



Fe₃O₄ nano assembly embedded in 2D-crumpled porous carbon sheets for high energy density supercapacitor

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ABSTRACT

Due to the copious development of industries and depletion of fossil fuels generate deteriorating environmental pollution and appalling economic crisis. Thus, there are increasing unmet for developing well-defined nano-structures to mitigate energy and environmental issues. Herein, we firstly report a unique concerted method to convert agro bio-waste into an economical wealth material. By the inspiration of nature, we selected a waste 2D garlic husk (*Allium sativum*) as a torchbearer to make a unique material. The garlic extract was applied for the synthesis of Fe₃O₄ NAs@2D-CCS composite nano-assemblies (NAs). Interestingly, the small-sized Fe₃O₄ nano-crystals (<20 nm) underwent nucleation in the presence of biogenic 2D-CCS and formed a pomegranate like a cluster (200 nm) forming a conglomerate on porous carbon layers. Most importantly, no secondary waste was generated in this work. This Fe₃O₄ NAs@2D-CCS composite affords high specific capacitance of 820F g⁻¹ at a current density of 0.5 A g⁻¹, which is nearly 5 to 3 times higher than pristine Fe₃O₄ NPs (<20 nm) electrode with an outstanding power density (3500–8000 W kg⁻¹) and specific energy density (115.5 to 65.9 Wh Kg⁻¹), which is superior among most of all reported iron oxide and graphitic carbon composites. This simple work stimulates a new door for the generation of waste to well-defined nanostructure materials for energy, catalysis, and environmental applications.

1. Introduction

Since ancient times, onwards carbon-based materials play a copious role in almost every aspect of human civilization, including the energy field [1,2]. Researchers has been developed a lot of new carbon allotropes, like fullerene, graphene, carbon nanotubes, and porous carbon, etc [3]. These carbon nanomaterials exhibit astonishing role in the various fields such as energy storage, catalyst support, gas separation, fuel cells and water purification etc [4–8]. The family of carbon materials are classified based on various dimensions like zero-dimension (0D) spherical in shape (carbon dots, nano-onions and buckyballs), one-dimension (1D) fibers in shape (nanotubes, nanowires, nanoribbons and nanopillars), two-dimension (2D) sheet-like shape (graphene, graphyne and gC₃N₄) and three-dimension (3D) solids (graphene aerogel, nanofoams and honeycomb) [9–11]. Moreover, by considering the fascinating properties like high surface area conjugated hexagonal network, chemically more reactive edge sites, durable mechanical

strength, open van der Waals gaps, and unique flexible atomic dimensions allow 2D carbon materials are a key component for energy storage and production [12].

Owing to the rapid development of many cities urge huge consumption of fossil fuel, the development of efficient energy storage and eco-friendly materials has great importance [13]. Researchers are developing various energy storage devices like batteries, fuel cells, electrolytic capacitors, and supercapacitors [14]. In recent years, significant attention has been paid to supercapacitors because of the fast charge–discharge rate, high specific power/energy density, long cycle stability, excellent reversibility, lightweight, and fewer maintenance costs compared to common batteries, capacitors, and fuel cells [15,16]. Based on the storage mechanism, supercapacitors are classified into electrochemical double-layer capacitors and pseudocapacitors. The charge is stored by electrostatically (non-Faradaic) in EDLCs because of the reversible ion adsorption at the electrode–electrolyte interface [17]. The carbon-based allotropes, including active carbon, carbon aerogels,

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carbon nanotubes, and graphene, can act as electrode materials for EDLCs. Among these carbon materials, 2D graphene is used as the most extensive electrode material for EDLCs [18]. Beside the advantages like high mechanical strength, 2D structure, and excellent electronic conductivity, the 2D graphene has several limitations such as high cost, low specific capacitance, and complicated synthesis procedure [19]. In addition, the 2D graphene sheets tend to aggregate due to potent van der Waals attraction and to form stacks, which reduces the active surface area leading to lower ionic and electronic conductivity of the materials [20]. Based on the surface corrugation of the 2D carbon materials, the properties can be altered. The 2D carbon materials also display surface corrugations, including wrinkles, crumples, and ripples [21]. Recently Luo et al. reported that crumple 2D graphene sheets have astonishing properties including resisting aggregation, compression, more open structure, and high specific surface area than flat carbon sheets [22].

In contrast to EDLCs, pseudocapacitors store the charge by electrochemically during the transfer of charge between electrode and electrolyte via redox faradic reaction, which allows achieving excellent specific capacitance and high energy densities [23]. Generally, owing to multiple valence states metal oxides like Co_3O_4 , Fe_3O_4 , ZnO , MnO_2 , NiO , RuO_2 , V_2O_5 , and WO_3 , etc., and conducting polymers (PANI, PPY, and PEDOT) exhibit pseudocapacitor behavior [24–31]. Of these, transition metal-based pseudocapacitor electrode materials, the most abundant, cost-effective, eco-friendly, easy synthesis, wide operating potential window, and high theoretical capacitance transition element-based electrode is Fe_3O_4 (magnetite) [32,33]. Based on these remarkable properties, Fe_3O_4 NPs have been employed in various fields like drug delivery, MRI contrast agent, water purification, catalysis and energy storage etc [34,35]. Nevertheless, poor cyclic stability during charging and discharging, crumbling rate capability and low conductance, which inadequate their practical applications [36]. EDLCs have poor specific capacitance, and pseudocapacitors have poor stability. In this juncture, to alleviate the obstacles of individual component electrodes, researches are developed binary ($\text{CNT}/\text{Fe}_3\text{O}_4$, $\text{LSG}/\text{Fe}_3\text{O}_4$, $\text{Fe}_3\text{O}_4/\text{RGO}$, $\text{Fe}_3\text{O}_4/\text{MnO}_2$, $\text{Fe}_3\text{O}_4/\text{CNF}$), ternary composite ($\text{Fe}_3\text{O}_4/\text{C}/\text{PANI}$, $\text{Fe}_3\text{O}_4/\text{PANI}/\text{MnO}_2$, $\text{Fe}_3\text{O}_4/\text{CNT}/\text{PANI}$, $\text{Fe}_2\text{O}_3/\text{RGO}/\text{Fe}_3\text{O}_4$) and quaternary composite ($\text{CNF}/\text{MWCNT}/\text{RGO}/\text{Fe}_3\text{O}_4$, $\text{h-CNF}/\text{CNS}/\text{Fe}_3\text{C}/\text{Fe}_3\text{O}_4$) materials combining the carbon precursor, polymers and metal oxide nanoparticles, which reveals distinguishing properties like excellent specific capacitance, high energy density and long cycle life [37–43]. However, most of the Fe_3O_4 NPs are embedded with graphene oxide, carbon nanotubes, and conductive polymers, which are expensive, complicated synthetic processes. At this juncture, the research on clean and renewable energy has become one of the hottest topics. The extensive literature reported that the biomass-derived active porous carbon is widely applied as electrode material [44]. Activated porous carbon illustrates multiple advantages like high specific surface area with micro to nanopore structure, abundant active sites, high conductivity, chemically stable, less corrosion and most importantly obtained from renewable natural resources [45]. Further, Fe_3O_4 NPs are synthesized by using various green (agro-extract) and organic solvents (toluene, benzyl ether) [46–48]. Besides, up to now, the Fe_3O_4 doped carbon composite materials were synthesized using individual precursors like activated carbon from biomass and composites from additional solvents [49,50]. Creating a new composite material having Fe_3O_4 NAs by using a single precursor is a great interest for future prospects. So far, to the best of our knowledge, there are no reports for the synthesis of Fe_3O_4 NAs@2D-CCS composite by using unique waste garlic husk.

In this study, a unique concerted method was developed by using waste garlic husk (*Allium sativum*) as a single precursor (solvent as well as 2D-crumpled porous carbon) for the synthesis of Fe_3O_4 NAs@2D-CCS composite. According to UN food and agriculture organization, South Korea is the 3rd place with 0.36 million tons of garlic per year [51]. The bio-inspired 2D-layered integument of garlic aroused to make biogenic active edge sites having a 2D-crumpled porous sheet (2D-CCS) [52], which is having significant advantages than the 2D graphene sheets.

Interestingly, the bare Fe_3O_4 NPs (20 nm) undergo nucleation by the 2D-crumpled network and produce a uniform Fe_3O_4 NAs with the size of 200 nm, without disturbing the 2D-crumpled porous sheet. This Fe_3O_4 NAs@2D-CCS composite affords high specific capacitance with an outstanding power density ($3500 - 8000 \text{ W kg}^{-1}$) and specific energy density (115.5 to 65.9 Wh Kg^{-1}) in a pseudocapacitor application. The simple approach may stimulate a new door for the generation of waste to well-defined nanostructures without secondary waste generation.

2. Experimental section

2.1. Materials

Waste garlic husk was collected in a local market from Seongnam, South Korea. Ferric chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) (97.0%), sodium acetate (CH_3COONa) ($\geq 99.0\%$), propylene glycol (PG) ($\geq 99.5\%$), Ethanol ($\text{C}_2\text{H}_5\text{OH}$) (99.8%) were purchased from Sigma Aldrich (Milwaukee, United States). Potassium hydroxide (95%) was purchased from Samchun chemicals (Gyeonggi-do, South Korea). All the solutions were prepared using deionized Millipore water.

2.2. Extraction of garlic husk and preparation of 2D crumpled carbon sheets (2D-CCS)

The collected garlic husk was washed thrice with deionized water to eluate the impurity particles and dried at room temperature. By using a mortar pestle, the washed husk was crushed to make a powder. 15 g of the powder was blended with 100 mL of deionized water in a 250 mL round bottom flask and refluxed for 3 h at 70°C and the color of the solution turns to pale yellow. The mixture was centrifuged and filtered with cheesecloth. The filtrate was stored at -4°C , and the reaming waste residue was dried at 100°C . Subsequently, the garlic husk powder (10 g) was immersed in 3 M KOH aqueous solution for 6 h and filtered out without washing. The collected filtrate was dried at 100°C overnight, and later the KOH activated residue husk was pyrolyzed in a tube furnace at 800°C with N_2 flow (50 cc min^{-1}) for 3 h. After that, the obtained carbonized powder (2D-CCS) was washed twice by 2 M HCl and distilled water. The pure 2D-CCS was obtained after drying at 120°C overnight.

2.3. Synthesis of Fe_3O_4 NAs@2D-CCS composite

For the synthesis of Fe_3O_4 NAs@2D-CCS composite, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (5 mmol) and CH_3COONa (50 mmol) were dissolved in garlic husk extract (36 mL) and 4 mL of PG and sonication for 10 min. Subsequently, the prepared 2D-CCS (1.00 g) was gradually added to the iron solution and sonication for 20 min, followed by vigorously stirred for 1 h at 80°C . Finally, the mixture was transferred to a Teflon-lined stainless-steel autoclave and heated at 180°C for 12 h. The composite was decanted by using an external magnetic field and washed thrice with ethanol and water. The above reaction tiny portion of PG worked as an additive to initiate the smooth reaction under high temperature. The final product was dried under vacuum oven at 130°C overnight and was stored in a glass vile until further use. A similar synthesis procedure was employed for the preparation of bare Fe_3O_4 NPs without the addition of 2D-CCS. The synthesis procedure of the Fe_3O_4 NAs@2D-CCS composite represented in Fig. 1.

2.4. Electrochemical experiments

The electrochemical properties of the electrode materials were tested in 6.0 M KOH aqueous electrolyte solution using three-electrode system at room temperature. The working electrode were prepared by mixing the active materials, acetylene black and polytetrafluoroethylene binder with the weight ratio of 90:5:5 in minor quantity of ethanol solution to make slurry, and then the mixture were fabricated onto nickel form (1

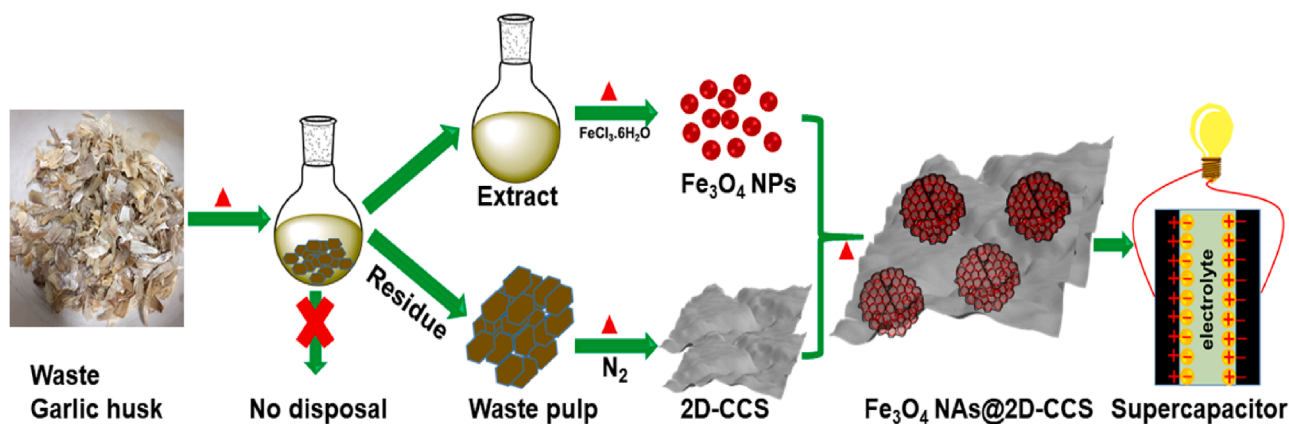


Fig. 1. Schematic illustration of the design concept of Fe_3O_4 NAs@2D-CCS composite and its supercapacitor behavior.

cm^2) current collectors. The electrodes were dried at room temperature for 24 h and then soak with 6 M KOH electrolyte before the electrochemical test. The electrochemical performance of the materials was measured by cyclic voltammetry (CV) and galvanostatic charge–discharge with electrochemical working station. A Platinum foil and Ag/AgCl were serving as a counter and reference electrodes, respectively in the three-electrode system. Furthermore, a symmetric capacitor by the Fe_3O_4 NAs@2D-CCS composite as positive electrode and negative electrode was assembled. The prepared Fe_3O_4 NAs@2D-CCS composite electrodes fitted with the separator (Whatman filter paper) and electrolyte solution (6 M KOH aqueous solutions), which were symmetrically assembled into sandwich-type cells construction (electrode/separator/electrode) with the active material loading mass of 1.5–2.0 mg. To calculate the overall performance of the device, the charge between positive and negative electrode needed to balance and the loading mass of active material can be optimized by following equation below:

$$C_m^+ \cdot \Delta V_{+} \cdot m_{+} = C_m^- \cdot \Delta V_{-} \cdot m_{-}$$

where C_m^+ and C_m^- are the specific capacitance (F/g), ΔV are the potential window (V) and m_{+} , m_{-} are the loading mass of the positive and negative electrodes, respectively.

The specific capacitance is calculated from the charge/discharge via Eq. (1):

$$C = I \Delta t / \Delta V m \quad (1)$$

where C denotes as a specific capacitance (F g^{-1}), I (mA) notified charge–discharge current, m (mg) mass of the active material within the electrode, ΔV (V), and Δt (s) is the potential range and total discharge time respectively.

2.5. Characterization

The phase purity of the bare Fe_3O_4 MNPs, 2D-CCS, and the Fe_3O_4 NAs@2D-CCS composite was analyzed by Rigaku Ultima III X-ray diffractometer equipped with a Cu sealed tube (wavelength of $\lambda = 1.54 \text{ \AA}$) with the conditions of 40 kV, 30 mA, an increment of 0.05° , and scan speed is 3 deg/min . The morphological structure and composition of the bare Fe_3O_4 NPs, 2D-CCS and Fe_3O_4 NAs@2D-CCS composite were determined by using TEM, HRTEM and SAED patterns were obtained with an accelerating voltage of 300 kV and camera constant of $28 \text{ mm \AA}$ (Tecnai G2). The STEM-EDS and HAADF-STEM were performed by JEM-2100F (FC-TEM20, JEOL). To determine the morphology of the composite in microscopic scale, a scanning electron microscope (SEM, S-4700, HITACHI, Japan) was used with an accelerating voltage of 20 kV. The morphological thickness of the 2D-CCS was analyzed by using Atomic force microscopy (AFM) with a JPK Nano Wizard II bio atomic force microscope in a contact mode. The detailed compositional and

structure studies were carried out using a Thermo Fisher Scientific (Quanta Master, Photon Technology International, Birmingham, NJ, USA) K-Alpha + X-ray photoelectron spectrometer (XPS) system equipped with 100 – 4000 eV range of motion, 180° double focusing hemispherical analyzer (Thermos scientific, Oklahoma City, OK, USA) with 128-channel detector (Thermos scientific, Oklahoma City, OK, USA), and with a monochromatic Al K α line X-ray setting (400 μm , 30 W, 12 kV). The functional groups of the materials were analyzed by using Fourier transform infrared spectra (FTIR) with a Thermo Nicolet iS50 spectrometer using a KBr pellet with a transmission mode, and Raman Spectrometry by using Micro Raman system (Ramboss 500 i) He-Ne laser beam at 633 nm, and 1800 lines per mm grating with 50 X objective lens at room temperature. The specific surface area and pore diameter of the synthesized materials were calculated from an N_2 adsorption isotherm measured using Micromeritics ASAP-2020; a high-purity N_2 gas (99.999%) was used for the measurements. Thermal gravimetric analysis (TGA) was employed on a Scinco TGA N-1000 instrument, at a heating rate of $10^\circ\text{C min}^{-1}$ under N_2 . A vibrating sample magnetometer (VSM, LakeShore-7404) was employed to analyze the magnetic behavior of the nanocomposites.

3. Results and discussion

3.1. Characterization of pure 2D-CCS, bare Fe_3O_4 NPs, Fe_3O_4 NAs@2D-CCS composite

The typical morphology and structure of the pure 2D-CCS, bare Fe_3O_4 NPs, and the Fe_3O_4 NAs@2D-CCS composite were examined by transmission and high-resolution transmission electron microscopy (TEM, HRTEM) techniques. Fig. 2a and b illustrate a precise 2D layered crumpled porous carbon sheets. Moreover, the high crumpled formation (yellow arrows Fig. 2b) is due to the interconnected crumpled and wrinkles rather than the stacking of graphene. Fig. 2c shows the bare Fe_3O_4 nanoparticles (NPs) with the size of 18 to 22 nm with semi-spherical shape and the SAED pattern indicates the presence of a bright diffraction dots reflection from the crystal planes of (220), (311), and (400) of cubic Fe_3O_4 NPs are crystalline in character Fig. 2d. However, the beauty of the 2D layer crumpled morphology allows nucleation growth of Fe_3O_4 NPs, which results in the Fe_3O_4 nano-assembly (NAs) with the size of 150–200 nm comprising small primary Fe_3O_4 nanocrystals ($\sim 20 \text{ nm}$). The Fe_3O_4 NAs are well dispersed and firmly internally integrated by 2D-CCS (Fig. 2e and f).

The high-resolution TEM images are shown in Fig. 3a–d. The 2D-layers crumple carbon sheets (yellow arrows) not only allow the formation of nucleation but also provide a fine carbon layer (yellow arrows) wrapped in between the Fe_3O_4 nanocrystals (white arrows), which resembles a pomegranate like Fe_3O_4 NAs (Fig. 3a and b). Moreover, Fig. 3c clearly illustrates the Fe_3O_4 NAs are present in the interstitial of

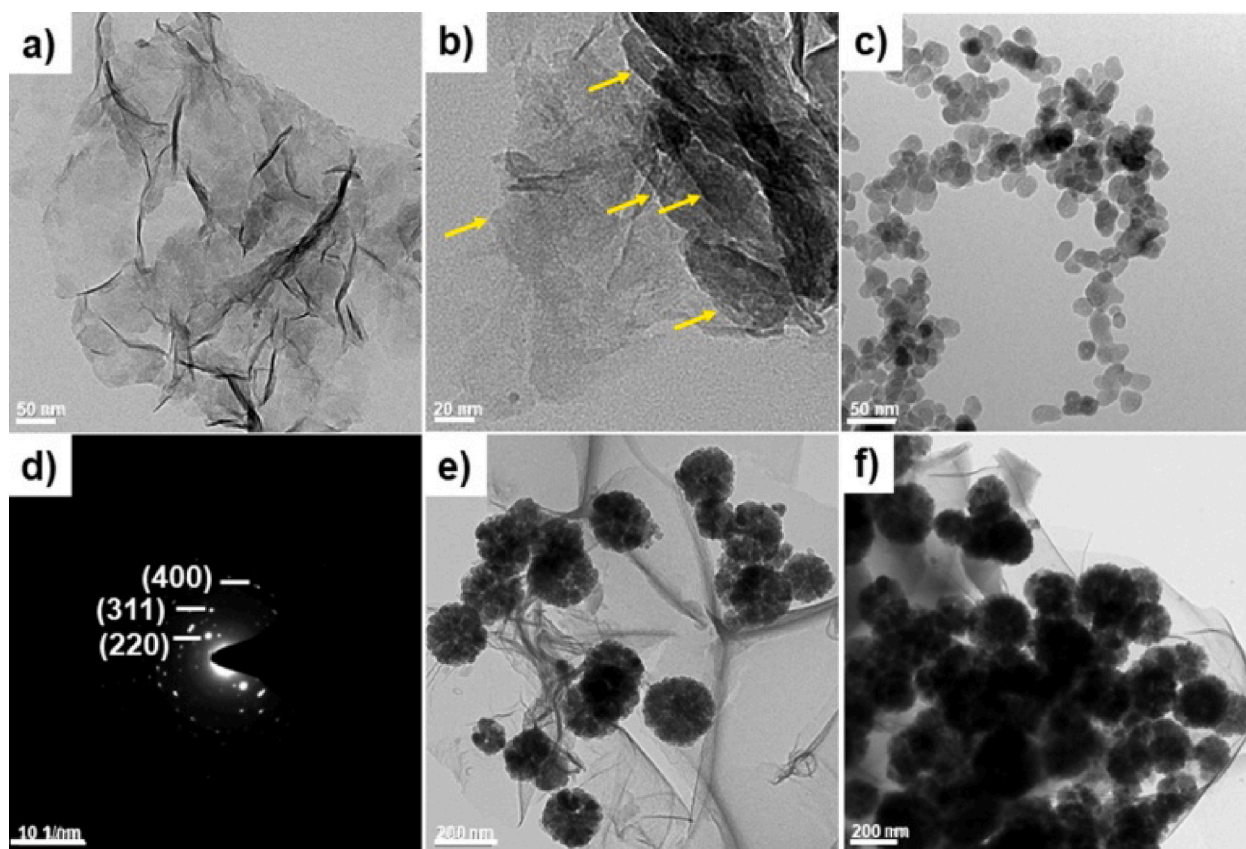


Fig. 2. (a, b) TEM images of pure 2D-CCS, (c, d) TEM and SAED images of bare Fe_3O_4 NPs, (e, f) TEM images of Fe_3O_4 NAs@2D-CCS composite.

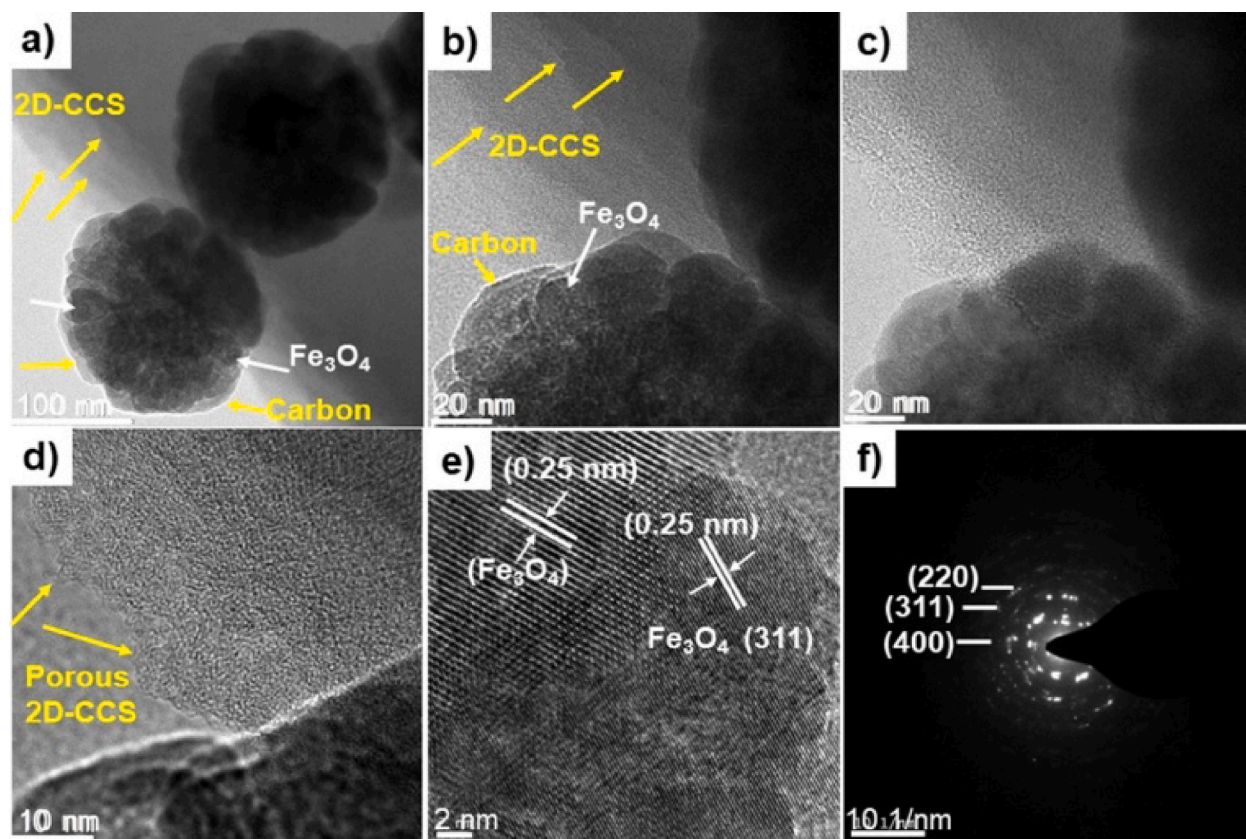


Fig. 3. (a-f) HRTEM and SAED images of Fe_3O_4 NAs@2D-CCS composite.

2D-CCS. In addition, Fig. 3d shows the disordered highly porous nature of the 2D-CCS, which is favorable for high electrolyte ions transportation. The well-indexed lattice fringes of the Fe_3O_4 NAs with an inter planar distance of 0.25 nm belongs to the d spacing of (3 1 1) plane of magnetite shown in Fig. 3e. The SAED pattern reveals the polycrystalline character of the Fe_3O_4 NAs with the diffraction dots of (2 2 0), (3 1 1), and (4 0 0) crystal planes Fig. 3f. This crumpled mesopores 2D carbon sheets internally connected via highly dispersed Fe_3O_4 NAs may

shorten the ion diffusion distance and facilitating the electron transportation between Fe_3O_4 NAs and 2D-CCS, which leads electrodes with distinctive performance.

To achieve further insight into the morphological structure of Fe_3O_4 NAs@2D-CCS composite, the high angular annular dark field (HAADF)-scanning transmission electron microscopy (STEM) imaging and STEM-energy dispersive X-ray spectroscopy (EDS) line scan analysis was conducted. The Fe_3O_4 NAs@2D-CCS composite HAADF-STEM image along

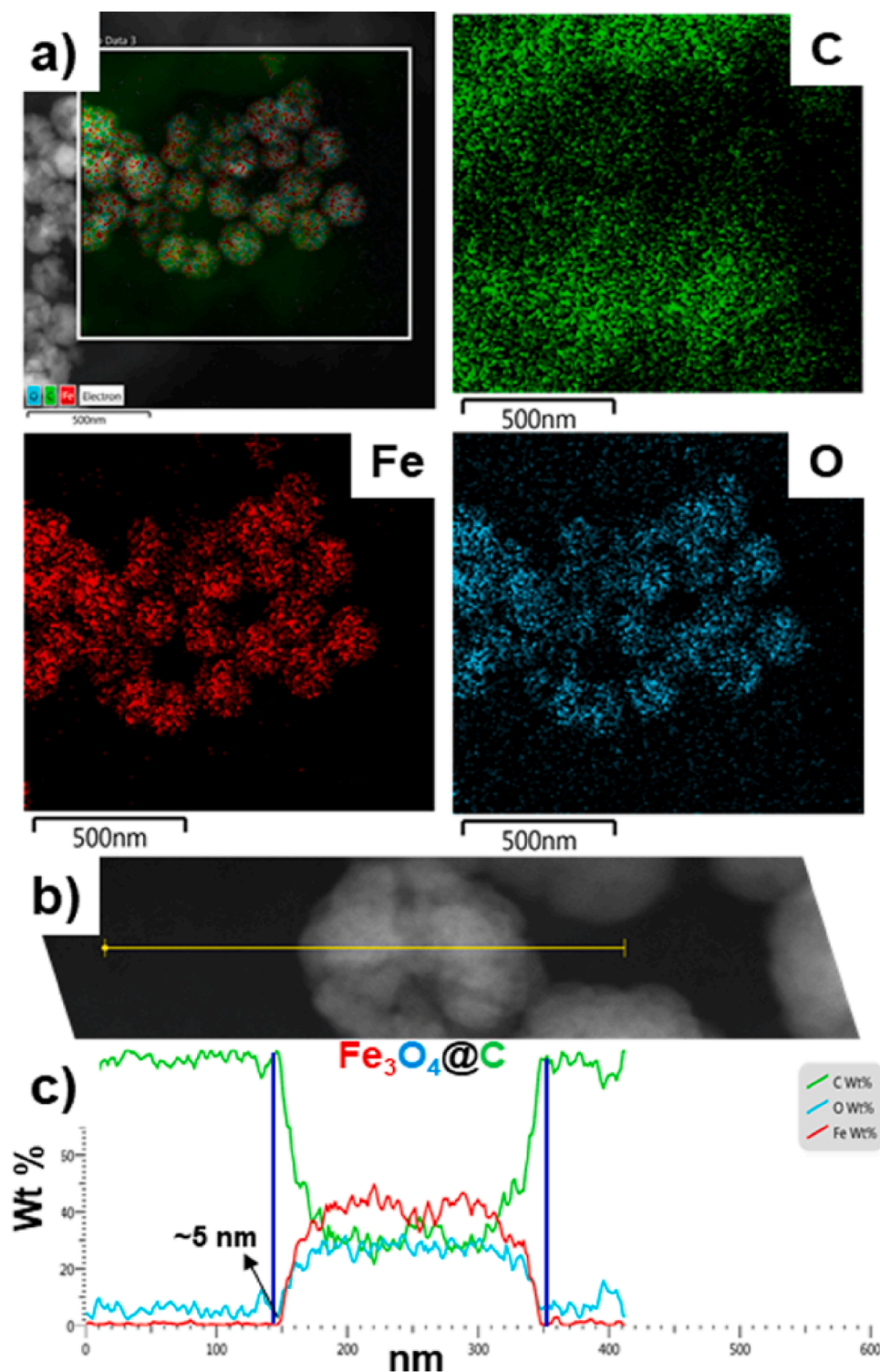


Fig. 4. (a) Fe_3O_4 NAs@2D-CCS composite HAADF image along with elemental mapping images of C, Fe, and O of individual particles. (b) HAADF-STEM image and (c) STEM-EDS linear scan spectra of the selected area of the Fe_3O_4 NAs@2D-CCS composite.

with EDS elemental mapping images of C, Fe, and O shows the homogeneous distribution of the Fe_3O_4 NAs in the composite (Fig. 4a). Especially, Fig. 4b, c illustrates the HAADF-STEM bright image location EDS liner scan spectra across the 2D-CCS interlinked Fe_3O_4 NAs (marked by a yellow line Fig. 3b). The line scan profile (Fig. 4c) clearly indicates that the carbon layer with thickness of nearly 5 nm covered (black arrow) on the surface of Fe_3O_4 NAs as well as internally conglomerate (the green line in-between Fe and O), which resembles pomegranate like structure with the diameter of 180 nm as shown in the TEM image (Fig. 3a). To show more details about the chemical nature of the composite, the SEM images and EDS data are also presented (Fig. S1a-c) in microscopic scale, which clearly indicates the presence of Fe_3O_4 NAs@2D-CCS composite. In addition, we included the composition of element calculated from EDS data is also presented in Table S1.

For more comprehensive on the structure of composite, the thickness of the 2D-CCS was analyzed using an atomic force microscope (AFM) technique. Fig. 5a shows that the overall average thickness of the biogenic 2D-CCS is 40 nm, and each 2D-CCS is having a thickness of 17 nm. Owing to agro-derived 2D carbon, the rough thinness has a composition of many carbon-oriented functional groups, which may lead to capillary force spurred evaporation of oxygenated molecules under the carbonization process, and causes wrinkling of the carbon sheets [53]. A height histogram profile (Fig. 5b) shows linear steps with parabolic disturbances in the 2D-CCS, which indicates that the 2D-CCS consisting of wrinkles in between each layer, which reduces the flatness of the carbon layer. This kind of 2D-CCS are highly advantaged for ion transport and worked as an energy storage bank. Further, Fig. 5c illustrates the AFM image of Fe_3O_4 NAs@2D-CCS composite, where the Fe_3O_4 NAs are visualized, which is also confirmed by 3D AFM image of composite (Fig. 5d), and the arrow marks indicate the Fe_3O_4 NAs exist in-between the sheets. The height histogram profile (Fig. 5e) shows the humps, which suggests that the Fe_3O_4 NAs successfully intercalated with 2D-CCS.

The crystalline phase purity and structure of the materials (2D-CCS, bare Fe_3O_4 , and Fe_3O_4 NAs@2D-CCS composite) were evaluated by PXRD patterns (Fig. 6). Fig. 6(i) shows broad peaks 2θ at 16.8° , 23.5° is assigned 2D-CCS is having amorphous (sp^3) as well as aromatic (sp^2) conglomerate carbon sheets. However, for bare Fe_3O_4 and Fe_3O_4 NAs@2D-CCS composite the major diffraction peaks of 2θ at 30.7° , 35.42° , 43.05° , 56.93° , and 62.52° are well indexed to the crystalline standard Fe_3O_4 (JCPDS card no. 82–1533) face-centered cubic inverse spinel structure with the planes of (220), (311), (400), (333) and (440) in Fig. 6(ii, iii). Moreover, the sharp peaks form Fe_3O_4 NAs composite represent the highly crystalline future Fe_3O_4 NAs, which will coincide with the HRTEM image of Fig. 3e. By using the Debye-Scherrer equation [54], the average crystallite size is calculated based on the (311) plane, is approximately 18 nm and is well-matched with the TEM result. Notably, no other phases (Fe_2O_3 , FeOOH) were detected, which reveals the excellent phase purity of the material. Meanwhile, the peak at 16.8° was disappeared, as shown in Fig. 6(iii), which states that the amorphous carbon developed the π -electron system in the 2D-CCS structure and interlinked with Fe_3O_4 NAs. The above results confirm the successful formation of the composite.

The detailed surface composition and oxidative status were analyzed by X-ray photoelectron spectroscopy (XPS). The full scan spectrum of 2D-CCS, bare Fe_3O_4 , and the Fe_3O_4 NAs@2D-CCS composite was presented in Fig. 7a (i-iii). The survey spectrum of 2D-CCS (line (i)) assigned two peaks at 284 eV, and 532 eV belongs to C1s and O1s, without any other residual hetero atoms. Along with C1s and O1s, several additional peaks at 710 eV to 725 eV corresponding to Fe2p of bare Fe_3O_4 and Fe_3O_4 NAs@2D-CCS composite shown in Fig. 7a (ii, iii). Fig. 7b (i, ii) shows the high-resolution spectrum of Fe2p of bare Fe_3O_4 and Fe_3O_4 NAs@2D-CCS composite. The peaks at 710.8 and 724.4 eV correspond to $\text{Fe}2\text{p}_{3/2}$ and $\text{Fe}2\text{p}_{1/2}$, respectively. Whereas, the disappearance of the satellite peak at 719.5 eV ($\gamma\text{-Fe}_2\text{O}_3$) indicates the phase purity of Fe_3O_4 with mixed oxide of Fe(II) and Fe(III). In addition, the presence of a peak

at 531.6 eV, and the absence of binding energies at 707 eV and 283.2 eV confirms the chelation of Fe_3O_4 with the nest of 2D-CCS is Fe-O-C bond rather than a Fe-C bond. The deconvolution O1s spectrum of 2D-CCS (Fig. 7c(i)) shows three binding energies at 532.3, 533.1, and 534.1 eV attributed C-O/C=O, C-OH, and O-C=O groups. The O1s spectrum of bare Fe_3O_4 NPs reveals two peaks at 530.08, 533.3 eV attributed to lattice oxygen (Fe-O), and -OH of Fe_3O_4 NPs (Fig. 7c(ii)). It is noticeable that compared to pure 2D-CCS the binding energies of O1s spectrum of Fe_3O_4 NAs@2D-CCS composite (Fig. 7d) a new peaks appeared at 530.01 and 531.6 eV attributed to Fe-O and Fe-O-C, [55] which indicate that the Fe_3O_4 NAs is conglomerate with 2D-CCS via oxygenated functional groups, leads the peak intensities of C-O/C=O, C-OH, and O-C=O groups decreases. The C1s deconvoluted spectrum of 2D-CCS Fig. 7e shows the photoelectron peaks at the binding energies of 284.7, 285.9, 286.8, and 288.6 eV indicates the presence of amorphous (C-C/C=C) sp^3/sp^2 carbon moiety, C-O, C=O and O-C=O groups respectively. Besides, Fe_3O_4 NAs@2D-CCS composite the C1s peak was (C-O, C=O, and O-C=O groups) shifted to the lower region, which indicates the functional groups play a crucial role for the growth of nucleation to form Fe_3O_4 NAs (Fig. 7f). These XPS and XRD results were confirmed the phase purity of the Fe_3O_4 NAs@2D-CCS composite.

To better understand the role of functional groups for the formation of composite material, FT-IR plays a vital character (Fig. S2(i)), which shows a broad peak at 3500 cm^{-1} and sharp peaks at 1755, 1710, 1030 cm^{-1} indicating the presence of -OH, C=O and O-C=O groups of garlic extract, respectively. However, the peaks at 3375, 2953, 2865, 1720, 1510, 1090, and 955 cm^{-1} attributed to the -OH, C-H, C=O, C=C, C-O, and aromatic C-H groups of 2D-CCS, respectively (Fig. S2(ii)). The garlic husk extract mediated bare Fe_3O_4 NPs showed the shift of a broad OH peak toward the lower wave number from 3500 to 3324 cm^{-1} , and the appearance of a new peak at 584.4 cm^{-1} indicating that the functional groups play a vital role for the formation of Fe_3O_4 NPs. The peak (Fig. S2 line (iv)) at 1090 cm^{-1} was shifted to 1038 cm^{-1} indicated the formation of Fe-O-C bonds, which is due to the carbothermal reaction. The peak at 584.7 cm^{-1} assigned to the lattice oxygen (Fe-O) of Fe_3O_4 NAs. The chemical structure of the nanocomposite was explored using Raman spectroscopy. The Raman spectra of 2D-CCS and Fe_3O_4 NAs@2D-CCS composite exhibit disorder-induced D bands at 1346 and 1341 cm^{-1} (Fig. S3 (i, ii)), which assigned vibration of the sp^3 carbon atoms. The in-plane vibrational G-band at 1578 and 1572 cm^{-1} indicates the presence of sp^2 graphitic carbon atoms. The intensity of the G-band is higher than that of the D-band, implying the partial graphitization of the material. In Fig. S3 it is observed that the I_D/I_G ratio of Fe_3O_4 NAs@2D-CCS composite (0.69) is lower than that of pure 2D-CCS (0.71) indicating the increasing of sp^2 nature of the composite [56]. Moreover, additional peaks at 531 and 669 cm^{-1} indexed to A_{1g} and T_{2g} modes of Fe-O and a weak peak at 320 cm^{-1} (Fig. S3 (ii) inset zoom) confirm the formation of pure Fe_3O_4 rather than that of maghemite and hematite [57]. The composite is maintaining the high degree of graphitization, which is beneficial for high electrical conductivity, excellent charge transportation during the charge/discharge process.

The porous feature and the specific surface area are one of the significant criteria for benign supercapacitors. Fig. 8a, b illustrates the N_2 adsorption-desorption isotherms were examined for 2D-CCS, Fe_3O_4 NAs@2D-CCS composite at 77 K. Fig. 8a, b shows the Brunauer-Emmett-Teller (BET) specific surface area of 2D-CCS, and the Fe_3O_4 NAs@2D-CCS composite was 1265 and $687\text{ m}^2\text{ g}^{-1}$, respectively. Both the samples exhibit type-IV isotherms with the hysteresis loop, indicating an amalgamation of a hierarchical porous structure [58]. The porosity was further confirmed by the density functional theory (DFT) pore size distribution analysis. The 2D-CCS possess several pores of various diameters in two main regions from 0.6 to 1.2 and 2.7 to 3.4 nm, suggesting that the 2D-CCS has both micro and mesoporous pores (Fig. 8a inset). However, Fe_3O_4 NAs@2D-CCS composite the porous are distributed in three main regions, namely 0.8–1.4, 2.9–3.6 nm, and 6.9 to 8.6 nm (Fig. 8b inset). Due to the presence of carbon wrapped Fe_3O_4

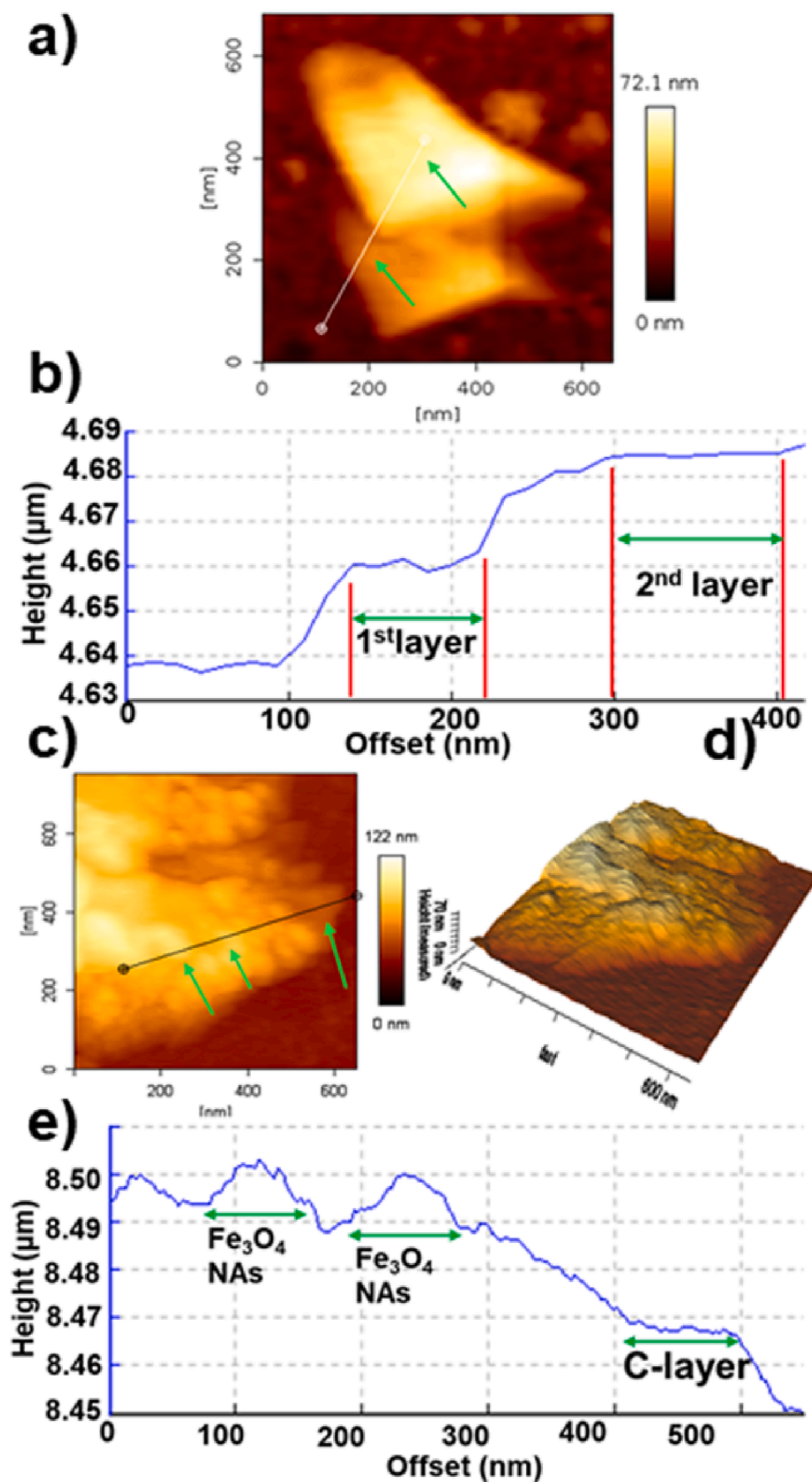


Fig. 5. (a, b) AFM image of pure 2D-CCS composite, and its height histogram profile. (c-d) AFM and 3D-AFM images of Fe_3O_4 NAs@2D-CCS composite. (e) height histogram profile of Fe_3O_4 NAs@2D-CCS composite.

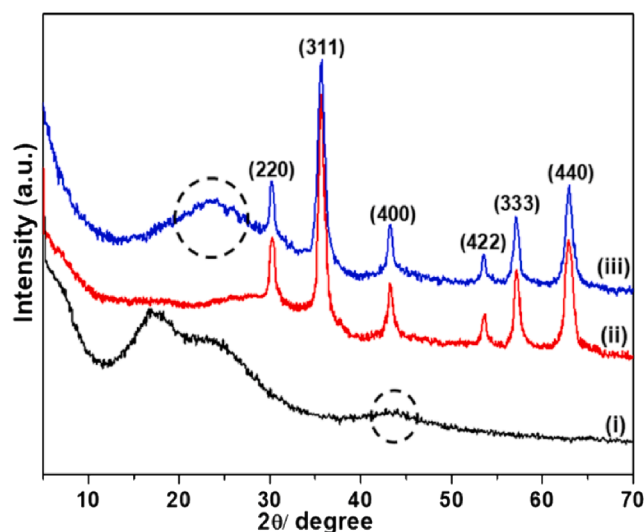


Fig. 6. XRD pattern of (i) pure 2D-CCS, (ii) bare Fe_3O_4 NPs, and (iii) Fe_3O_4 NAs@2D-CCS composite.

moiety, the composite can have a more mesoporous character. The total pore volume of the 2D-CCS and Fe_3O_4 NAs@2D-CCS composite was $0.8775 \text{ cm}^3 \text{ g}^{-1}$ at $P/P_0 = 0.9943$ and $0.5777 \text{ cm}^3 \text{ g}^{-1}$ at $P/P_0 = 0.9947$, respectively. The Fe_3O_4 NAs@2D-CCS composite shows excellent micro to the mesoporous surface area, which boosts up to achieve excellent specific capacitance with high cyclic stability. Further, green synthesized bare Fe_3O_4 NPs having a specific surface area of $55.96 \text{ m}^2 \text{ g}^{-1}$ with a pore size (Fig. S4 inset) of 40.3 nm indicates the hierarchical porous structure.

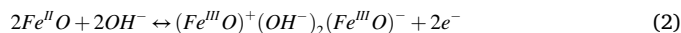
Thermogravimetric analysis (TGA) was employed to estimate the thermal stability of the 2D-CCS, bare Fe_3O_4 , and Fe_3O_4 NAs@2D-CCS composite. The 2D-CCS exhibited (Fig. S5, line (i)) a stepwise weight loss occurred at 130°C , $260\text{--}480^\circ\text{C}$, and $530\text{--}670^\circ\text{C}$, which is due to 1) the loss of adsorbed water molecules, 2) the removal of oxygenated functional groups, and 3) decomposition to in the form of carbon dioxide, resulting a total weight loss of 67% at 900°C . Fe_3O_4 NAs@2D-CCS composite shows a total weight loss of 26%. The lesser weight loss at high temperature is due to the hydroxylated and carbonyl functional are chelated, and the 2D-carbon layer is wrapped to Fe_3O_4 NPs and formed a NAs. The bare Fe_3O_4 NPs show a total weight loss of 5.5% because of the removal of water molecules and the hydroxyl functional groups. The results confirm that the composite is more stable than pure 2D-CCS, which is more advantageous for energy storage systems.

Fig. S6 shows that magnetic behavior of the bare Fe_3O_4 and Fe_3O_4 NAs@2D-CCS composite, performed by using vibrating sample magnetometer (VSM) at room temperature with the magnetic field range of 10,000 to -10000 G . The saturation magnetization value of bare Fe_3O_4 is 43.5 emu g^{-1} with hysteresis loop (upper inset enlarged hysteresis loop (black) Fig. S6(i)), and nonzero remnant magnetization (M_r), coercive force (H_c) shows a ferromagnetic behavior. However, after reacting with 2D-CCS the saturation magnetization value decreases 32.7 emu g^{-1} with narrow hysteresis loop (upper inset enlarged hysteresis loop (red), Fig. S6(ii)) and shows a weak ferromagnetic characteristic because Fe_3O_4 NAs (190 nm) is composed of many crystalline Fe_3O_4 NPs ($\sim 20 \text{ nm}$). The decrease in the saturation magnetization can be mainly attributed to the existence of the nonmagnetic carbon layer on the surface of Fe_3O_4 NAs, and the magnetic behavior of the composite (Fig. S6 right inset). These results also confirmed that the carbon layer covers the Fe_3O_4 NAs interspace.

3.2. Electrochemical study

The electrochemical behavior of bare Fe_3O_4 NPs, and the Fe_3O_4

NAs@2D-CCS composite was studied by using cyclic voltammetry (CV), galvanostatic charge/discharge, and EIS techniques. To distinguish the difference between the non-Faradic and Faradic reactions, CV considered a suitable tool. Fig. 9a (i) shows the CV curves of the bare Fe_3O_4 NPs at various scan rates of 20, 40, 60, 80, 100, and 120 mV s^{-1} in potential range from -0.2 to 1.0 V . A pair of redox peaks appears in various scan rates indicating the existence of Faradaic reactions during the charging and discharging processes. The alkaline mediated redox reaction of Fe_3O_4 is expressed by the following electrochemical reaction equations [59].



The CV curves obtained for Fe_3O_4 NAs@2D-CCS composite (Fig. 9a (ii)) shows a quasi-rectangular with humps, rather than pure rectangular shape, confirming the significant faradaic pseudo-capacitive and the double layer capacitance behavior [60,61]. Besides, a potential shift of the CV peaks in Fig. 9a (ii) can be attributed to the electrode polarization at a higher scan rate [62]. Wrapping of each tiny Fe_3O_4 NPs with porous carbon layers owing to the pomegranate arrangement of Fe_3O_4 NAs results in the unique pseudocapacitor property of the material. This result is coinciding with previous reports [35]. In addition, the shape of the CV curves does not change at various scan rates, which reveals that the Fe_3O_4 NAs@2D-CCS composite possesses excellent reversibility and rate capability. The CV area of Fe_3O_4 NAs@2D-CCS composite was much larger than that of bare Fe_3O_4 , at the scan rate of 120 mV s^{-1} illustrating the Fe_3O_4 NAs inter chelation with porous 2D-CCS and facilitating the electron transportation between Fe_3O_4 NAs and 2D-CCS, leading the electrodes with distinctive performance with higher specific capacitance (820 F g^{-1}). The detailed mechanism was shown in Fig. 10.

To further assess the capacitive performance of the synthesized materials, the galvanostatic charge–discharge was conducted. Fig. 9b (i–ii) shows the charge–discharge curves of bare Fe_3O_4 NPs, and Fe_3O_4 NAs@2D-CCS composite with a potential range of -0.2 to 1.0 V at various current densities from 0.5 to 10 A g^{-1} . The charge–discharge characteristics of bare Fe_3O_4 NPs and Fe_3O_4 NAs@2D-CCS composite nearly similar to the triangle discharge curve, but the charging–discharging of the composite was very longer than individual components (Fig. 9b (i)). This discharge curve in Fig. 9b (ii) indicates the composite exhibits faradaic pseudo-capacitive behavior accompanied by the EDLC process [59]. From the galvanostatic charge–discharge curves, the calculated specific capacitance of bare Fe_3O_4 NPs using Eqn. (1) were found to be 166, 83, 55, 41, 33, 15 F g^{-1} at a current density of 0.5, 1.0, 2.0, 4.0, 6.0 and 10 A g^{-1} , respectively (Fig. 11 (i)). Interestingly, the as-synthesized Fe_3O_4 NAs@2D-CCS composite can reach up to 820 F g^{-1} at a charge–discharge current density of 0.5 A g^{-1} (Fig. 11 (ii)). On the other hand, the composite further can deliver 680, 530, 412, 367, and 340 F g^{-1} , respectively. Fig. 11 (ii) illustrates that the specific capacitance of Fe_3O_4 NAs@2D-CCS composite is higher than that of bare Fe_3O_4 NPs each current density. The excellent performance of the Fe_3O_4 NAs@2D-CCS composite electrode materials is mainly attributed to its unique structure and the following steps a detailed study. (i) The macro spherical size of Fe_3O_4 NAs consisting of many tiny Fe_3O_4 nanocrystals having active redox sites, which are interconnected with porous crumpled carbon sheets, and trigger the longer discharge process. (ii) The 2D-CCS having wide gaps between the layers with high surface area, which can prevent the agglomeration of Fe_3O_4 NAs and can pave a path for electron transport, subsequently boost the rate performance. (iii) Due to the crumpled nature of the porous carbon, it not only acts as a host for Fe_3O_4 NAs but also prevents restacking, which leads cooperative behavior with excellent dispersibility in the electrolyte solution and dissemination of the electrolyte ions via high porous channels for excellent redox reactions, simultaneously enhances the charge storage phenomena. Notably, the specific power, energy densities and capacitance of the Fe_3O_4 NAs@2D-CCS composite is one of the best

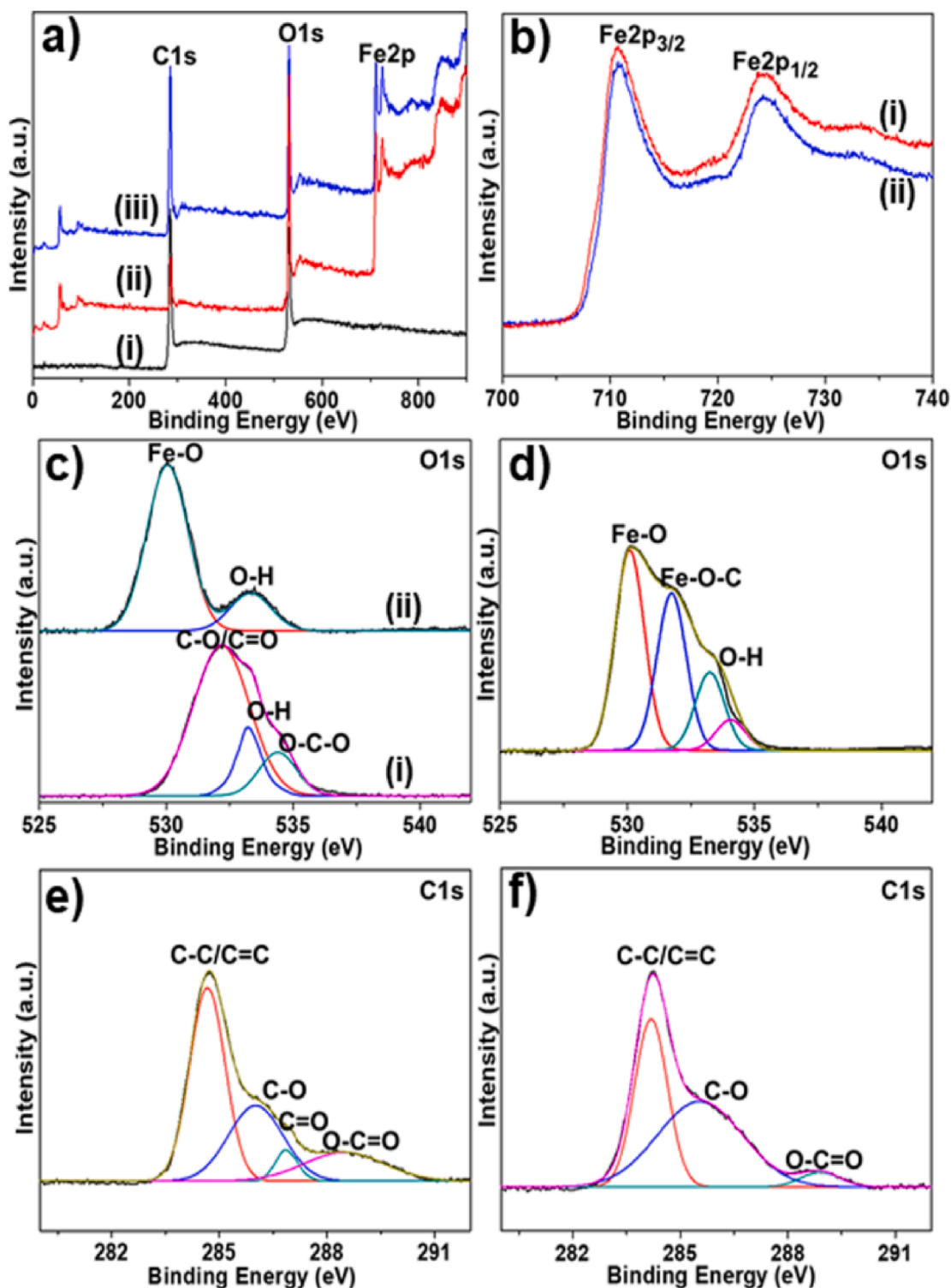


Fig. 7. (a) XPS survey scan spectra of pure 2D-CCS (i), bare Fe_3O_4 NPs (ii), and Fe_3O_4 NAs@2D-CCS composite (iii). (b) high-resolution XPS spectra of bare Fe_3O_4 NPs (i), and Fe_3O_4 NAs@2D-CCS composite (ii). (c (i, ii), d) deconvolution spectrum of O 1s of 2D-CCS, bare Fe_3O_4 NPs, and Fe_3O_4 NAs@2D-CCS composite. (e, f) deconvolution spectrum of C 1s of bare Fe_3O_4 NPs, and Fe_3O_4 NAs@2D-CCS composite.

electrochemical performances among those of iron oxide carbon-based reported materials as shown in Table 1 [60,62-73].

Most critical criteria for the practical application of a supercapacitor is the synthesized material should possess a long cycle life. Fig. S7 (i-ii) shows the cyclic stability of electrodes prepared with bare Fe_3O_4 , and the Fe_3O_4 NAs@2D-CCS composite was evaluated by a 2000 cycle at the current density of 0.5 A g^{-1} . The Fe_3O_4 NAs@2D-CCS composite

electrode can keep 90% of its initial capacity after 2000 cycles (Fig. S7 (ii)). Whereas, the capacitance of bare Fe_3O_4 diminution to 64% (Fig. S7 (i)). The excellent stability is attributed to its unique structure, which promotes the electron transport efficiency between Fe_3O_4 NAs and 2D-CCS (Fig. 10), with an increase in reaction time. Fig. S8 (a-d) shows the TEM images and SAED pattern of the Fe_3O_4 NAs@2D-CCS composite after 2000 cycles. Importantly, even after 2000 cycles, the structure of

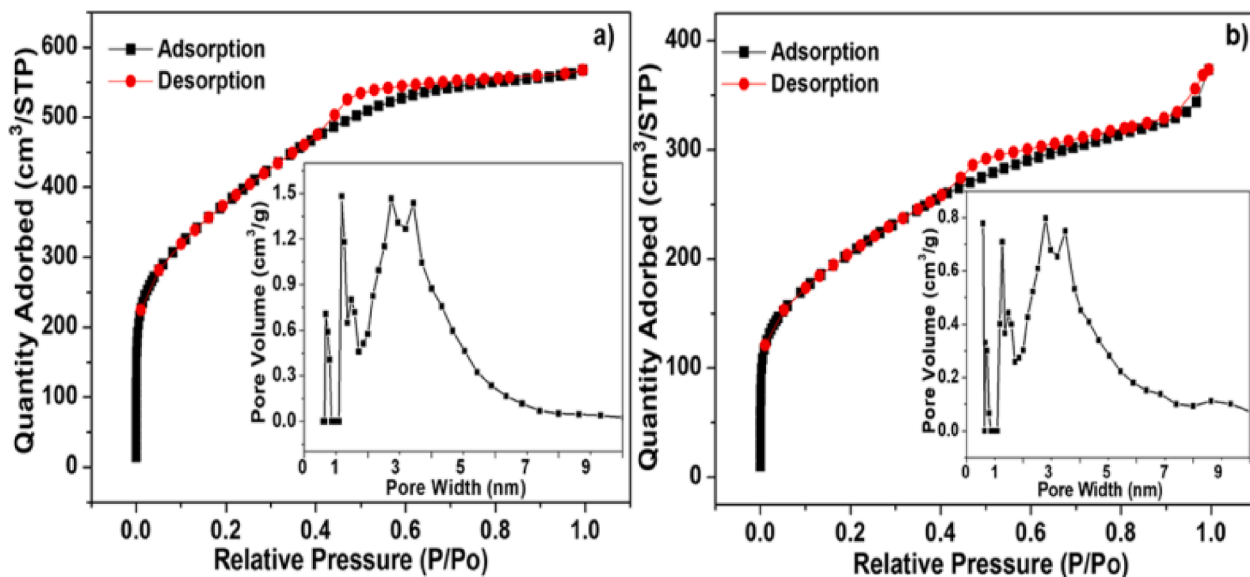


Fig. 8. N_2 adsorption-desorption isotherms of (a) pure 2D-CCS and (b) Fe_3O_4 NAs@2D-CCS composite. Inset pore size distribution calculated by NLDFT method.

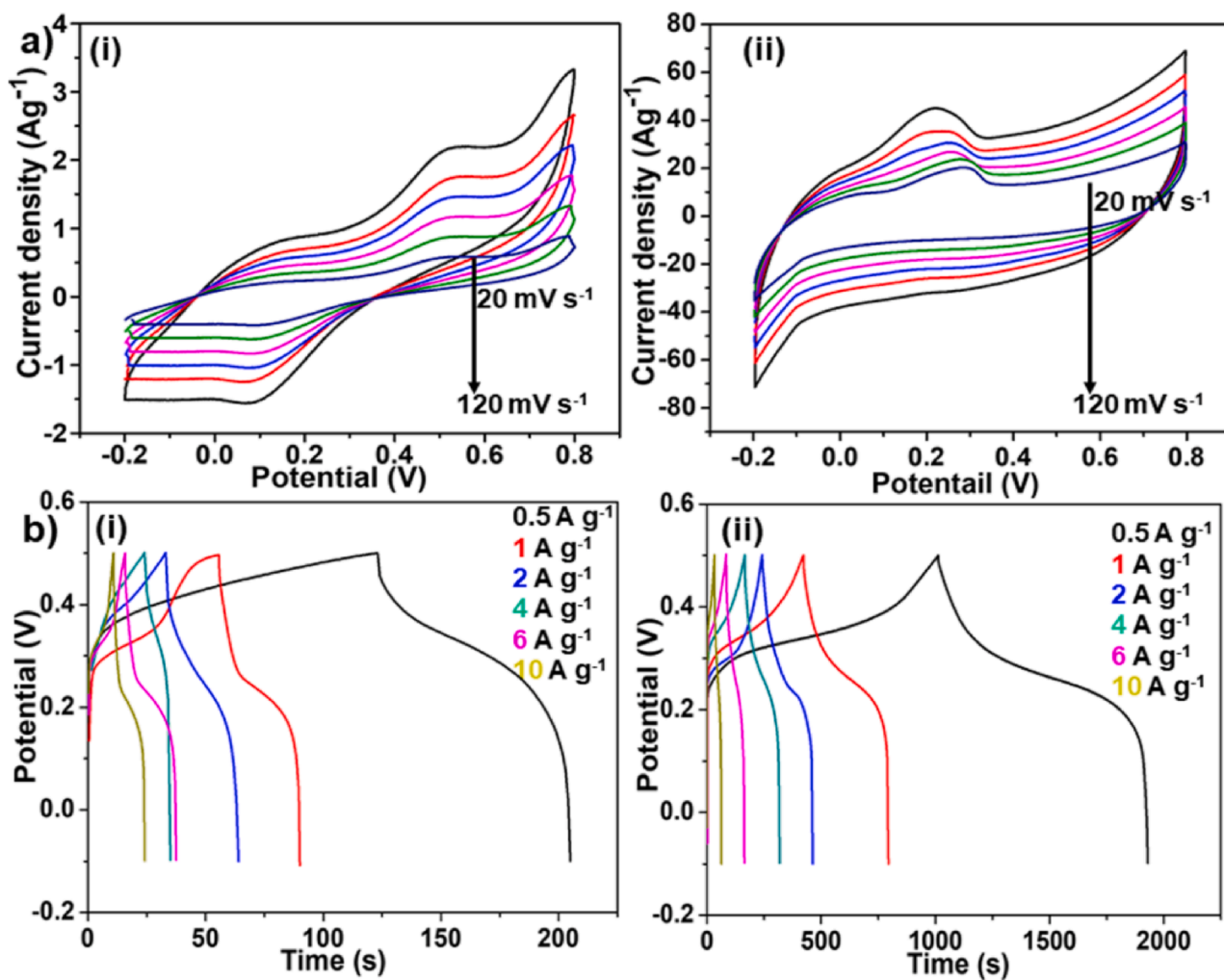


Fig. 9. (a) Cyclic voltammograms of (i) bare Fe_3O_4 NPs, and (ii) Fe_3O_4 NAs@2D-CCS composite at different scan rates from 20 to 120 mV s^{-1} , (b) galvanostatic charge-discharge of (i) bare Fe_3O_4 NPs, and (ii) Fe_3O_4 NAs@2D-CCS composite at various current densities 0.5 to 10 A g^{-1} .

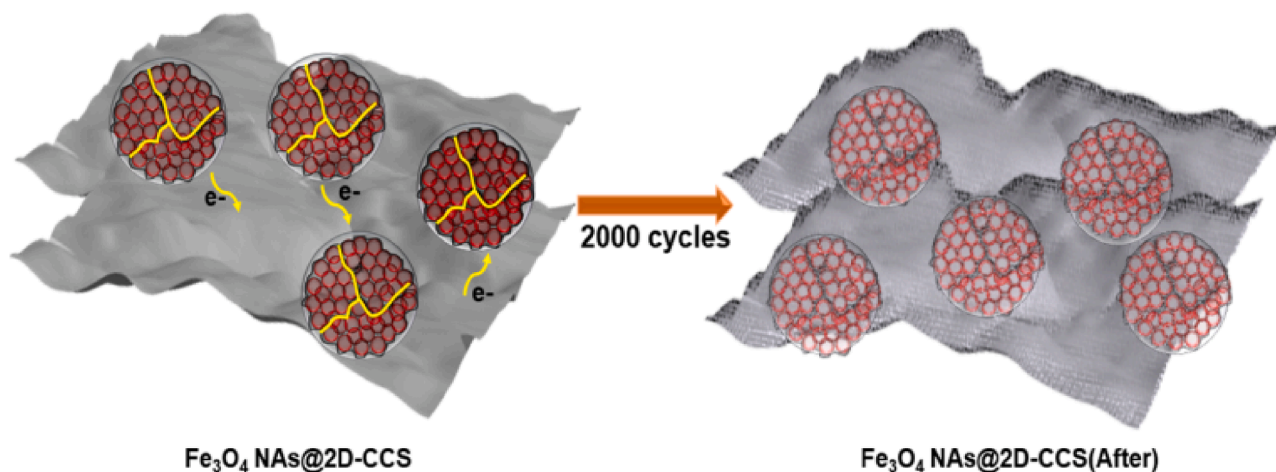
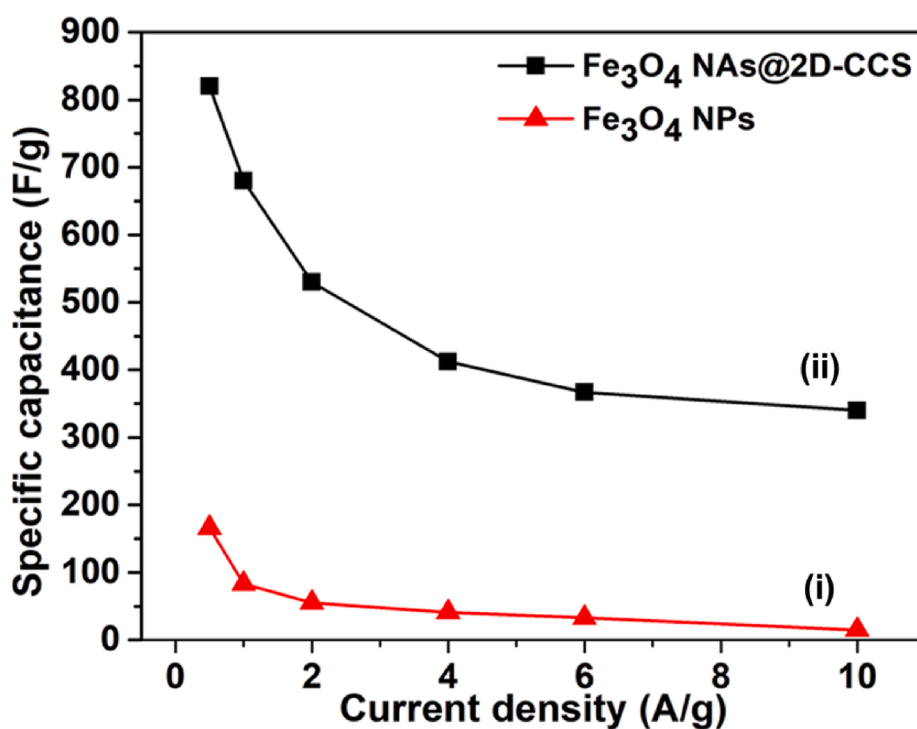
Fe₃O₄ NAs@2D-CCSFe₃O₄ NAs@2D-CCS(After)Fig. 10. Energy storage behavior of Fe₃O₄ NAs@2D-CCS composite before and after 2000 cycles.Fig. 11. Specific capacitances of (i) bare Fe₃O₄ NPs, and (ii) Fe₃O₄ NAs@2D-CCS composite as a function of current density.

Table 1

A comparison study of recently reported iron oxide carbon-based electrodes electrochemical performance.

Composite	Current density (A g ⁻¹)	Specific capacitance (F g ⁻¹)	Power density (W kg ⁻¹)	Energy density (Wh kg ⁻¹)	Reference
Fe ₃ O ₄ @GO	5	480	5506	67.0	[62]
Fe ₃ O ₄ @GNS	2	358	225	07.0	[64]
rGO/Fe ₃ O ₄ /PANI	1	283	550	47.4	[65]
Fe ₃ O ₄ @Carbon nanosheet	10	586	351	18.3	[66]
CNT-Fe ₃ O ₄ -PANI	20 mV S ⁻¹ (scan rate)	201	5300	28.0	[67]
Fe ₃ O ₄ /Fe-CNT	1	1065	897.1	29.9	[68]
Fe ₃ O ₄ /Graphene	0.05	187	150–2587	147–86	[69]
Au-Fe ₂ O ₃	1	570	2730	34.2	[70]
Porous Fe ₃ O ₄ /C	2	868	801.1	24.2	[71]
CC/CW/Fe ₃ O ₄ @C	1	463	1384	91.1	[72]
Fe ₃ O ₄ @CNT@MnO ₂	1	643	849.9	52.9	[73]
PANI@Fe ₃ O ₄ @CFs	0.5	245	1047.5	78.6	[74]
C/Fe ₃ O ₄	3	536	14,500	42	[75]
Fe ₃ O ₄ NAs@2D-CCS	0.5	820	3500–8000	115.5–65.9	This work

Fe_3O_4 NAs@2D-CCS composite does not change, and the presence of a bright diffraction dots indicates the presence of crystalline nature of Fe_3O_4 NAs. This result suggests that the high stability of Fe_3O_4 NAs@2D-CCS composite material is excellent for energy storage applications. In addition, tapped density of the material is also important for a practical application. The calculated tapped density of the Fe_3O_4 NAs@2D-CCS composite was 0.35 and 0.42 g cm^{-3} , respectively, which is modest value among the reported electrode material for a pseudocapacitor. Therefore, the compositing the material can provide better method for the preparation of practically useful material.

The electrochemical impedance spectroscopy (EIS) is a non-destructive versatile technique for evaluation of electron transfer rate of reaction and capacitive information of bare Fe_3O_4 NPs, and Fe_3O_4 NAs@2D-CCS composite. The Nyquist plots were analyzed at the frequency range of 0.1 MHz to 0.01 Hz (Fig. 12). In the high-frequency region, the equivalent series resistance (ESR) of Fe_3O_4 NAs@2D-CCS composite (Fig. 12(ii)) is 2.9 Ω , which is smaller than that of their bare Fe_3O_4 NPs (65.3 Ω), (Fig. 12(i)). The lower ESR indicated the higher electrical conductivity of the Fe_3O_4 NAs@2D-CCS composite electrode. The presence of interlinked Fe_3O_4 NAs and the 2D-crumpled porous structure can significantly improve the electrical conductivity of the composite. In addition, the absence of the semicircle region assigned the composite coaxial configuration leads to low charge transfer resistance (R_{ct}) and low Faradaic resistance in the electrolyte [66,74]. The results demonstrate that the presence of interlinked Fe_3O_4 NAs and 2D-crumpled porous structure can significantly improve the electrical conductivity of the composite. Furthermore, we studied the EIS of the Fe_3O_4 NAs@2D-CCS composite after the 2000 cyclization (Fig.S9). The equivalent series resistance (ESR) of Fe_3O_4 NAs@2D-CCS composite is increased from 2.9 Ω to 4.6 Ω . The distortion of architecture may occur in the composite material during the cycling experiment, which leads the decreased in conductivity of the material [75].

The power performance of the bare Fe_3O_4 NPs, and Fe_3O_4 NAs@2D-CCS composite is illustrated in the Ragone plot. The energy and power densities of asymmetric supercapacitor are achieved based on the galvanostatic charging and discharging curves by using the following equations:

$$E = (it\Delta E/m)/2 \quad (3)$$

$$P = E/t \quad (4)$$

where E is energy density, i is the current in amps used for charge/discharge cycling, t is the discharge time, m is the mass of active material in grams and ΔE is the operating potential window in volt of charge and discharge, P is the power density and t is the discharge time.

Fig. 13 (i, ii) shows the Ragone plot of the synthesized materials, and it shows the Fe_3O_4 NAs@2D-CCS composite having outstanding specific energy density from 115.5 to 65.9 Wh Kg^{-1} at the power densities ranging from 3500 to 8000 W Kg^{-1} (Fig. 13 (ii)). However, bare Fe_3O_4 NPs showed a specific energy density of 4.5 Wh Kg^{-1} (Fig. 13 (i)). Finally, the eco-friendly, economically viable nanocomposite shows outstanding energy density as well as superior power density, which is much needful for practical sustainable industrial applications. For practical application, an electrode cell configuration was used to test the performance of an asymmetric supercapacitor in 6 M KOH aqueous electrolyte solution. The device is first connected with a 3 V battery for charging 90 sec. After that, the supercapacitor device was able to glow the LED, as shown in Fig. 13 inset. The developed waste to valuable eco-friendly material is excellent for energy, catalysis, and environmental applications.

4. Conclusion

By the inspiration of nature, we have successfully developed an economically viable concerted method for pomegranate like (0D) Fe_3O_4 nano-assembly (NAs) embedded 2D-crumpled porous carbon sheet (2D-CCS) composite materials with zero-waste generation. The waste garlic husk derived extract and residue are act as a solvent and 2D-carbon template. Interestingly, instead of the regular 2D carbon sheet, we achieved more active edge sites having 2D-crumpled porous carbon sheets. Moreover, the spherical uniformly dispersed Fe_3O_4 NPs with a size of < 20 nm was successfully obtained by the absence of biogenic 2D-CCS. Importantly, after the addition of biogenic 2D-CCS, a pomegranate like Fe_3O_4 NAs (200 nm) (having several tiny Fe_3O_4 nanocrystals)

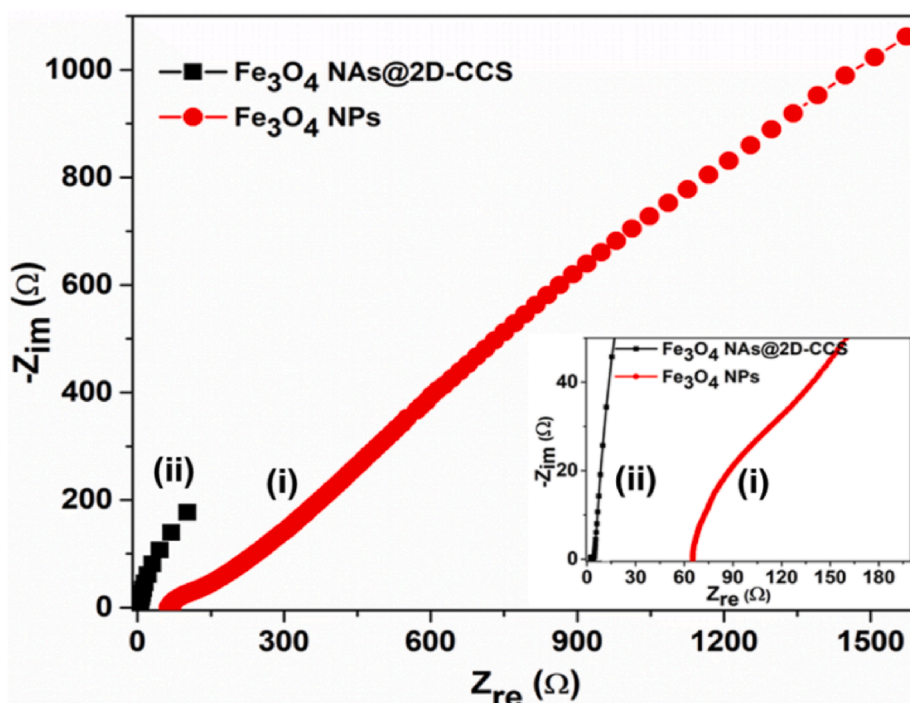


Fig. 12. The Nyquist plots of (i) bare Fe_3O_4 NPs, and (ii) Fe_3O_4 NAs@2D-CCS composite. (inset image: zoomed Nyquist plots in a Z_{re} range of 0-190 Ω).

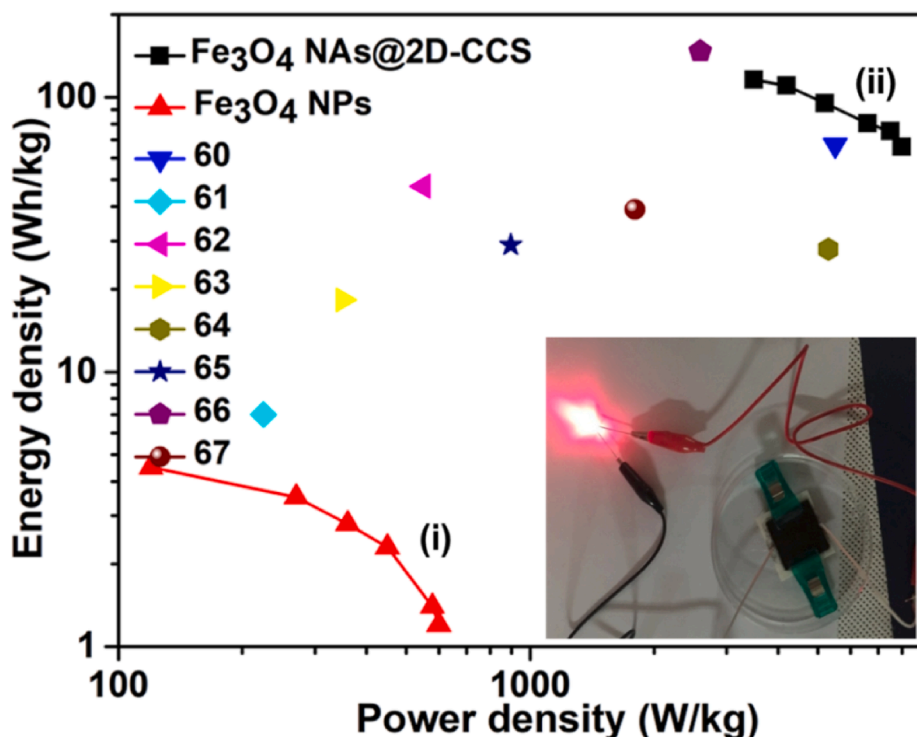


Fig. 13. Ragone plots of (i) bare Fe_3O_4 NPs, and (ii) Fe_3O_4 NAs@2D-CCS composite. Inset photograph of LED lighted up brightly by asymmetric device with Fe_3O_4 NAs@2D-CCS composite.

generated and internally connected within the 2D-CCS skeleton. Moreover, the 2D-crumpled nature of the pores carbon prevents the restacking and agglomeration of Fe_3O_4 NAs, which leads to cooperative behavior with excellent diffusion of the electrolyte ions via high porous channels, holding up-and-coming applications in energy storage systems. The Fe_3O_4 NAs@2D-CCS composite exhibit high specific capacitance of 820 F g^{-1} at a current density of 0.5 A g^{-1} and shows excellent cycle stability with 90.1% retention of its initial specific capacitance after 2000 cycles. In addition, the composite shows outstanding power density ($3500 - 8000\text{ W kg}^{-1}$) and specific energy density ($115.5 - 65.9\text{ Wh Kg}^{-1}$), which is superior among most of all reported iron oxide carbon materials. This eco-friendly, economically viable work stimulates a universal new door for the generation of waste to valuable materials compared to the several carbon allotrope materials like $\text{Fe}_3\text{O}_4/\text{rGO}$, $\text{Fe}_3\text{O}_4/\text{CNT}$, and $\text{Fe}_3\text{O}_4/\text{GNS}$, etc., and mitigate the environmental and energy crisis. Furthermore, this developed method acts as a torch-bearer for producing other transition metal oxide-based nano-assembly embedded 2D crumpled carbon composite materials for unprecedented energy storage applications.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Author Contributions

All authors contributed to this work. All authors have given approval

to the final version of the paper.

Appendix A. Supplementary data

Further experimental details; Electrochemical measurement, FT-IR analysis, Raman analysis, TGA analysis, BET analysis, VSM analysis, cyclic stability, and TEM analysis are available Supplementary data to this article can be found online at <https://doi.org/10.1016/j.cej.2020.127584>.

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