish-brown colour powder, which is the characteristics colour of Hematite. FTO (Fluorine doped tin oxide) substrate was clean with isopropanol; soap water followed upon by dip-coated in the supernatant solution to obtain thin films of the same. It was then dried and further heat-treated at 500°C for 3 hours to get the Hematite film. The thickness of the hematite film is shown in Figure S3, and it is 0.95µm. The RMS roughness of the hematite film before sonication is found to be 7.6 nm. We have used the centrifugation process in the isolation of akageneite powders. We have also used the centrifuged process in the isolation and calculation of sonicated Hematene sheet yield. It is a new amendment, as described below.

2.1.2. Synthesis of Hematene Sheets and Flakes containing Hematite Films

For the synthesis of Hematene sheets, Hematite nanopowders obtained are ultrasonicated for 5 min in Ethanol in a glass vial. The obtained solution is further applied for TEM characterization to confirm the presence of Hematene. The Hematene flake is formed by the ultrasonication of as obtained Hematite film for 5 min in Ethanol. Films are taken out and characterized further with FESEM to confirm the presence of Hematene flakes.

The exfoliation yield of the process is calculated by following the protocol as described elsewhere [52]. Here, the weight of the empty centrifugation tube is first taken. Then the Hematene sheet solution is centrifuged for 10 min at a speed of 10000 rpm/hr. After this, the weight of the Hematene

116 sheet along with the tube is retaken. The difference comes out as 1 mg, which is a low exfoliation

117 yield.

118 **2.2. Characterization of obtained powder and thin films:** Hematite nanoparticle's morphology and

119 lattice imaging are studied with high-resolution transmission electron microscopy (model: Thermo

120 Scientific Talos F200S scanning/transmission electron microscope (S / TEM). The TEM sample

121 preparation was done with nanoparticle dispersion in Ethanol with an ultrasonication for 5 min

122 followed by drop cast on a TEM grid. They were then drying it to evaporate the Ethanol in an

123 Eppendorf tube. This result in Hematene sheets like morphology is further studied with the same

124 TEM model with higher resolution. The FESEM and XRD of Hematite nanoparticles are studied

125 with Field Emission Scanning Electron Microscopy (FESEM) JEOL model JSM7100F, equipped

126 with energy dispersive X-rays (EDX) spectrometer operating at 15 keV and Powder X-Ray

127 diffractometer (Rigaku, Ultima IV X-Ray Diffractometer, Cu Kα radiation). The morphology and

128 EDX mapping of the same is carried out with FESEM (same model). The optical properties of

129 Hematite nanoparticles and thin films are studied with UV-Vis spectroscopy (Shimadzu UV-1800

130 UV-Vis spectrometer). The surface topography of thin films was investigated on Atomic Force

131 Microscopy (Agilent Technologies, model 5000) in tapping mode. The phase compositions of the

132 thin films were studied on X-ray diffractometer (XRD) Rigaku, Smartlab XRay Diffractometer

133 model with CuKα radiation of wavelength 1.54 Å in the 2θ range of 5 to 80˚ in parallel beam

134 (grazing incidence) mode. The Reflectance spectra corresponding to thin films were obtained on a

135 UV-VIS-NIR/DRS instrument Perkin Elmer, Lambda 750 in the range 190-700 nm. The emission

136 spectra of thin films were procured from a spectrofluorometer (Horiba Jobin Yvon, FL-1039/40),

137 with 50 W ozone free Xe source and double Czerny Turner optics having 1200 g/mm rating blazed

138 at 500 nm. The XPS spectra were recorded by an ESCA, Kratos Analytical, Axis Supra, U.K.

139 spectrometer equipped with AlKα 600W, X-ray source. The analysis software used here is Image J

(Fiji TEM package) for HRTEM FFT, FESEM analysis, Dwyydion for AFM data analysis, Casa XPS for XPS core level data analysis.

2.2.1. Photoelectrochemical characterization. The photocurrent density of Hematite film before and after ultrasonication was measured in an Electrochemical Workstation from C.H. instruments, CHI660D Potentiostat model with a Potential range of −10 to 10 V and Current range of 250 mA. The measurement setup consists of the photoelectrochemical cell (custom built from Borosil) beaker having a 3-electrode system configuration with 1MKOH (pH = 13.6) as the electrolyte. Ag/AgCl on sat. KCl and platinum wire were used as the reference and counter electrode, respectively. A LED lamp (100mW) from Tec. Inc. USA [tec light] with embedded electronic shutter option was used as the light source to measure the photocurrent density. The transient photocurrent density is taken using the same light source using the built-in light on-off shutter option with both fast and slow interval modes.

3. Results and discussion

Before discussing Hematene sheets and flakes formation, we will first explain the force hydrolysis reaction to form hematite nanoparticles and films. Here, the forced hydrolysis is defined as a reaction of iron trichloride with water [Figure 1- I], and this yields many different morphologies. In this case, we have also used Urea, whose role is to control nanoparticles' shape. Due to an acidic bi-product (carbonic acid) formation, Urea mainly controls nanoparticle morphology, as established in a separate study. It adsorbed on the specific crystal planes of growing nanocrystals [30]. From the SEM characterization of the as-prepared Hematite powders [Figure 1- II], we found that the morphology shows a rod-like pattern, which is a characteristic of the formation of akageneite rods on top of which Hematite nanoparticle nucleates [31]. The heat treatment at 500°C results in spherical shape nanoparticles. A similar morphological transition and its growth have been reported

163 in earlier literature [32]. The mean nanoparticle size of rod-shaped particles found here is 34 nm,

164 while hematite nanoparticles are 115 nm [Figure S5]. Next, from the XRD of Hematite

165 nanoparticles, it is found that (104) Bragg planes have the maximum XRD peak intensity than that

166 of (110) plane reveals it as the most exposed crystallographic plane [33]. The XRD patterns of the

167 sample in their powder form have been illustrated in Figure 1-II C and matched well with the JCPDS

168 no. 34-1266, which is usually indexed for akageneite (β-FeOOH) phase and, upon thermal treatment

169 of it at 500°C, undergoes a phase transformation into Hematite (α-Fe$_2$O$_3$). The two prominent peaks

170 (104) and (110), indexed to the JCPDS no. 33-0664, grow from (004) and (11-2) of the Akageneite

171 XRD pattern (before calcination). [33].

3.1. Sonochemical Exfoliation of Hematene sheets and flakes

173 The sonochemical exfoliation process has been carried out for both Hematite nanoparticle powders

174 and the thin film to get Hematene sheets and flakes, as shown in Figure 1-III in a one-pot setup. We

175 called it ultrasonic or sonochemical exfoliation because we observed such nano sheet-like materials

176 after the ultrasonic preparation of nanopowder and film. On ultrasonication for 5 minutes in

177 Ethanol, hematite surface layers are exfoliated, forming both flakes for thin film and sheet-like

178 morphology for nanoparticles. While, in the regular LPE (liquid phase exfoliation) process, the

179 materials to be exfoliated is kept in the ultrasonication for more than 24 hours and results in 2D

180 layers or flakes [22, 26, 27]. In this case, exfoliation is accomplished with a short period of

181 ultrasonication though it is not ideally a 2D layer material with a thickness range of 2- 3 nm.

182 We will first discuss the HRTEM results obtained for the Hematene sheets to shed light on their

183 structural and morphological characteristics. Afterwards, we will discuss the result obtained from

184 the FESEM investigation of the Hematene flakes. Whether these materials possess any

185 characteristics for photoelectrochemical functionality, we have further studied its detailed

structural, topological, morphological, optical and surface composition investigation with advanced microscopy as well as spectroscopic and diffraction tools.

3.2. Detail atomic structure investigation of Hematene sheet with HRTEM

We have performed the HRTEM (High-resolution transmission electron microscopy) investigation of ultrasonically dispersed nanoparticles [Figure 2A] to probe the morphologies. Nanoparticles show an aggregate like feature resembling cauliflower in the first observation. Next, we have found a partially hexagonal sheet-like morphology at a 20 nm scale, which on close inspection at the higher resolution, shows the lattice structure of Hematite [Figure 2 B - E]. Comparing this morphology with the existing literature report [20], the terminology of Hematene comes from a similar lattice structure observed during the ultrasonic exfoliation of naturally available iron ores [20]. The atomic structure of the Hematene sheet formed is further investigated by lattice imaging of Hematene sheet edges, as shown in Figure 2F. Here, the interlayer spacing between two atomic planes of Hematene is 2.66 Å, corresponding to the (104) plane of Hematite crystallographic structure. The FFT (Fast Fourier Transform) of HRTEM lattice imaging results in the electron diffraction patterns of hexagonal symmetry, as shown in Figure 2G. A similar hexagonal symmetry is also observed for Hematene obtained by Balan et al. [22]. However, we do not have here direct evidence about the crystallographic projection to know the basal planes. Whereas in other studies, it is the (001) plane [22].

The indexing of diffraction spots reveal (131) planes with d - spacing value closely matched to the JCPDS pattern of Hematite with the rhombohedral crystal system. These observations indicate the crystallographic origin of Hematene nanosheet exfoliated from Hematite lattice with the ultrasonication procedure, and the formation of a free-standing 2-D Hematene sheet is well confirmed. We have made another exciting observation by looking at different edges (yellow

209 rectangular portion) of the Hematene sheet lattice fringes. Here, we have obtained a superlattice

210 arrangement of the atomic assembly for the nanocrystallites, as shown in Figure 2H. The d-spacing

211 matches well with (012) Bragg planes, and the plane at a 75° angle is (104). A closer look at it

212 reveals an evolutionary pattern of the atomic arrangement in a hexagonal order [Figure 2I]. There

213 are two types of atomic layers observed. The inward layer and outer layers are repeating in ordered

214 manners refer to the formation of a single layer Hematene sheet [22, 27].

215 Nevertheless, we strictly not confirmed it by molecular dynamic simulation as described elsewhere

216 [22], which shows a thickness of 20 Å. The FFT of the corresponding lattice fringes [Figure 2J]

217 also indicates the formation of hexagonal spots corresponding to each atom constituting the

218 Hematene crystallographic structure and repeating in a similar pattern. The FFT diffraction spot

219 corresponds to the (131) planes of Hematite. A similar atomic arrangement is observed for the

220 Hematite nanocrystal with a bitruncated dodecahedron shape [29].

221 Next, we have performed the HRTEM of nanoparticle clusters in different ROI (region of interest)

222 with the selected area electron diffraction pattern (SAED) to get further details about the atomic

223 arrangement of hematite nanocrystallites Hematene is exfoliated. The TEM of Hematite

224 nanoparticles (Figure 2 K1) again shows aggregate like features, which offer usual lattice fringes

225 (Figure 2 K2), proves its crystalline nature. The selected area diffraction pattern (SAED) of the

226 crystallites and its analysis (Figure 2 L and M) with Fiji TEM package of Image J shows ring

227 patterns, where ring numbers 4 and 9 match with Bragg planes of Hematite (202), (315)

228 respectively. The presence of a diffraction spot further confirms that the base material from which

229 Hematene is exfoliated has a Hematite crystallographic structure.

230 **3.3. How Hematene form?**

The mechanism of Hematene exfoliation and temporal control in understanding the surface energies of most exposed crystallographic planes is shown in Figure 3. Note that, to understand the same, first we have to know the surface energies of (104) planes in our finding and the naturally obtain Hematite ores which have basal planes (0001) lying along the foliation plane [34]. Followed by this, we will emphasize the hydroxylation of the Hematite surface. It takes a minute to an hour for the hydroxylation, depending on the surface reactivity of each plane. It is a well-established fact that the Hematite surface usually contains Fe atoms with an unoccupied state, acts as Lewis acids, and reacts with Lewis bases such as hydroxyl ions via the available electron pair [33]. Due to the same, hydroxyl ions adsorb on the surface of iron oxide via coordination with Fe atoms. The heat treatment removes the surface hydroxyl group and forms water molecules due to the surface condensation, and the same is desorbed later. The dehydroxylated Hematite nanoparticle on exposure to ambient temperature forms three types of coordination based on the earlier study [30] due to water vapour adsorbed by the (104) exposed facet. The hydroxylation of the Hematite surface depends on the surface energies of exposed crystal facets. For instance, the surface energy of the (104) plane of nanoparticles described here is around 2.64 J / m^2 [36], while that of (001) basal planes in the case of naturally abundant Hematite ores are 1.53 J/m^2 [37]. So, the hydroxylation time of both cases will differ and will finally affect the exfoliation step run by a secondary process such as ultrasonication and solvent interaction with metal oxide surfaces. In this case, this hydroxylation step is faster due to the more exposed (104) plane, leaving the exposed hydroxyl group, which will further react with the absolute alcohol.

Next, the metal oxide is well known for the dehydration of alcohol and beta elimination reaction, in which unsaturated organic compounds such as ethylene get produced according to the literature described elsewhere [38]. Here, the alcohol hydrogen atom intercalates to the Fe-O-Fe linkage's

oxygen, forming a hydroxyl moiety (O- H) covalent bond between two metal atoms. It takes place

on (104) crystal facets leaving stress on the planes, which will finally lead to the formation of

Hematene sheets. It is bound initially by non-van der Waal forces. Besides this, this hydroxyl

moiety acts as a knob to control the magnetoelectric coupling in ferroelectrics such as $Ca_3Mn_2O_7$.

It is also formed by hydrogen intercalation and, due to the same antiferromagnetic metal oxides,

shows ferrimagnetic properties [39]. It is also evident in the case of Hematene, which shows

ferrimagnetic behaviour, as stated above [23].

3.4. Formation of Hematene Flakes

So far, we have described the formation of a free-standing Hematene nanosheet. The free-standing

Hematene sheets are challenging to apply directly for device application. Nevertheless, to use them

as a functional material, we need a handful of systems where their influence can be observed

towards a specific functionality. In this regard, our goal is to use this type of 2D material for

photoelectrochemical water splitting applications. So, to achieve the same, as described above, we

ultrasonically transform Hematite nanoparticle film [Figure 1-III] into an exfoliated film with the

generation of flakes, which we called Hematene flakes by the 2D morphological characteristics as

observed by the FESEM. Here, Hematite film is sensitized by Hematene flakes after the

ultrasonication process. From here on, we will designate both Hematite films before and after

ultrasonication as B. S. and A. S. The homogenous solution mixture is used for thin-film coating,

as shown in Figure 1-I A, which on calcination at 500°C results in a Hematite film by following the

procedure described elsewhere [40].

3.5. FESEM and EDX investigation of Hematene flakes sensitized thin film

We have performed field emission scanning electron microscopy (FESEM) studies of Hematene flakes to observed their morphology. It is followed by a detailed compositional characteristic of the Hematene flakes to confirm the presence of Fe and O only, which composed the usual iron oxide bulk counterpart. The morphology of calcined Hematite thin films (A.S. and B.S.), before and after ultrasonication, has been studied, and their images are presented in Figures 4 A and B, respectively. The FESEM image of the B.S. [Figure 4 A] obtained by the dip-coating methodology described in our earlier study [41] shows anisotropic nanoparticles with the fusion of two nanoparticles in an elongated pattern. The A.S. morphology is shown in the FESEM image [Figure 4 B]. Here, the particle morphology remains the same but the exfoliation results in more porous like features. In B.S., particles have been uniformly deposited and possess a smooth surface, as confirmed from the FESEM image of the thin film. While upon sonication, in figure 4B, the smooth surface was converted to rough, as the particles from the film exfoliated.

Further, in Figure 4C, we have shown a FESEM image representing 2D flakes like structure formed on the top of A.S. The flakes are also deposited freely on a coverslip [Inset; Figure 4B]. The purpose is to understand that the 2D flakes like materials are originated from base Hematite nanoparticles. Next, to determine the rough estimate of Hematene sheets and flakes thickness, 3D transformed their corresponding HRTEM and FESEM images with Image J. The result obtained as shown in Figure S4 reveals that the thickness is around 20 nm for the Hematene sheet after carefully looking at the intensity scale bar of spectrum LUT images on the right side of the image. Similarly, the thickness of Hematene flakes [Figure 4 D] is found to be 200 nm.

Further, to rule out the presence of other elements or any external foreign objects such as dust particles, we have made the EDX mapping and the line scan analysis of Hematene flakes. Here, the EDX mapping [Figure 4 E] study confirms the distribution of Fe and O elements besides Sn, which mostly come from the substrate. Note that we have F- doped SnO_2 as a substrate to deposit the

Hematite film. The line scan analysis also confirms the presence of the same elements. From this observation, it is concluded that flakes like 2D materials are exfoliated due to the ultrasonication process. This structure is made of Hematene, as confirmed from the EDX mapping. It is also confirmed with the transparent nature of flakes, which shows the underneath FTO crystal. The usual Hematite SEM is devoid of this kind of morphology. The atomic % wise distribution of elements [Fe= 4%, O = 30%] confirms the stoichiometry of the Hematite. In this case, the formation of the hematite phase by XRD investigation directly confirms the α-Fe_2O_3 stoichiometry (Hematite phase) of the materials described below.

Next, we have also carried out the AFM measurement of the Hematene sheet and flakes to determine their thicknesses. However, the result obtained [Figure S1] does not reveal the image found during the TEM and FESEM investigation. To determine the thickness of corresponding hematite nanoparticles, sheets and films, we have plotted the RMS roughness of the surface for each sample. The result obtained is shown in Figure S2. For the Hematene sheet, the surface roughness decreases, while for Hematene flakes, it increases after the ultrasonication process. We have compared the FESEM of free-standing Hematene flakes (high magnification) with the one obtained on the thin film [Figure S 11] at a bulk level. Here, the surface roughness in both cases does not show any significant difference, and it appeared to be smooth on close inspection of FESEM images.

3.6. Optical and Crystallographic properties of Hematene flakes and sheets

We have measured the optical property of Hematene sheet, flakes and film before and after ultrasonication (B.S. and A.S.) to understand light absorption characteristics and electronic properties with UV-Vis spectroscopy in both liquid and solid-state conditions. It is studied by the analysis of the absorption maxima λ_{max} shifting and energy bandgap (E_g) calculation for indirect bandgap semiconductors with Tauc methodology. The understanding of Hematene flakes light

absorption property is essential to decipher its role in the photoelectrochemical properties. For the free-standing Hematene sheet, we have taken the exfoliated Hematite nanoparticle solution obtained by the ultrasonication process. For the Hematene flakes, the exfoliated particles were used for UV-Vis analysis by making an ethanol dispersion. Note that after exfoliation of thin film by ultrasonication, we have obtained reddish-brown dispersion, which we believe the presence of Hematene flakes and exfoliated nanoparticles from the film. The UV-Vis spectra of all samples, including free-standing Hematene sheet, flakes, A.S. and B.S are shown in Figure 5 A. We have observed the absorption intensity maintain its maxima 550 nm ($\lambda_{max\_}$) for both Hematene flakes and Hematene sheet. The absorption spectra of both A.S. and B.S are shifted towards a shorter wavelength $\lambda_{max} = 525$ nm.

In contrast, an additional absorption band appears at 400-450 nm in all cases, a characteristic spectral signature of the Hematite UV-Vis spectrum, where two absorption bands at 400 nm and 550 nm are typically observed [30]. Hematene flakes show the maximum absorption intensity of all cases, making them a good absorber material for photoanode development. Next, we have seen that its peak intensity decreases at 450 nm compared to the Hematene sheet, which still absorbs photons below this range. It might be due to the concentration difference of the materials understudied as the flakes like materials form diluted solution due to less density of it compared to the nanosheet. In contrast, nanosheets are easily exfoliated into Ethanol solution and develop a reasonably concentrated solution. However, a detailed electronic calculation understanding is needed from the density functional theory to understand these sharp differences. It is also evident that the light absorption intensity profile in the range from 550 nm - 700 nm follows a different trend than that of the B.S. and A.S. to be discussed next. It is an impressive result considering the panchromatic light-harvesting ability of this particular Hematite based 2D material, a new finding

346 to the best of our knowledge. It can be further extended in the interaction study of free-standing

347 Hematene sheets with light-harvesting proteins and pigments in hybrid organic optoelectronics.

348 Hematene flakes obtained in the ultrasonicated film mentioned above in the photoanode

349 functionality for light-harvesting are the primary evaluation criteria. It is found that the absorbance

350 intensity is more for the A.S. than B.S. [Figure 5 A]. Whether this increase in absorbance directly

351 influences Hematene flakes, we have plotted the UV-Vis absorbance spectrum of Hematene flakes

352 with that of A.S. and B.S., followed by a differential spectrum between A.S. and B.S. [Figure 5 B]

353 to understand it further. The differential spectrum shows the exact shape of the absorption spectrum

354 as that of Hematene flakes. The shape resembles the convoluted Hematene flakes absorbance

355 spectra, confirming its formation on the pristine Hematite film after the ultrasonication.

356 Whether the size of Hematene flakes or sheet has any influence on the spectral shape, we have

357 accordingly isolated three fractions of Hematene sheet suspension and measure their UV-Vis

358 spectra. It is shown in Figure S10. From the result obtained, it is evident that the shape of the

359 absorption spectrum does not change irrespective of the isolated fractions. It is concluded that the

360 spectral shape is independent of the size of the nanosheets present in the suspension.

361 We have plotted Tauc plots, as shown in Figure 5[C, E- H], of all samples for the indirect bandgap

362 of Hematite to know the effect of optical property changes on the electronic structure. Here, it is

363 evident that the Tauc profile for both Hematene sheet and flakes deviating from the standard pattern

364 of Tauc plots for B.S. and A.S. From here, it reveals that the energy bandgap (E_g) of (Hematene

365 sheet= 2.6 eV & flakes = 2.4 eV) significantly differs from that of pristine Hematite. In comparison,

366 Hematene flakes sensitized film (A.S.) shows the usual band gap value of 2.1 eV. The Hematite has

367 an indirect phonon-assisted bandgap transition value of 1.9-2.2 eV [42]. The associated shift in

368 bandgap energy is attributed to the blue shift of the small Hematene nanostructures. Hematene

369 formation results in the rise of the conduction band and the lowering of the valance band, thereby

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resulting in a broader band gap value and blue shift of the absorption edge [43]. The same result agrees with the band gap value of the Hematene obtained by the ultrasonication of natural Hematite ores [22].

Next, we have presented the photoluminescence spectrum, as shown in Figure 5D. Here, on excitation with 320 nm wavelength, we have observed the emission spectra at 640 nm. Hematite film A.S. and B.S. indicate that the emission peak shows a doublet pattern while the Hematene sheet shows singlet. The size of the iron oxide nanoparticle controls the changes in peak shape, a common observation found in the X-ray emission spectra [44].

The scattering contribution and its quantitative analysis are also understood here to consider the scattering contribution to optical properties. It is carried out by measuring the diffuse reflectance spectrum of Hematite Film B.S. and A.S., followed by the Hematene sheet. Here we have applied the Kubelka -Munk function to the diffuse reflectance spectrum with the following equation:

$$f(R) = \frac{(1-R)^2}{2R} = k/s$$

R is the diffuse reflectance of the layer relative to a standard such as magnesium oxide, k is the molar absorption coefficient, and s is the scattering coefficient of the sample. The diffuse reflectance spectra of all samples are shown in figure 6 A. We have observed a similar type of diffuse reflectance pattern for both Hematite film A.S. and Hematene sheet while Hematite film B.S. shows high reflectance till 600 nm, afterwards the reflectance lowers to 400 nm. To understand the same, we have plotted the scattering coefficient (s) and found that it varies significantly for pristine Hematite film, but for Hematite film A.S. and Hematene sheet, the pattern looks almost the same [Figure 6B]. It further confirms that the morphology of the Hematene sheet and flakes are the same as the scattering contribution, which is almost similar for both cases, whether film or dispersion. For pristine hematite film, the scattering gets higher from 550 nm onwards. Hence the

absorbance changes due to different scattering coefficients for all samples. It is also found that the scattering and absorption coefficients of Hematite changes for morphology and size of the nanoparticle [30].

Our previous study [40] shows that the forced hydrolysis of iron chloride salts in the presence of Urea always results in maximum peak intensity for (104) Bragg planes, as confirmed by XRD. Here, we have studied the detailed crystallographic properties of the Hematene flakes. We have carried out the thin film XRD investigation of all three materials such as Hematene sheet, hematite film B.S. and hematite film A.S. As shown in figure 6 C, we found that all the Bragg diffraction peak shows the typical crystallographic structure of Hematite according to the JCPDS pattern. The diffracted intensity of (110) plane decreases after the ultrasonication process for the Hematite Film A.S. Next, on expanding the (104) and (110) peak [Figure 6D], it is evident that a new peak splitting has been observed for (104) plane in case of Hematite film A.S. The (104) peak intensity after the ultrasonication process decreases while a new peak appeared at 0.6˚ from the original Bragg angle. It further signifies the hydroxyl ion intercalation along the (104) peak described in the mechanism [Figure 3]. A similar type of peak splitting is observed in the in-situ X-ray diffraction pattern of chloroaluminate ion intercalation in Aluminium batteries [45].

3.7. Surface properties of Hematene flakes and sheet from XPS study (X-Ray photoelectron spectroscopy)

The XPS (X-Ray photoelectron spectroscopy) is performed for hematite nanoparticle film obtained from the heat treatment of rod-shaped particle, the hematite film A.S. and Hematene sheet (dispersion) followed by a control measurement of substrate FTO (Fluorine doped tin oxide) on which hematite film is deposited. The survey scan of all samples is shown in Figure S6. The composition shows the variation in atomic ratio both before and after ultrasonication.

The O1s core level spectrum of all samples is shown in Figure 7 A. The first peak at 529 eV comes from the hematite lattice, while a second peak at 532 eV is considered a defect peak, which is usual of Hematene electronic structure as mentioned elsewhere [22]. The oxygen 1s core level scan of FTO reveals a peak at around 531.70 eV [46], and this peak deviates itself from the defect mediated peak. The Fe2p core level scan of hematite thin film B.S. and A.S. is shown in Figure 7B. Here, the change in the oxidation state has not been observed after the ultrasonication process. Next, we have fitted the oxygen 1s core level spectrum with multiple peaks deconvolution [Figure 7 C - F]. For both hematite films, B.S. and A.S., the lattice peak, as mentioned above, comprises O^{2-} and $O.H.^{-}$ signatures followed by the formation of oxygen defect signature at 532 eV. Next, it is observed that the intensity of this particular signature is more in hematite film A.S. than Hematite film B.S further confirming the formation of Hematene flakes. Next, we have deconvoluted the O1S peak from the Hematene sheet, signifying a pure defect-related peak at 532eV. Finally, fitting the O1S spectrum of FTO reveals a small spectral weight at 529 eV, pointing towards Hematite coating.

3.8. Photoelectrochemical properties of Hematene flakes sensitized thin film

We have applied Hematene flakes sensitized Hematite film for the photoelectrochemical response study due to its light absorption properties, as discussed above. We have not performed any measurement for the sheet-like Hematene materials as it is challenging to make a stable dispersion. There is a way to sensitize any photoanode materials with these Hematene materials like Graphene sensitized photoanode encountered in many studies. With this regard, Hematene coated titanium dioxide is published elsewhere as a sensitizing material [22]. Also, its application for the photoelectrochemical water splitting reaction is worth investigating due to the direct photoanode functionality of both bare Hematite and doped counterpart in terms of PEC water oxidation and matching of the valence band edge position with water oxidation potential [18]. Here, our goal is

to see any difference in the photoelectrochemical response of this Hematene flakes sensitized photoanode from that of the Hematite film. For the same, we have measured the photocurrent density of both B.S. and A.S. in 1M KOH, as shown in Fig. 8A.

It depicts a comparison between the light and dark current densities for the B.S and A.S. In all photocurrent density patterns, the usual photocurrent plateau is not observed, which mainly seen for the nanostructured Hematite photoanode. In this case, the Hematite from which Hematene flakes are exfoliated is the direct conversion of Akageneite, crystal which usually results in more resistive action, while doped Hematite already well established to show higher photocurrent density [44]. Despite not having a Plateau-like feature, the photocurrent density of film A.S is higher than that of B.S. and displayed a photocurrent density of 50 $\mu A/cm^2$. Here, the photocurrent density of bare Hematite film before sonication is very low in the 30 $\mu A/cm^2$ at 0.6 V. The slight increase in photocurrent density can be attributed to the more opening in the porosity of the photoanode materials (A.S.) due to the ultrasonication process. It is evident from the morphology discussion with the FESEM study, which shows a rougher surface for A.S. At the same time, the dark current density for A.S. is lower than that of B.S. Our earlier studies show that the Hematite films show considerable dark current density due to the presence of Fe^{2+} site, which on electrochemical oxidation result in extra electrons with a direct effect of Faradaic current density in the dark condition [41]. While in the A.S. film, as the ultrasonication process removes surface layers as exfoliated ones, the dark current density is low. The photocurrent density mentioned here is also not that high, but the ultrasonication process leads to a better photocurrent density, a new finding in this domain. We believe the direct role of Hematene flakes in the overall photocurrent density is due to the maximum absorbance shown by these flakes, followed by the A.S. film absorbance is higher than that of B.S. Besides these, Hematene also shows extra panchromatic light-harvesting above 550 nm, and the additional increase in the photocurrent density is due to the collective action

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of the same. Besides these, the IPCE (incident photon to current conversion efficiency) of Hematene coated TiO_2 photoelectrode shows increase efficiency in this region [22]. However, these ultrasonication methods will give rise to more efficient photoanodes, which are already well established. So, we keep it as the next objective for our future study with this new material.

3.8.1. A qualitative understanding of the charge transfer process from the transient photocurrent density

Does the following question arise how Hematene flakes sensitized film (A.S.) shows its photoinduced charge transfer action compared to the Hematite film? The underlying physical phenomena for the same need to be understood. Here, we have carried out the transient photocurrent density study of films (A.S. and B.S.) under light ON-OFF configuration and results are shown in Figure 8 B. If we consider the light ON part of the resultant data, the photocurrent density is considerably high for A.S. film than that of the B.S. Also, the spike spreads across both anodic and cathodic directions. The enhancement of both the anodic and cathodic spike intensity signifies bulk and excitonic surface recombination. If we carefully observe at 0.4 V [Figure 8 C], the intensity of this spike in the anodic direction is more than that of the cathodic direction.

In comparison, it is remaining the same for both cases for pristine Hematite film. If we consider the 2D Hematene nanosheet, the surface oxygen defect is validated by the XPS study as described above [Figure 7 C and D]. Also, an operando synchrotron soft x-ray absorption spectroscopy study by Braun et al. reveals that the formation of the hole for the O2p band or charge transfer band brings its maximum contribution photocurrent density at 0.4 V [47]. So, from here, we can justify that increase in the magnitude of spike formation in the anodic direction at 0.4 V is nothing but the function of the oxygen ligand present partially in 2D Hematene flakes along with the rest of oxygen ligands in the entire Hematite film after ultrasonication, which contributes to the formation of the

hole and subsequent recombination. However, the experimental finding of the same is not done yet. We here qualitatively propose a suggested physicochemical mechanism.

The photocurrent density reaches around 50 $\mu A/cm^2$ at the light - ON mode, while it relaxes back to the zero current during the light - OFF mode. The presence of a cathodic transient spike is due to the bulk electron-hole recombination [48]. It is a direct first kind of study with Hematene. Next, we have plotted the comparative limited chopped light current density profile of both films, as shown in Figure 8 D. Here, *limited* stands for the slow speed of the shutter, which is embedded in the light source. We have observed a different trend in the photocurrent relaxation phenomena for exfoliated materials (A.S.) in both anodic and cathodic directions. Here, we see that current density decayed in a delayed response. Before light–OFF mode, the photocurrent is excited for a while, forming an additional spike until it reaches equilibrium. It falls again towards the cathodic direction. Similarly, during the light-ON step, the photocurrent rises with a delayed intermediate response in the cathodic regime before reaching the maximum magnitude in the anodic region. If we compare the same with the film without ultrasonication (B.S.), we can also see a trend in the transient photocurrent density.

The basic understanding and observation of a transient photocurrent spike need to be understood regarding the photoinduced charge transfer effect. As described elsewhere [49, 50], the photocurrent transient spike reaches a peak in the upward direction followed upon by decay to the steady-state when light is turned on. After 10 seconds of photon illumination, if the light is turned off, the zero current occurs and re-spiking when the light is turned back on again. The physical significance of the falling photocurrent density is the conduction band electrons rapid removal into the bulk, and spike formation occurs due to the recombination of electron holes by the surface state. The sub- spike feature we discussed above is assigned as a sub-surface state generated peak. Now coming back to our discussion about the transient photocurrent characteristic of A.S and B.S

Hematite film, we have noticed that the light chopping with faster interval (figure 8 B) does not show this sub spike feature. Only when the light chopping speed is slow with longer intervals, this specific feature is observed. The extra spike points towards slow removal of electrons, and in other words, it shows back-reaction: the recombination of electrons and holes with sub-surface states as a first glimpse, while a direct confirmation with different spectroscopic techniques is not available. Finally, the extra spike is absent in other Hematite nanostructured films synthesized by an oleic acid route [40]. It is evident when we compare the transient photocurrent density [Figure 8 E] of a nano octahedron dispersed Hematite film [Figure 8 F] with hematite film obtained by the water-mediated route. The precursor chemistry leads to two different Hematite films with changes in the surface electronic and atomic structure, as revealed by the extra spike-like feature. However, to get detailed insight into the initial claim of surface and atomic structure changes, we need to do synchrotron XRD and XAS, which is out of scope for the time being out of scope COVID-19 constraint. Our goal is to report here only the formation of Hematene sheets and flakes with their photoelectrochemical properties. Also, the Hematene formation for oleic acid-derived Hematite nano octahedron has not been studied. However, it will be the subject of further study.

4. Conclusions

The sonochemical treatment of hematite film leads to the formation of Hematene nanosheet and flakes as supported by the detailed HRTEM investigation with the observation of both inward and outward layers arrangement of atoms nanocrystallites. A thorough atomic structure understanding with the d-spacing calculation reveals that the Hematene originated from the Hematite as it also shows the crystallographically more exposed (104) plane. Based on the same, its formation mechanism is proposed and predictive that hydroxylation is faster due to more reactive surface due to the high surface energy of (104) planes. The XPS study validates the usual oxygen defect signature of Hematene at 532 eV, which further confirms the enhanced photoelectrochemical

535 functionality of the Hematite film after ultrasonication treatment and the formation of the sub-
536 surface state. The photocurrent density increased up to $50\mu A/cm^2$ for Hematene flakes sensitized
537 Hematite photoanode due to its enhanced light-harvesting action, while the pristine shows current
538 density up to $30\mu A/cm^2$. Though it is not a fantastic performance, the future outlook of such
539 sonochemical modification and making of Hematene flakes on champion photoanode will boost its
540 efficiency further for the solar water-splitting process.

541 **Supporting Information**

542 Electronic Supplementary Information (ESI) is available: AFM data statistics, FESEM images, Size
543 distribution, XPS survey scan, Fe2p core level scan and fitted spectrum, UV-vis spectrum of Hematene
544 extracts.

545 **Conflicts of interest**

546 There are no conflicts to declare.

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