RSC Advances



PAPER



View Article Online



Cite this: RSC Adv., 2024, 14, 25347

Agile soft template array fabrication of onedimensional (1D) polyaniline nanocomposite fibers for hydrogen storage

Ameena Parveen, a S. Manjunatha, M. Madesh Kumar and Aashis S. Roy **D**de

Polyaniline-Zn/V₂O₅ nanocomposites were prepared in the presence of toluene-4-sulfonic acid monohydrate as an anionic surfactant *via* an *in situ* oxidation polymerization method. The structural study of the nanocomposites was carried out using FTIR and XRD analysis, and their surface morphology was characterized through SEM analysis. The BET surface area of a 3 wt% nanocomposite was 386 m² g⁻¹, which is higher compared to that of PANI. The Kelvin two probe method was used to study DC conductivity, and it was found that the conductivity increases with increasing temperature. Among all the PANI nanocomposites, 3 wt% PANI-Zn/V₂O₅ shows a high conductivity of 13.8 S cm⁻¹. Cyclic voltammetry results show the characteristic oxidation–reduction peaks at 0.93 V and 0.24 V for polyaniline and its nanocomposites, respectively. Hydrogen absorption studies were carried out using volumetric sorption measurement technique. At room temperature, it was found that the hydrogen adsorption capacity of polyaniline fibres is about 4.5 wt%, and its absorption capacity increases two-fold upon increasing the temperature up to 60 °C. Conversely, the 3 wt% PANI-Zn/V₂O₅ nanocomposite showed a high absorption capacity of 6.6 wt% compared with other compositions, which is may be due to the presence of nitrogen (N) molecules in polyaniline and its particular porous fiber architecture.

Received 28th June 2024 Accepted 25th July 2024

DOI: 10.1039/d4ra04710a

rsc.li/rsc-advances

1. Introduction

The unique benefits of nanostructured polymer materials in green hydrogen energy conversion and hydrogen storage technologies have been significantly improved. Various structures of polyaniline can be prepared using different synthesis methods, such as in situ oxidative polymerization, electrochemical, and interfacial methods. B. Senthilkumar et al.1 reported on hydrogen adsorption on pure polyaniline of various structures. They determined that the hydrogen adsorption capacities of polyanilines with irregular granular, spherical and fibrous structures are 1.56 wt%, 3.3 wt% and 5.3 wt%, respectively. Hydrogen energy has become increasingly important in recent years owing to its potential to replace fossil fuels. Hydrogen is abundant in the universe and can be used to generate electricity and power vehicles. It can be generated from renewable sources, such as water streams and biomass, making it a clean and sustainable energy source.2 Hydrogen is nontoxic, environmentally friendly, efficient, cost-effective, and readily available,

The storage medium needs to be reversible and able to hold its energy even after being charged with hydrogen several times. Making materials that can store and release gas at standard pressure and temperature is therefore essential. Metal hydrides and their complexes have been the material of choice for hydrogen storage for most of the past 10 years. Metal hydrides, particularly magnesium hydrides, can contain 6.5 H atoms per cm³ compared to liquid hydrogen's density of only 4.2 H atoms per cm³. This advantage makes it possible to maintain a safe vessel while attaining significant hydrogen gravimetric absorption. Most of the materials in this class are metal hydride complexes of lithium, aluminum, beryllium, magnesium, and sodium because of their low atomic weight. Hydrogen atoms dissociate on the metal surface, absorb into the substance, and then form chemical bonds within the lattice complex's interstitial sites. The "bottleneck" of this material is the activation energy required to break the interstitial bonds and liberate the hydrogen atoms from the material.4

The importance of lightweight metal oxide nanomaterials, which are directly related to a wide range of alternative technological solutions, is particularly crucial. There are difficult technical problems in the use of hydrogen as petroleum energy for automobiles *via* the development of efficient hydrogen

making it a possible alternative to fossil fuels. This makes hydrogen a much better option for reducing air pollution than fossil fuels, which release carbon dioxide and other pollutants into the atmosphere.³

^{*}Department of Physics, Government Degree College, Yadgir-585201, Karnataka, India

*Department of Physics, SSA Government First Grade College, Ballari-583101, India

^cDepartment of Physics, REVA University, Bangalore-560064, Karnataka, India ^dDepartment of Chemistry, S. S. Tegnoor Degree College, Gubbi Colony-585104,

[&]quot;Department of Chemistry, S. S. Tegnoor Degree College, Gubbi Colony-585104 Karnataka, India. E-mail: aashisroy@gmail.com; Tel: +91-9108809031

^eDepartment of Industrial Chemistry, Addis Ababa Science and Technology University Addis Ababa 500013, Ethiopia

storage systems.5-7 The adsorption of hydrogen on the vanadium pentoxide (010) surface is a selected reaction step in the nucleophilic oxidation of hydrocarbons for V₂O₅ cluster models, as per the ab initio Hartree-Fock method. Three different oxygen adsorption sites are considered: the vanadyl site, the bridging oxygen site between two surface vanadyl groups $(V^{2+},$ V3+), and the bridging oxygen site between two surface vanadium centres. This suggests that for the vanadyl sites, hydrogen binds to the surface oxygen with a fairly strong bond, leading to the formation of stable surface groups that are bound to the surface vanadium atoms.8 The proton is localized and forms a hydride bond with vanadium. The electrons are also localized, creating V2+ and V3+ paramagnetic centres. The exchange interaction between these two paramagnetic species is the origin of chemosorption. In contrast, hydrogen approaching the bridging oxygen sites forms an even stronger surface O-H bond, but that particular surface oxygen becomes mobile so that the surface OH species can desorb with only a small or no activation barrier, leaving behind an oxygen vacancy.9,10 Storing H2 in nanostructured polymer fibers by means of a physisorption mechanism is an easy-to-control process that allows reversible H₂ absorption and release, as well as quick adsorption/ desorption kinetics.11-14

The most fascinating materials are conducting polymers because of their easy synthesis, environmental stability, low cost, and tunable electrical properties. Owing to these properties, they can be used in suitable technological applications, such as energy storage, battery, super capacitor and sensor applications. 15-17 However, there are problems with the crystallinity of the polyaniline and mechanical robustness. To overcome these constraints, many researchers have recently focused on creating hybrid organic-inorganic nanocomposite systems consisting of nanostructured metal oxides and conducting polymer fibers. 18-20 Here, we have prepared a polyaniline fiber shape at ice temperature with the ability to modify its electrical and mechanical properties to produce desired synergistic effects. PANI has also been demonstrated to be a well-known material with prospective applications in sensors, supercapacitors, corrosion, solar cells, and light-emitting diode devices.21 Recently, one-dimensional hybrid heterojunction-based nanocomposites have been investigated for use in hydrogen storage applications, owing to their high aspect ratios and high surface areas. Polyaniline can be prepared in one-dimensional fiber nanostructures using soft templates or template-less methods. 22-24 The controlled modified polyaniline surface enhances the physical and chemical absorptions, owing to the rich structural modification chemistry, anisotropic geometry of the nanofiber structures, high surface area, smaller infiltration depth for marked molecules, and roomtemperature operation.25

Therefore, we have made an attempt to prepare polyaniline nanofibers doped with porous ${\rm Zn:V_2O_5}$ nanocomposites with different weight percentages. The prepared nanocomposites were characterized by Fourier transform infrared (FTIR) spectroscopy and X-ray diffraction (XRD) pattern analysis, and their surface morphologies were studied by employing scanning electron microscopy (SEM). The DC conductivity was measured using the Kelvin two-probe method, and the activation energy

was calculated. A CH Instruments 660D electrochemical work station was used for electrochemical impedance experiments, and a picoamp (pA) booster was used to identify the current and voltage. Volumetric isothermal analyses were carried out using Hy-Energy PCTPro 2000 sorption equipment.

2. Materials and methods

All chemicals were used in analytical grade for the preparation of Zn/V_2O_5 nanoparticles and polyaniline. The following products were purchased from Sigma-Aldrich Pvt Ltd, India and used exactly as is: toluene-4-sulfonic acid monohydrate ($C_7H_8-O_3S \cdot xH_2O$) with mol. wt. 172.20 and 98.6% purity; zinc acetate anhydride ($Zn(CH_3COO)_2 \cdot (H_2O)$) with 99% purity; vanadium acetate ($V(C_2H_3O_2)_5$) with 99.99% purity; orthophosphoric acid (H_3PO_4) with 99.99% purity; hydrogen peroxide (H_2O_2) with 99.9% purity; hydrogen peroxide (H_2O_2) solution with mol. wt. 34.01, concentrated hydrochloric acid with mol. wt. 36.46; ammonium persulfate ($(NH_4)_2S_2O_8$) with 99.9% purity; and acetone with 99.8% purity.

2.1 Synthesis of porous Zn/V₂O₅ nanoparticles

Using a round-bottom flask, 4.5 g of zinc acetate anhydride $(Zn(CH_3COO)_2 \cdot (H_2O))$, 100 ml of ethanol, 100 ml of vanadium acetate (V(C₂H₃O₂)₅), and 200 ml of ethanol solvent were used to dissolve 4.5 g of sodium hydroxide (NaOH) to create Zn/V₂O₅ nanoparticles using the sol-gel technique. First, we combined the zinc acetate and vanadium acetate solutions in a 500 ml beaker at an equimolar ratio, while constantly stirring for 20 minutes. Subsequently, a sodium hydroxide solution was gradually added to the previously mentioned solution, and then hydrogen peroxide (H2O2) was added while stirring continuously at room temperature for three hours. The pH was maintained between 5.6 and 5.9. Less than 8.0% ethanol was used to modify the pH, such that the white colloidal solution could settle for five hours. After transferring the white colloidal solution into centrifuge tubes, the mixture was centrifuged for 15 minutes at 10 000 rpm. The liquid supernatant was disposed, and the white residue was repeatedly cleaned with distilled water. The residue was collected, dried for 60 minutes at 60 °C, and then annealed in a temperature-controlled muffle furnace for two hours at 450 °C. The annealed Zn/V2O5 (ZVO) nanoparticle residue was then crushed into tiny particles for use in the fabrication of nanocomposite materials.26-28

2.2 Synthesis of the polyaniline nanofiber

0.1 M of aniline aqueous solution in 100 ml of distilled water was mixed with 100 ml of 1 M HCl and 1 M toluene-4-sulfonic acid monohydrate (PTSA) solution to form an aniline hydrochloro-toluene-4-sulfonic acid solution. The mixture was soaked in ice pores by submersion in an ice bath. Then, at ice temperature, 0.25 M of 100 ml ammonium persulfate (APS) was added gradually with constant stirring. Following the addition of all of the APS, the reaction mixture was placed in a deep freezer under ice temperature to react slowly for 48 hours without stirring, resulting in the formation of a greenish-spongy

precipitate. After filtering the precipitate, it was repeatedly washed with distilled water to get rid of any salt deposits, followed by 0.1 M HCl to eliminate all of the unreacted monomers. Then, the precipitate was washed with acetone to remove the water from the nanocomposite, and dried under a dynamic vacuum drier for 24 hours at 60 °C to achieve a constant weight.^{29,30}

2.3 Synthesis of the polyaniline- $\text{Zn/V}_2\text{O}_5$ nanocomposite fibers

The preparation of the Zn/V₂O₅-doped polyaniline nanocomposites followed an identical procedure to that of the polyaniline synthesis. The aniline hydrochloro-toluene-4-sulfonic acid solution was combined with varying weight percentages (1, 2, 3, and 4 wt%) of Zn/V₂O₅ nanoparticles during a 30 minute stirring period in this synthesis procedure. Then, at ice temperature, 0.25 M of 100 ml ammonium persulfate (APS) was added slowly with continuous stirring. Then, the reaction mixtures were put in the deep freezer at ice temperature and allowed to react slowly for 48 hours without being agitated, resulting in the formation of a greenish-spongy precipitate once all of the APS was added. After filtering the precipitate and repeatedly washing it with distilled water to eliminate any salt build up, 0.1 M HCl was added to remove any remaining unreacted monomers. After rinsing with acetone to eliminate any remaining water from the nanocomposite, the precipitate was dried under dynamic vacuum drier for 48 hours at 60 °C to achieve a constant weight.31,32 Schematic diagram 1 shows how the PANI-Zn/V₂O₅ nanocomposite was prepared (Fig. 1).

3. Characterization

Polyaniline and PANI-Zn/V₂O₅ nanocomposite were characterized via Fourier transform infrared (FTIR) spectra recorded on a PerkinElmer spectrophotometer (model 1600) within the wave number range of 400-4000 cm⁻¹. After combining the produced PANI samples with KBr in a 1:5 ratio to create a uniform palette, the mixture was compressed using a hydraulic press to create a plate with a diameter of 10 mm. The surface morphologies of PANI and PANI-Zn/V2O5 nanocomposites were examined by scanning electron microscopy (SEM) with goldcoated particles via sputtering. Electrochemical studies were conducted using the CH Instruments 660D-electrochemical workstation; the current and voltage were detected using a picoamp booster. Three electrodes were used in the electrochemical investigations: a platinum counter electrode, a saturated calomel electrode (SCE) as the reference electrode, and polyaniline and its nanocomposite mixed with carbon black and polyvinylidene fluoride in a 8:1:1 ratio in N-methyl-2pyrrolidone were used to prepare a uniform paste coated over the nickel plate to create the working electrodes.

4. Results and discussion

4.1 Fourier transform infrared (FTIR) spectroscopy

Fourier transform infrared (FTIR) spectroscopy was used to analyse the structural properties of the synthesised PANI and PANI-Zn/V₂O₅ nanocomposites, as shown in Fig. 2. The C-N and C-S stretching vibrations are located at 602 cm⁻¹ and 687 cm⁻¹,

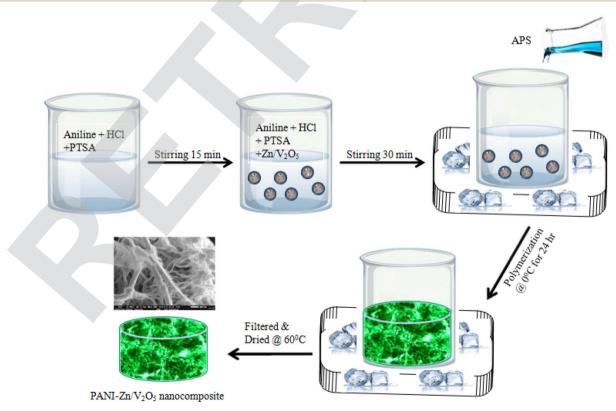


Fig. 1 Schematic of the PANI-Zn/V₂O₅ nanocomposite.

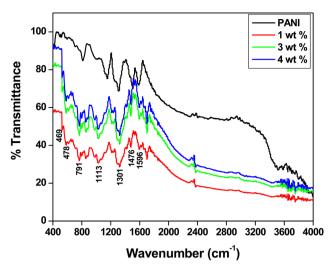


Fig. 2 FTIR spectra of PANI, ${\rm Zn/V_2O_5}$ nanoparticles and 3 wt% of PANI-ZVO nanocomposites.

respectively, for the PANI. The C-H bending vibrations are found at 842 cm⁻¹, the para di-substituted ring stretching vibrations at 842 cm⁻¹, the C-N in-plane stretching vibrations at 1113 cm⁻¹, the C=N stretching band of the aromatic ring at 1301 cm⁻¹, the benzenoid ring stretching vibrations at 1476 cm⁻¹, the quinoid ring vibrations at 1596 cm⁻¹, and the O-H stretching vibrations of water molecules. 33-35 The Zn/V₂O₅ nanoparticle-doped nanocomposites show a peak at 469 cm⁻¹, which corresponds to the Zn-O in-plane bending, 478 cm⁻¹ is due to the vibrational mode of Zn-V-O symmetrical twisted inplane bending, 1013 cm⁻¹, which is related to the in-plane O-V stretching vibration, and 3456 cm⁻¹, which is related to the O-H stretching mode of the hydroxyl group. The nanocomposites exhibit a shift of the peaks due of the loss in mass and strong chemical interaction between the nanoparticles and polyaniline, generating a red shift in the spectra that indicates the presence of Zn/V₂O₅ in polyaniline nanocomposites.³⁶

4.2 X-rays diffraction study

X-ray diffraction (XRD) was used to analyse the structure of the produced metal oxide and nanocomposites, as illustrated in Fig. 3. Due to the semicrystalline nature, it was discovered that the PANI exhibits the characteristic diffraction peak values at the (121), (113), and (220) planes, which correlate to 25.4 Å, 26.5 Å, and 30.4 Å, respectively (JCPDS no. 053-1890).37 The modified sol-gel method was used to prepare the porous Zn/V₂O₅ nanoparticles. The observed diffraction peaks were observed at the (001), 9110), (101), (110), (111), (002), (102), (11), (380), and (212) planes. These correspond to 2θ values of 21.1 Å, 25.4 Å, 25.6 Å, 36.8 Å, 39.2 Å, 45.1 Å, 47.3 Å, 69.8 Å, 72.4 Å, and 72.6 Å, indicating the orthorhombic α -phase with an interlayer spacing of 0.425 nm (JCPDS card no. 041-1426). The Debye Scherrer equation, $D = K\lambda/\beta \cos \theta$, is used to calculate the crystallite size, and the result is 32 nm. Here, D stands for the crystalline size of the metal oxide nanoparticles, K is the Scherrer constant, λ is the wavelength of 1.54, and β is the full width at half maximum (FWHM) of the crystallographic peaks.38 Similar hkl peaks of the

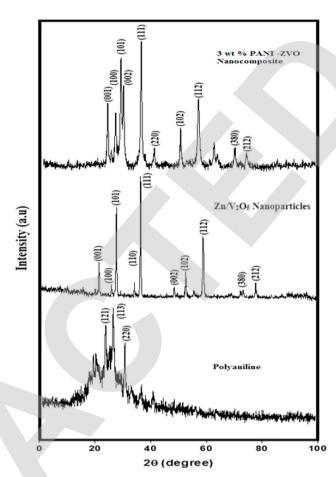


Fig. 3 $\,$ XRD of PANI, $\rm Zn/V_2O_5$ nanoparticles and 3 wt% of PANI-ZVO nanocomposites.

 $\rm Zn/V_2O_5$ nanoparticles in polyaniline nanocomposites can be observed at the (001), (100), (101), (002), (111), (2200, (102), (112), (380) and (212) planes, corresponding to the same 2θ values, which suggests the presence of the same crystal structure without distortion when doped in polyaniline. The observed superposition of polyaniline semicrystalline peaks in 3 weight percent of PANI-Zn/V₂O₅ nanocomposites suggests that the cause might be the nanoparticles embedded in the polymer matrix.

4.3 Scanning electron microscopy

Polyaniline and its nanocomposites were prepared by *in situ* polymerization technique in the presence of an anionic surfactant. The prepared PANI, Zn/V₂O₅ and PANI-Zn/V₂O₅ nanocomposites were characterized *via* SEM to understand the desirable manipulation of the surface morphology that would be suitable for hydrogen application. Fig. 4(a) shows the pristine polyaniline prepared in ice in the presence of toluene-4-sulfonic acid monohydrate surfactant, which helps to form the one-dimensional polyaniline (1D PANI) fibers.³⁶ It was observed that the prepared polyaniline is around 200 nm in length, forming a well-ordered network among each other without any agglomeration in the ice template. Nanocomposites

were prepared by doping porous Zn/V_2O_5 nanoparticles synthesized by sol–gel method. The metal oxide formed a flower-like spherical and small fiber-like structure, and exhibited very high porosity with the size of 23 nm, as shown in Fig. 4(b). It was observed that the Zn/V_2O_5 nanoparticles were homogeneously distributed and completely embedded in the polyaniline fibers. In 1 wt%, 2 wt% and 4 wt%, the cluster of small broken fibers (Fig. 4(c), (d) and (f)) causes a low surface area and less adsorption sites on the PANI nanocomposites surface.³⁹ However, it was observed that the 3 wt% of PANI-Zn/ V_2O_5 nanocomposite shows the proper fiber form (Fig. 4(e)), which is suitable for hydrogen adsorption application.

4.4 Surface studies

4.4.1 Nitrogen physisorption. The N_2 adsorption-desorption isotherm for (a) PANI and (b) porous Zn/V_2O_5 nanoparticles and 3 wt% of PANI- Zn/V_2O_5 nanocomposite are shown in Fig. 5(a) and (b). It was found that the curve is of type IV with a hysteresis loop at high pressure, which is a basic characteristic

property of mesoporous nanocomposites. The hysteresis loop at the relative pressure (P/P_0) range from 0.4 to 0.8 is indicative of type H1, which is generally present for fiber or cylindrical pores.40 Conversely, at high pressure, a type H3 hysteresis loop indicates the irregular slit-shaped pores. The nanocomposite shows a mixture of pores that may be due to the presence of surfactant toluene-4-sulfonic acid monohydrate (PTSA), which induces the nucleation of monomers through ice pores in one dimension that helps to form a polyaniline fiber network with nanoparticles at the junction. For the nanocomposite, the N2 adsorption-desorption isotherms indicates a H1 hysteresis loop, followed by a type H3 hysteresis, suggesting that Zn/V₂O₅ retains its mesoporous nature even after incorporation in polyaniline. However, some pore shrinkage is found in the distribution of the pore size. The specific surface area of PANI, Zn/ V₂O₅ and 3 wt% of PANI-Zn/V₂O₅ nanocomposite are 62.53 m² g^{-1} , 89 m² g^{-1} and 386 m² g^{-1} , respectively. As the crystal size increases, the surface area was found to be increased.41 From Fig. 6, it is evident that the doping of the Zn/V₂O₅ nanoparticles increases the porosity. This behaviour of the polyaniline

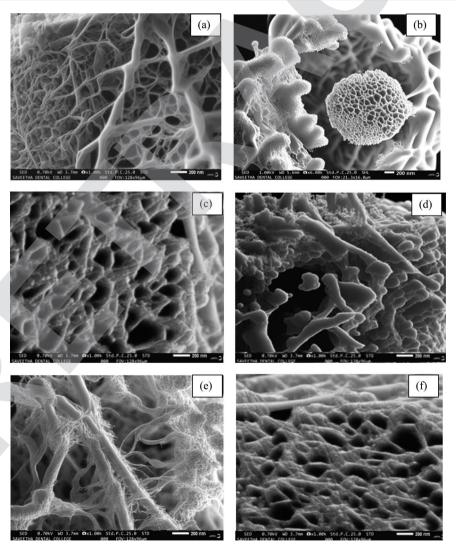
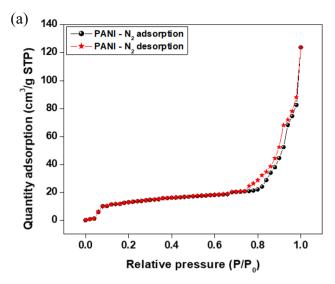


Fig. 4 SEM image of (a) PANI, (b) porous Zn/V_2O_5 nanoparticles, and (c-f) 1 wt%, 2 wt%, 3 wt% and 4 wt% of PANI-Zn/ V_2O_5 nanocomposites.



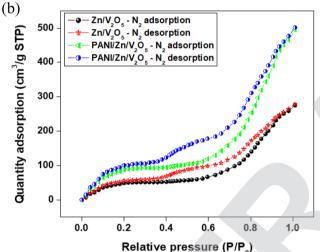


Fig. 5 Surface area analysis using Brunauer–Emmett–Teller (BET) analysis: N_2 adsorption–desorption isotherm of (a) PANI, Zn/V_2O_5 and (b) 3 wt% of the PANI- Zn/V_2O_5 nanocomposite.

nanocomposite can also be explained based on the concept of nucleation and crystal development. In the case of the nanoparticles, the number of crystal defects decreases with an increase in concentration. This may be due to the lower number of atoms per unit area.⁴²

The Barrett-Joyner-Halenda (BJH) method is employed to determine the distribution of pore size in the polyaniline nanocomposite, as shown in Fig. 6. It is observed that the average pore size of the PANI, $\rm Zn/V_2O_5$ and 3 wt% of PANI-Zn/ $\rm V_2O_5$ nanocomposite was found to be 1.93 nm, 3.86 nm and 1.89 nm, respectively.⁴³ It is important to note that the nanocomposites have a mesoporous structure after doping nanoparticles, and the pore diameter increases as the specific surface area decreases. The mesoporous structure and abundant gaps in the nanocomposite have advantages for achieving the desired hydrogen storage capacity of the nanocomposite.⁴⁴

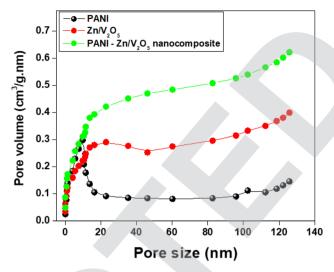


Fig. 6 BJH pore size & volume analysis-Brunauer-Emmett-Teller (BET) of PANI, Zn/V_2O_5 and 3 wt% of PANI- Zn/V_2O_5 nanocomposite.

DC conductivity

The temperature-dependent DC conductivities of polyaniline and PANI-Zn/ V_2O_5 nanocomposites fibers are shown in Fig. 7. The results obtained from the temperature-dependent conductivity of polyaniline and its nanocomposite fiber shows the increase of conductivity with an increase in temperature from 25 °C to 200 °C. This may be due to the linear enhancement in the hopping of polarons and bipolarons from the valence band to the conduction band. The increase in DC conductivity due to the increase in temperature because of the reduction in activation energy (E_a) is related to a shift in the Fermi level of doped Zn/V_2O_5 nanocomposites, as shown in Table 1. The temperature reliance of the conductivity of the PANI nanocomposites demonstrates a distinctive semiconductor nature, and it can be articulated by the one-

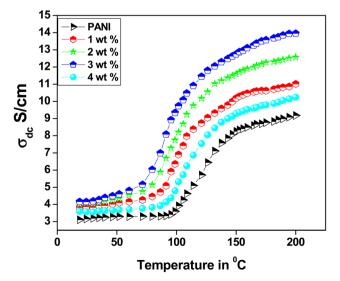


Fig. 7 DC conductivity of PANI and its nanocomposites.

Table 1 Activation energy of the nanocomposites

Sl no.	Samples	Slope value (B)	Energy (J)	Activation energy (E_a) in eV
1	PANI	0.42457	3529,291	-2.202
2	1 wt%	0.49131	4084.751	-2.549
3	2 wt%	0.56573	4703.229	-2.935
4	3 wt%	0.59763	4968.695	-3.101
5	4 wt%	0.47091	3896.186	-2.431

dimensional variable range hopping (1D-VRH) model predicted by Mott and Davis, and is as follows;

$$\rho(T) = \rho_0 \exp\left[\left(\frac{T_0}{T}\right)^{1/p}\right]$$

where T_0 is the characteristic hopping temperature, ρ is the exponential factor, and the pre-exponential factor ' ρ_0 ' is because of the lower temperature 'T'. According to Mott and Davis, the significant change in the DC conductivity shows that the conduction transpires largely in extended polymer chain states. 39 A smaller value of σ_0 denotes a large variety of localised states, and indicates that the conduction transpired via the hopping of charge carriers from the valence bands to the conduction bands. The values of σ_0 in the polyaniline fibre configuration are of the order of 13.8 S cm⁻¹ for 3 wt% of PANI-Zn/V₂O₅ nanocomposites, amplifying conduction due to the hopping of charge carriers. This is because of the wide range of localised states available within the nanocomposites. We may infer from the results that the increase in the nanocomposite conductivity is due to the hopping process. 46-48 The conduction mechanism can also be explained by the formation of polarons and bipolarons. The transport characteristics of polyaniline nanocomposites are significantly affected by the charge injection caused by polarons and bipolarons. Due to the strong lattice interaction, these self-localized defects are linked to various polyaniline backbone deformations and quantum states that are located in the energy gap.49

Three stages of conductivity are visible in the polyaniline nanocomposites' conductivity as a function of temperature. The first step's nearly constant temperature range of 25 to 100 degrees celsius could be caused by the polarons and bipolarons not having enough energy to shift from one low energy state to a higher one. In the second step, the mobility of the electron charge system causes a progressive increase in conductivity between 100 and 150 °C. In the third step, an exponential increase in conductivity is observed between 150 and 200 °C. This could be because of the usual behaviour of polyaniline semiconductors, which is the hopping of polarons and bipolarons from the lower energy state to the excited state. The highest conductivity of a 3 wt% of the polyaniline-Zn/V₂O₅ nanocomposite is reported to be 13.8 S cm $^{-1}$.

6. Cyclic voltammetry

A functioning electrode was created using a polyaniline-coated polyester sheet. As a conducting substance, polyaniline and

its nanocomposites were used, while polystyrene (PS) was used as a coating material. Unaccompanied polyaniline cannot generate a covering with adequate mechanical properties. As a result, polystyrene was coated as a support material in the fabrication of a covering comprising conductive polyaniline. The coating solution is produced and deposition is performed as follows. 1 g polyaniline and 1.27 g camphorsulfonic acid $(C_{10}H_{16}O_4S)$ (CSA) were dissolved in 20 cm³ of chloroform. After that, 1.00 g of polystyrene was added to the solution. The coating solution was created by magnetically swirling the solution for 24 hours. A polyaniline and camphorsulfonic acid chloroform solution was prepared, and a polystyrene solution was added to it. A polymer coating solution was made from the resultant solution. Using the aniline monomeric unit to calculate polyaniline, camphorsulfonic acid and polyaniline is combining to form a PANI-CSA salt in a 2:1 molar ratio. The polyaniline and CSA salt was readily soluble in chloroform at this ratio. This blend was sufficiently conductive; thus, the experiment's PANI: PS weight ratio was set at 1:1.55-58 The electric double layer capacitance (EPLC) properties are shown by the cyclic voltammetry (CV) curves of PANI and PANI-Zn/V₂O₅ nanocomposite in Fig. 8, which have a rectangular shape. On the other hand, the PANI CV curve displays the typical CV feature of PANI, which is ascribed to the reduction-oxidation peaks of 0.93 V and 0.24 V. The two peaks are assigned to PANI's redox conversion from a semiconducting to a conducting state and pernigraniline.59

7. Hydrogen sorption measurements of the PANI nanofiber

Volumetric hydrogen sorption experiments are critical for PANI fiber reactions when storing hydrogen. Experiments on hydrogen absorption were carried out at 60 $^{\circ}$ C in a high-pressure (H₂ 80 bar) reservoir. The volumetric isothermal analyses were performed on the Hy-Energy PCTPro 2000 sorption apparatus. This device is fully automated and has an

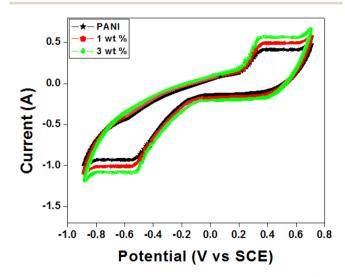


Fig. 8 Cyclic voltammetry (CV) curves of PANI and PANI-Zn/ V_2O_5 nanocomposites.

integrated 170 bar PID-pressure regulator controlled to meet Sievert's specifications. The HyDataV2.1 Lab-View program was used to inspect subroutines software for purging hydrogen, leak testing, and PCT.

A Schlenk flask with a rubberized cap was filled with the anionic surfactant of toluene-4-sulfonic acid monohydrate (PTSA)-based polyaniline and PANI-Zn/V₂O₅ nanocomposite fibres. The flask was then dried under vacuum at 70 °C for 60 minutes. Before being transferred to a high-pressure hydrogen reactor in a glove box with inert nitrogen gas, polyaniline and its nanocomposites were thoroughly dried.60-63 To assess the sorption performance, a volumetric setup with high hydrogen pressure was connected to the reactor and it was completely enclosed. Fig. 9 illustrates how pressure-applied hydrogen absorption changes at room temperature. Research has shown that when the pressure increases, so does the hydrogen adsorption capability.64 The hydrogen adsorption capacity of the polyaniline fibre is around 4.5 weight percent at ambient temperature, but it doubles to approximately 10.8 weight percent at 60 degrees celsius. The nitrogen (N) molecules in polyaniline are the hydrogen bond donor, and have a large number of hydrogen bond receptor sites in their molecular structure. The 3 wt% of PANI-Zn/V₂O₅ nanocomposites exhibit a high absorption capacity of 6.6% compared to other compositions of nanocomposites.65 It has been discovered that when pressure is released from 9.4 MPa to 1 MPa and the temperature is raised from room temperature to 60 °C, the hydrogen desorption rises. The increasing temperature enhances the kinetic energy of the molecules, thereby facilitating more effective interactions between absorbent materials and target substances. This phenomenon is particularly evident in gas absorption processes, where the elevated thermal conditions lead to greater molecular agitation, resulting in heightened adsorption rates. Consequently, the increased energy levels promote a more efficient transfer of species across phases. 66 It is also crucial to remember that the desorption process is

extremely sluggish at room temperature, which could be because the polyaniline backbone molecules have strong N=H bonds. At room temperature, polyaniline and PANI-Zn/ V_2O_5 nanocomposites exhibit hydrogen desorption at rates of 78% to 86% for 3 weight percent, respectively.⁶⁷

Hydrogen can adsorb two ways, as shown in Fig. 10. First, an enhanced electronic transition that interacts with the hydrogen atoms is produced by the two receptors in conductive groups on the polyaniline backbone that increase in relation to the quinoid diimine units (N=B=N).⁵⁷ The H-H bond breaks through the heterolytic path to produce a hydride, bonding to the Zn^{2+} , Vi^{2+} and Vi^{3+} sites, and a proton bonds to one oxygen to generate the (H^+-H) species in the next phase, the physisorption of H_2 molecules $(H_2^*$ species).

Later, the H⁺ on the VO²⁺ + 2e⁻ + 4H⁺ \rightarrow VO³⁺ + 2H₂O site is shifted to the neighboring oxygen atom, resulting in homogenous splitting and the configuration of 2O–H hydroxyl groups is labeled (H⁺–H⁺). As seen in Fig. 8, this phase is followed by the transport of two electrons to surface vanadium oxygen sites that become reduced.^{68–70}

Fig. 11 illustrates the first hydrogen uptake of polyaniline and PANI-Zn/V₂O₅ nanocomposite fibres, which are prepared *via in situ* polymerization in an ice bath over a period and formed at room temperature. It is discovered that the absorption of the polyaniline nanocomposite fiber reaches saturation in less than 60 minutes, meaning that a temperature increase of 60 °C results in an increase of 88% of the true uptake capacity to 10.8 weight percent. However, the hydrogen gas desorption takes a longer time of 147 minutes, causing the strong N=H bonding of the polyaniline backbone benzenoid molecules and the hygroscopic nature of the Zn/V₂O₅ nanoparticles.⁷¹ To determine the hydrogen sorption efficiency, a room-temperature pressure–composition–temperature (PCT) investigation was conducted on the polyaniline fiber.⁷² After 80 minutes, an effective hydride of around 6 bar is formed by

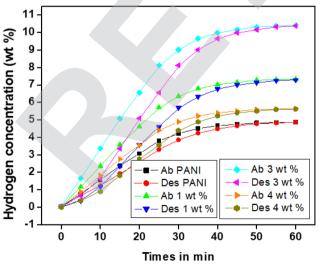


Fig. 9 Hydrogen absorption/desorption as a function of applied pressure.

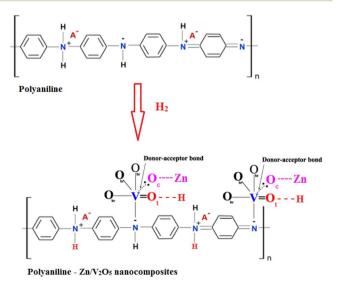


Fig. 10 Hydrogen absorption mechanism of the PANI-Zn/ V_2O_5 nanocomposites.

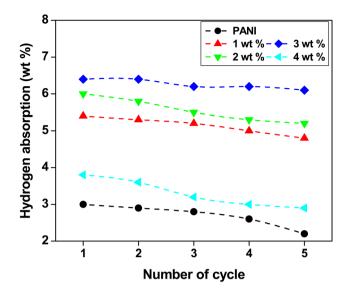


Fig. 11 Stability of the PANI nanocomposites for different cycles.

a separate variable pressure. With a linear zone of 4.5 weight percent, it reduces PANI's hydrogen uptake exponentially up to 90%. At room temperature, the total desorption capacity of 3 weight percent $\rm Zn/V_2O_5$ -doped PANI nanocomposites decreased from 10.8% to 6.6%.

8. Conclusion

Polyaniline-Zn/V₂O₅ nanocomposites were prepared by in situ oxidation polymerization method in the presence of an anionic surfactant. The prepared nanocomposites were subjected for structural analysis by FTIR and XRD studies. An FTIR spectrum confirms the characteristic peaks of the benzenoid ring stretching vibration, quinoid ring and metal oxide peaks. The XRD pattern confirms the orthorhombic structure with the α phase of Zn//V₂O₅, which has an interlayer spacing of 0.425 nm. The SEM surface morphology confirms the formation of polyaniline nanofibers, and also revealed that doping above 3 wt% interfered with the formation of the polyaniline fibre structure. The specific surface area of PANI, Zn/V2O5 and 3 wt% of the PANI-Zn/V₂O₅ nanocomposite is 62.53 m² g⁻¹, 89 m² g⁻¹ and 386 m² g⁻¹, respectively. The DC conductivity confirms that the conductivity increases with an increase in temperature. Among all nanocomposites, 3 wt% of PANI-Zn/V2O5 shows a high conductivity of 13.8 S cm⁻¹. Cyclic voltammetry studies were performed for polyaniline and its nanocomposites. The characteristic peaks of oxidation-reduction is observed at 0.93 V and 0.24 V. Hydrogen absorption studies were carried out by volumetric sorption measurement technique. It was confirmed that at room temperature, the pristine polyaniline fibre has a hydrogen adsorption capacity of about 4.5 wt%. However, at 60 °C, its capacity doubles to around 10.8 wt%. In comparison, 3 wt% of PANI-Zn/V₂O₅ nanocomposite shows a high absorption capacity of 6.6 wt% compared with other nanocomposite compositions, which is due to the particular structural design and shape. This indicates the porous fiber in nature, and the

nitrogen (N) molecules present in the benzenoid and quinoid rings in polyaniline. Hydrogen desorption of PANI and PANI-Zn/ $\rm V_2O_5$ nanocomposites increases with the decrease of pressure from 9.4 MPa to 1 MPa by an increase in temperature from ambient temperature to 60 °C. It was also confirmed that the hydrogen absorption–desorption capacity was stable up to 96% for 3 wt% Zn/V₂O₅-doped PANI nanocomposites at room temperature.

Data availability

Data will be available on request to author.

Author contributions

Ameena Parveen: data creation, conceptualization, methodology, writing – original draft and editing, Aashish Roy: methodology, writing – original draft and editing, S. Manjunatha: conceptualization and methodology, M. Madesh Kumar: methodology and data analysis, Ameena Parveen & Aashis S. Roy: final drafting and editing.

Conflicts of 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.

Acknowledgements

The authors would like to thank the PolyTech Research Laboratory, and are grateful for partial financial support from VGST during revision of the manuscript vide ref. no. KSTEPS/VGST/KFIST-L1/GRD-1151/2022-23/672; Dated: 05.02.2024. M. Madesh Kumar acknowledge the REVA University management for funding and support for this work through a seed money grant.

References

- 1 B. Senthilkumar, P. Ashok and A. Shanmugavani, 8 Polyaniline-based nanocomposites for hydrogen storage, in Woodhead Publishing Series in Composites Science and Engineering, Polymer-Based Nanocomposites for Energy and Environmental Applications, ed. M. Jawaid and M. M. Khan, Woodhead Publishing, 2018, pp. 219–238.
- 2 N. Mahato, H. Jang, A. Dhyani and S. Cho, Recent Progress in Conducting Polymers for Hydrogen Storage and Fuel Cell Applications, *Polymers*, 2020, 12(11), 2480.
- 3 Y. Sun, D. Liu, W. Liu, H. Liu, J. Zhao, P. Chen, Q. Wang, X. Wang and Y. Zou, Fabrication of porous polyaniline/MWCNTs coated Co9S8 composite for electrochemical hydrogen storage application, *J. Phys. Chem. Solids*, 2021, 157, 110235.
- 4 B. Sakintuna, F. Lamari-Darkrim and M. Hirscher, Metal hydride materials for solid hydrogen storage: A review, *Int. J. Hydrogen Energy*, 2007, 32, 1121–1140.

- 5 N. F. Attia, S. M. Lee, H. J. Kim and K. E. Geckeler, Nanoporous polypyrrole: Preparation and hydrogen storage properties, *Int. J. Energy Res.*, 2014, 38, 466–476.
- 6 Y. Sun, D. Liu, W. Liu, H. Liu, P. Chen, J. Zhao, Y. Cheng, Q. Wang and X. Wang, Preparation of porous polyaniline/RGO composite and its application in improving the electrochemical properties of Co9S8 hydrogen storage alloy, *Int. J. Hydrogen Energy*, 2021, 46(80), 40239–40250.
- 7 N. F. Attia and K. E. Geckeler, Polyaniline as a Material for Hydrogen Storage Applications, *Macromol. Rapid Commun.*, 2013, 34, 1043–1055.
- 8 D. Tinet, M. H. Legay, L. Gatineau and J. J. Fripiat, Properties of the vanadium pentoxide hydrogen bronzes $(H_{2x}V_2O_5)$, *J. Phys. Chem.*, 1986, **90**(5), 948–952.
- 9 M. Witko and K. Hermann, Hydrogen adsorption and OH desorption at vanadium pentoxide surfaces: ab initio cluster model studies, *J. Mol. Catal.*, 1993, **81**(2), 279–292.
- 10 H. Wu, J. Du, F. Cai, F. Xu, W. Wei, J. Guo and Z. Lan, Catalytic effects of V and V2O5 on hydrogen storage property of Mg17Al12 alloy, *Int. J. Hydrogen Energy*, 2018, 43(31), 14578–14583.
- 11 G. Illing, K. Hellgardt, R. J. Wakeman and A. Jungbauer, Preparation and characterization of polyaniline based membranes for gas separation, *J. Membr. Sci.*, 2001, **184**, 69–78.
- 12 X. Gao, Z. Zhong, L. Huang, Y. Mao, H. Wang, J. Liu, L. Ouyang, L. Zhang, M. Han, X. Ma and M. Zhu, The role of transition metal doping in enhancing hydrogen storage capacity in porous carbon materials, *Nano Energy*, 2023, 118, 109038.
- 13 J. Germain, J. Frechet and F. Svec, Nanoporous, hypercrosslinked polypyrroles: Effect of crosslinking moiety on pore size and selective gas adsorption, *Chem. Commun.*, 2009, 12, 1526–1528.
- 14 Z. Ding, Y. Ma, D. Peng, L. Zhang, Y. Zhao, Y. Li and S. Han, Effects of the hierarchical pyrolysis polyaniline on reversible hydrogen storage of LiBH₄, *Progress in Natural Science: Materials International*, 2018, 28(4), 529–533.
- 15 S. Virji, R. B. Kaner and B. H. Weiller, Hydrogen sensors based on conductivity changes in polyaniline nanofibers, *J. Phys. Chem. B*, 2006, **110**, 22266–22270.
- 16 Y. Chen, H. Zhu and Y. Liu, Preparation of activated rectangular polyaniline-based carbon tubes and their application in hydrogen adsorption, *Int. J. Hydrogen Energy*, 2011, 36, 11738–11745.
- 17 A. Rahy, T. Rguig, S. J. Cho, C. E. Bunker and D. J. Yang, Polar solvent soluble and hydrogen absorbing PANI nanofibres, *Synth. Met.*, 2011, **161**, 280–284.
- 18 A. R. Phani, R. M. T. De Britto, S. Srinivasan and L. Stefanakos, Polyaniline Nanofibers Obtained by Electrospin Process for Hydrogen Storage Applications, *Int. J. Environ. Res. Dev.*, 2014, 4, 375–386.
- 19 S. S. Srinivasan, R. Ratnadurai, M. U. Niemann, A. R. Phani, D. Y. Goswami and E. K. Stefanakos, Reversible hydrogen storage in electrospun polyaniline fibers, *Int. J. Hydrogen Energy*, 2010, 35, 225–230.

- 20 W. Shen, S. Han, Y. Li, S. Yang and Q. Miao, Effect of electroplating polyaniline on electrochemical kinetics of La-Mg-Ni-based hydrogen storage alloy, *Appl. Surf. Sci.*, 2012, 258(17), 6316-6320.
- 21 M. U. Jurczyk, A. Kumar, S. Srinivasan and E. Stefanakos, Polyaniline-based nanocomposite materials for hydrogen storage, *Int. J. Hydrogen Energy*, 2007, 32, 1010–1015.
- 22 B. H. Kim, W. G. Hong, S. M. Lee, Y. J. Yun, H. Y. Yu, S.-Y. Oh, C. H. Kim, Y. Y. Kim and H. J. Kim, Enhancement of hydrogen storage capacity in polyanilinevanadium pentoxide nanocomposites, *Int. J. Hydrogen Energy*, 2010, 35, 1300–1304.
- 23 J. Germain, J. M. J. Frèchet and F. Svec, Hypercrosslinked polyanilines with nanoporous structure and high surface area: Potential adsorbents for hydrogen storage, *J. Mater. Chem. A*, 2007, 17, 4989–4997.
- 24 Y. Chen, X. Cao, H. Zhu and Y. Liu, Preparation of a porous carbon from ferrocene-loaded polyaniline and its use in hydrogen adsorption, *Int. J. Hydrogen Energy*, 2012, 37, 7629–7637.
- 25 M. M. Li, C. C. Wang, Y. T. Zhou and C. C. Yang, Clarifying the polyaniline effect on superior electrochemical performances of hydrogen storage alloys, *Electrochim. Acta*, 2021, **365**, 137336.
- 26 M. U. Niemann, S. S. Srinivasan, A. R. Phani, A. Kumar, D. Y. Goswami and E. K. Stefanakos, Room temperature reversible hydrogen storage in polyaniline (PANI) nanofibers, *J. Nanosci. Nanotechnol.*, 2009, 9(8), 4561–4565.
- 27 M. Patel, S. Mishra and R. Verma, Synthesis of ZnO and CuO nanoparticles via Sol gel method and its characterization by using various technique, *Discover Materials*, 2022, **2**, 1–7.
- 28 J. N. Hasnidawani, H. N. Azlina, H. Norita, N. N. Bonnia, S. Ratim and E. S. Ali, Synthesis of ZnO Nanostructures Using Sol-Gel Method, *Procedia Chem.*, 2016, 19, 211–216.
- 29 P. Y. Gorobtsov, T. L. Simonenko, N. P. Simonenko, E. P. Simonenko and N. T. Kuznetsov, Preparation of V_2O_5 Thin Film by Sol–Gel Technique and Pen Plotter Printing, *Colloids Interfaces*, 2023, 7(1), 20.
- 30 A. S. Roy, Antistatic and Dielectric properties of one-dimensional ${\rm Al^{2^+}:Nd_2O_3}$ nanowire doped polyaniline nanocomposites for electronic application, *Sens. Actuators*, *A*, 2018, **280**, 1–7.
- 31 R. D. Balikile, A. S. Roy, A. Parveen, G. Ramgopal and N. Badi, Hybrid Nickel Ferrite Nanotubes Doped Polyaniline Nanocomposite and Its Dielectric Properties, *J. Electron. Mater.*, 2020, **49**, 833–841.
- 32 R. D. Balikile, A. S. Roy, S. C. Nagaraju and G. Ramgopal, Conductivity properties of hollow ZnFe₂O₄ Nanofibers doped Polyaniline Nanocomposites, *J. Mater. Sci.: Mater. Electron.*, 2017, **28**, 7368–7375.
- 33 J. N. Ansari, S. Khasim, A. Parveen, O. A. Al-Hartomy, Z. Khattari, N. Badi and A. S. Roy, Synthesis, Characterization, Dielectric and Rectification Properties of PANI/Nd₂O₃:Al₂O₃ Nanocomposites, *Polym. Adv. Technol.*, 2016, 27, 1064.
- 34 J. Zheng, C.-G. Wang, H. Zhou, E. Ye, J. Xu, Z. Li and X. J. Loh, Current Research Trends and Perspectives on

Paper

Solid-State Nanomaterials in Hydrogen Storage, *Research*, 2021, 23, 3750689.

- 35 U. Eberle, G. Arnold and R. von Helmholt, Hydrogen storage in metal-hydrogen systems and their derivatives, *J. Power Sources*, 2006, **154**, 456–460.
- 36 R. K. Joshi, S. Krishnan, M. Yoshimura and A. Kumar, Pd nanoparticles and thin films for room temperature hydrogen sensor, *Nanoscale Res. Lett.*, 2009, 4(10), 1191–1196.
- 37 H. A. Al-Aoh, N. Badi, A. S. Roy, A. M. Alsharari, S. Abd El Wanees, A. Albaqami and A. Ignatiev, Preparation of Anionic Surfactant-Based One-Dimensional Nanostructured Polyaniline Fibers for Hydrogen Storage Applications, *Polymers*, 2023, 15(7), 1658.
- 38 F. Liu, Z. Chen and G. Fang, V₂O₅ Nanospheres with Mixed Vanadium Valences as High Electrochemically Active Aqueous Zinc-Ion Battery Cathode, *Nano-Micro Lett.*, 2019, 11, 25–35.
- 39 P. Nagaraju, Y. Vijayakumar, M. V. Ramana Reddy and U. P. Deshpande, Effect of vanadium pentoxide concentration in ZnO/V₂O₅ nanostructured composite thin films for toluene detection, *RSC Adv.*, 2019, **9**, 16515.
- 40 C. Sandaruwan, H. M. P. C. K. Herath and T. S. E. F. Karunarathne, Polyaniline/palladium nanohybrids for moisture and hydrogen detection, *Chem. Cent. J.*, 2018, 12, 93.
- 41 S. Nawaz, Y. Khan, S. A. M. Abdelmohsen, S. Khalid, E. M. Björk, M. A. Rasheed and M. Siddiq, Polyaniline inside the pores of high surface area mesoporous silicon as composite electrode material for supercapacitors, *RSC Adv.*, 2022, 12, 17228–17236.
- 42 R. Rahman, P. Rani, S. Ghosh, A. Midya, A. Pathak and T. K. Nath, Engineering Hierarchical Self-Assembled PANI-/1T@2H MoS2 Nanostructure toward Ultrahigh Performance Supercapacitor Electrodes, *ACS Appl. Energy Mater.*, 2023, 6(21), 11012–11029.
- 43 H. Tan, D. Xiao, R. Navik and Y. Zhao, Facile Fabrication of Polyaniline/Pristine Graphene–Bacterial Cellulose Composites as High-Performance Electrodes for Constructing Flexible All-Solid-State Supercapacitors, ACS Omega, 2021, 6(17), 11427–11435.
- 44 B. Liu, X. Zhang, D. Tian, Q. Li, M. Zhong, S. Chen, C. Hu and H. Ji, In Situ Growth of Oriented Polyaniline Nanorod Arrays on the Graphite Flake for High-Performance Supercapacitors, ACS Omega, 2020, 5(50), 32395–32402.
- 45 U. Akhter, M. Miran, M. Susan, M. Mollah and M. Rahman, Preparation and characterization of polyaniline-silica composite material, *Bangladesh J. Sci. Ind. Res.*, 2012, 47(3), 249–256.
- 46 M. Rahim, S. Yaseen and R. Ullah, Electrochemical supercapacitor based on polyaniline/bismuth-doped zinc oxide (PANI/Bi–ZnO) composite for efficient energy storage, *J. Phys. Chem. Solids*, 2023, 182, 111610.
- 47 A. Parveen and A. S. Roy, Enhancement of microwave absorption of polyaniline-PbTiO₃ composites prepared by using sodium dodecyl benzene sulfonoic acid (SDBSA), *J. Mater. Res.*, 2013, **28**, 840–847.

- 48 A. S. Roy, H. Shruti Gopalkrishna and A. Parveen, Synthesis, Characterization, Ac Conductivity and Diode Properties of Polyaniline-CaTiO₃ Composite, *Polym. Adv. Technol.*, 2014, **25**, 130–135.
- 49 B. Getiren, H. Altınışık, F. Soysal, Z. Çıplak and N. Yıldız, N-doped reduced graphene oxide/MnO₂/co-doped polyaniline ternary nanocomposites for electrochemical energy storage applications, *J. Electroanal. Chem.*, 2023, 932, 117243.
- 50 D. Tian, H. Cheng, Q. Li, C. Song, D. Wu, X. Zhao, S. Hu, S. Chen and C. Hu, The ordered polyaniline nanowires wrapped on the polypyrrole nanotubes as electrode materials for electrochemical energy storage, *Electrochim. Acta*, 2021, 398, 139328.
- 51 K. Ran, X. Hou, Y. Huang, W. Ye, J. Wen, Y. Zhang, S. Wang, K. Cao, W. Wang, W. Xue and R. Zhao, Preparation of polyaniline intercalated V2O5 composites and study of their self-charging mechanism, *Colloids Surf.*, A, 2023, 671, 131703.
- 52 A. R. Dhanya, P. Haridoss and R. Sundara, EDA/PANI derived FeNxC with Fe-Nx active sites as room temperature hydrogen storage material, *J. Alloys Compd.*, 2024, **970**, 172596.
- 53 Y. Chen, H. Zhu and Y. Liu, Preparation of activated rectangular polyaniline-based carbon tubes and their application in hydrogen adsorption, *Int. J. Hydrogen Energy*, 2011, 36(18), 11738–11745.
- 54 M. Turgeman, G. Bergman, A. Nimkar, B. Gavriel, E. Ballas, F. Malchik, M. D. Levi and D. Sharon, Unique Mechanisms of Ion Storage in Polyaniline Electrodes for Pseudocapacitive Energy Storage Devices Unraveled by EQCM-D Analysis, ACS Appl. Mater. Interfaces, 2022, 14(41), 47066-47074.
- 55 J. Yun, I. Echols, P. Flouda, S. Wang, A. Easley, X. Zhao, Z. Tan, E. Prehn, G. Zi, M. Radovic, M. J. Green and J. L. Lutkenhaus, Layer-by-Layer Assembly of Polyaniline Nanofibers and MXene Thin-Film Electrodes for Electrochemical Energy Storage, ACS Appl. Mater. Interfaces, 2019, 11(51), 47929–47938.
- 56 W. Xinming, W. Qiguan, Z. Wenzhi, *et al.*, Enhanced electrochemical performance of hydrogen-bonded graphene/polyaniline for electrochromo-supercapacitor, *J. Mater. Sci.*, 2016, **51**, 7731–7741.
- 57 G. Mashao, K. D. Modibane, S. B. Mdluli, *et al.*, Polyaniline-Cobalt Benzimidazolate Zeolitic Metal-Organic Framework Composite Material for Electrochemical Hydrogen Gas Sensing, *Electrocatalysis*, 2019, **10**, 406–419.
- 58 J. Hu, F. Yang, C. Lai, *et al.*, Researches on a conductive polyaniline-acetylene black composite to suppress the hydrogen evolution reaction in lead-acid batteries, *J. Solid State Electrochem.*, 2022, **26**, 1153–1161.
- 59 L. Li, Y. Zhang, H. Lu, *et al.*, Cryopolymerization enables anisotropic polyaniline hybrid hydrogels with superelasticity and highly deformation-tolerant electrochemical energy storage, *Nat. Commun.*, 2020, **11**, 62.
- 60 A. Arslan and E. Hur, Electrochemical storage properties of polyaniline-, poly(N-methylaniline)-, and poly(N-ethylaniline)-coated pencil graphite electrodes, *Chem. Pap.*, 2014, **68**, 504–515.

- 61 K. Y. Yasoda, M. S. Kumar and S. K. Batabyal, Polyaniline decorated manganese oxide nanoflakes coated graphene oxide as a hybrid-supercapacitor for high performance energy storage application, *Ionics*, 2020, 26, 2493–2500.
- 62 H. D. Kyomuhimbo and U. Feleni, Catalytic and Energy Storage Applications of Metal/Polyaniline Nanocomposites: A Critical Review, *J. Electron. Mater.*, 2022, 51, 5568–5585.
- 63 S. Wang, M. Gao, K. Xian, Z. Li, Y. Shen, Z. Yao, Y. Liu and H. Pan, LiBH₄ Nanoconfined in Porous Hollow Carbon Nanospheres with High Loading, Low Dehydrogenation Temperature, Superior Kinetics, and Favorable Reversibility, ACS Appl. Mater. Interfaces, 2020, 3(4), 3928–3938.
- 64 S. Wang, M. H. Wu, Y. Y. Zhu, Z. L. Li, Y. X. Yang, Y. Z. Li, H. F. Liu and M. X. Gao, Reactive destabilization and bidirectional catalyzation for reversible hydrogen storage of LiBH₄ by novel waxberry-like nano-additive assembled from ultrafine Fe₃O₄ particles, *J. Mater. Sci. Technol.*, 2024, 173, 63–71.
- 65 M. Wu, M. Gao, S. Qu, Y. Liu, W. Sun, C. Liang, X. Zhang, Z. Li, Y. Yang and H. Pan, LiBH₄ hydrogen storage system with low dehydrogenation temperature and favorable reversibility promoted by metallocene additives, *J. Energy Storage*, 2023, 72, 108679.
- 66 E. Boateng, J. van der Zalm and A. Chen, Design and Electrochemical Study of Three-Dimensional Expanded Graphite and Reduced Graphene Oxide Nanocomposites Decorated with Pd Nanoparticles for Hydrogen Storage, *J. Phys. Chem. C*, 2021, **125**(42), 22970–22981.

- 67 Z. Li, M. Gao, J. Gu, K. Xian, Z. Yao, C. Shang, Y. Liu, Z. Guo and H. Pan, In Situ Introduction of Li₃BO₃ and NbH Leads to Superior Cyclic Stability and Kinetics of a LiBH₄-Based Hydrogen Storage System, *ACS Appl. Mater. Interfaces*, 2020, 12(1), 893–903.
- 68 Y. Du, N. Li, T.-L. Zhang, Q.-P. Feng, Q. Du, X.-H. Wu and G.-W. Huang, Reduced Graphene Oxide Coating with Anticorrosion and Electrochemical Property-Enhancing Effects Applied in Hydrogen Storage System, *ACS Appl. Mater. Interfaces*, 2017, 9(34), 28980–28989.
- 69 I. Hussain, C. Lamiel, M. S. Javed, M. Ahmad, S. Sahoo, X. Chen, N. Qin, S. Iqbal, S. Gu, Y. Li, C. Chatzichristodoulou and K. Zhang, MXene-based heterostructures: Current trend and development in electrochemical energy storage devices, *Prog. Energy Combust. Sci.*, 2323, 97, 101097.
- 70 C. K. Maity, S. De, K. Verma, M. Moniruzzaman and S. Sahoo, Nanocellulose: A versatile nanostructure for energy storage applications, *Ind. Crops Prod.*, 2023, 204, 117218.
- 71 H. Liu, W. Liu, Y. Sun, P. Chen, J. Zhao, X. Guo and Z. Su, Preparation and electrochemical hydrogen storage properties of Ti₄₉Zr₂₆Ni₂₅ alloy covered with porous polyaniline, *Int. J. Hydrogen Energy*, 2020, 45(20), 11675–11685.
- 72 Y. Chen, H. Zhu and Y. Liu, Preparation of activated rectangular polyaniline-based carbon tubes and their application in hydrogen adsorption, *Int. J. Hydrogen Energy*, 2011, 36(18), 11738–11745.