



Copper and zinc oxide anchored silica microsphere: A superior pseudocapacitive positive electrode for aqueous supercapacitor applications



Narthana Kandhasamy^a, Gopal Ramalingam^b, Govindhasamy Murugadoss^{a,*},
Manavalan Rajesh Kumar^c, Gunasekaran Manibalan^d, Rajabathar Jothi Ramalingam^e,
Hemraj M. Yadav^f

^a Centre for Nanoscience and Nanotechnology, Sathyabama Institute of Science and Technology, Chennai 600119, Tamil Nadu, India

^b Quantum Materials Research Lab (QMRL), Department of Nanoscience and Technology, Alagappa University, Karaikudi 630003, India

^c Institute of Natural Science and Mathematics, Ural Federal University, Yekaterinburg 620002, Russia

^d Department of Chemistry, Indian Institute of Technology Bombay, Mumbai 400076, India

^e Chemistry Department, College of Science, King Saud University, P.O. Box 2455, Riyadh 11451, Saudi Arabia

^f Department of Biological and Environmental Science, College of Life Science and Biotechnology, Dongguk University, Biomedical Campus, Gyeonggi-do 10326, South Korea

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ABSTRACT

Synthesis of metal and metal oxides with silica (SiO₂) for catalyst purpose is an important topic in energy application. However, preparation of the silica-based catalyst with controlled size is still limited, leading to the loss of the catalytic activity and reusability performance. Improving conductivity and surface properties of SiO₂ by decorating of suitable metal/metal oxides is a novel route to utilise the earth abundant silica for diverse application. Herein, we report highly uniform copper (Cu) and zinc oxide (ZnO) anchored SiO₂ synthesised by facile sol-gel method. The crystalline structure of SiO₂ (amorphous), Cu (cubic) and ZnO (hexagonal) were confirmed by X-ray diffraction (XRD). Chemical composition and the oxidation state of the elements present in the composites were confirmed by X-ray photoelectron spectroscopy (XPS). Microstructural and compositional information of the silica-based nanoparticle were investigated using Laser Raman, field emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM) analysis. The size of the anchored tiny nanoparticles (Cu and ZnO) on SiO₂ surface was determined from the FESEM and TEM analysis. The charge-discharge result showed high specific capacitance of 423 F g⁻¹ and 227.5 F g⁻¹ for SiO₂-Cu and SiO₂-ZnO at 4 mA g⁻¹, respectively. It was clearly observed that the silica-based composites with improved physical and electrochemical performances will be considered as promising candidate for achieving high electrical energy storage capacitor as a positive electrode.

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1. Introduction

In recent years, huge demand in energy requirement has been increased significantly due to elevate utilisation of electricity and lack of conventional energy conversion and supplies. Therefore, design and development of efficient energy storage devices is more important for supply uninterrupted energy to household and industry applications. To fulfil the requirement, renewable energy resources particularly wind, solar and hydro are considered as major

resources. However, intermittent natures of such sources are unable to provide surplus electricity during the peak hours. Therefore, the converted electricity from such an intermittent resource must be stored and utilised upon their requirements. In this regard, electrochemical energy storage (EES) devices such as battery and supercapacitor are the more ideal devices to deliver high energy and high-power density. The electrochemical capacitors (ECs) have been considered as a novel energy storage device because it has unique features like fast charge and low discharge rate, excellent power density than the lithium-ion batteries, high energy density than the conventional capacitors and has long cycle life [1–3]. In such devices, electrode materials play an important role because it determines the voltage range, capacitance and cycle life of the devices. Hence,

* Corresponding author.

E-mail address: murugadoss_g@yahoo.com (G. Murugadoss).

fabrication or selection of electrode materials is a significant process. A good electrode material should be electrochemically active, good reversibility, good rate capability, excellent specific capacity, and environmentally friendly, high stable and long cycle life, earth abundant and low cost which is being a main focus by many researchers, in recent years [4–6]. The recent progresses in nanotechnology empower the utilisation of nanomaterials in energy storage systems, especially it is a novel route for increasing power density and energy density. This size reduction improves the surface area of the materials, shortens the ion diffusion lengths, and sometimes suppresses the phase transformations in battery and supercapacitor materials [7,8]. Great interest to develop low-cost materials which is used to enhance the capacitance property in electrochemical energy storage system, carbon derivatives, transition metal oxides or hydroxides, sulphides, and conducting polymers are used as suitable electrode materials for supercapacitor. In this perspective, transition metal oxide (TMOs) electrodes-based energy storage devices have attracted great attention in research due to their high specific capacity, elevated safety, low cost and toxicity, widespread availability, multiple oxidation states and fast redox reactions [9–11]. Hence it reached a great attention owing to its numerous applications including batteries, fuel cells and especially in supercapacitors. The development of energy related research is mainly depending on the type of materials used, morphology and applications of TMOs such as size, shape, dimensionality and crystallinity [12,13]. Various TMOs like NiO, CoO, TiO₂, MnO₂, RuO₂, CuO, ZnO, SiO₂, CeO₂ and the combination of metal oxides such as, Co₃O₄/SiO₂, ZrO₂/SiO₂ and MnO₂/SiO₂ were used as electrode materials in supercapacitor in the recent years [14–21]. Among the oxides, silica dioxide (SiO₂) nanoparticles is an environmentally friendly, earth abundant, high mechanical and chemical stable and less toxic in nature [22]. Silica nanoparticles are well-known as a large number of applications like agricultural, food industries, energy storage & conversion. Interestingly, theoretical specific capacitance of SiO₂ (800 F g⁻¹) is high compared to the all-reported results with low energy density and poor cycling stability [23]. The current drawback of SiO₂ such as low electrical conductivity, and limited surface area can be overcome by using combined transition metal and metal oxides.

Therefore, composite or integrate other compound to SiO₂ to propose a signification cause on energy storage process. Several works are being done on SiO₂-based nanostructures as electrode material for supercapacitors by modifying its composition, as composite with other materials using aqueous electrolyte. For example, high specific capacitance achieved by Zhang et al. using SiO₂@C/TiO₂ hollow spheres synthesised via a template method and the specific capacitance of the fabricated electrode was achieved as 1018 F g⁻¹ at 1 A g⁻¹ [24]. Recently, Ramesh et al. synthesised SiO₂-based composite for symmetric supercapacitor fabrication using aqueous electrolyte. The composite attained higher discharge current density of 16.6 A/g with 57% retention of the initial capacitance. The role of the SiO₂ was increased specific capacitance due to the redox reaction and electrode's stability [25]. Sui et al. were achieved a high areal specific capacitance of 470.8 mF/cm² at 20 mV/s and superior cycling stability with the retention of 99.29% after 5000 cycles using SiO₂ based MnO₂/VG/ SiO₂/Si supercapacitor in aqueous electrolyte [26]. Chandra Sekhar et al. synthesised SiO₂-based electrode that Co@NiO-SiO₂ for superior electrochemical response, it demonstrated a higher capacity of 41.7 μ Ah cm⁻² and sustained up to 10,000 cycles by retaining 95.5% of its initial capacity. The SiO₂ was played as major role that improve the surface area and bestow more redox-active sites [27]. Baig et al. synthesised NiFe₂O₄/SiO₂ nanocomposite as a potential electrode material for high performance

supercapacitors. The prepared electrode demonstrated a high capacitance of 925 F g⁻¹ (154.1 mAh/g) at 1 A/g, with 95.5% capacitance retention after 5000 cycles at 20 mA/cm² [28]. Cu₂O/SiO₂ nanowires prepared at ambient temperature for electrochemical supercapacitor by Maity et al. [29], the prepared transparent composite exhibited high specific capacitance value of 550 F g⁻¹ at a scan rate of 10 mV/s. as a result, the combination of nanostructured metal or metal oxides with SiO₂ have given unique morphology, crystal structure, redox-active sites [30–33]. Therefore, the main goal of this present work is utilisation of transition metal and metal oxides along with SiO₂ for achieve better specific capacitance and capacitance retention. Particularly, Cu and ZnO are well known electroactive materials to improve electrical conductivity, surface area and specific capacitance. Herein, it is designed a simple sol-gel method for synthesis the SiO₂-based electrodes for high performance of electrochemical supercapacitor application. As a result, the as fabricated SiO₂-Cu electrode materials exhibited a superior specific capacitance of 423 F g⁻¹ at 4 mA g⁻¹ and outstanding capacitance retention of 86.3% at 5 mA g⁻¹ even after 3000 cycles.

2. Experimental details

2.1. Materials

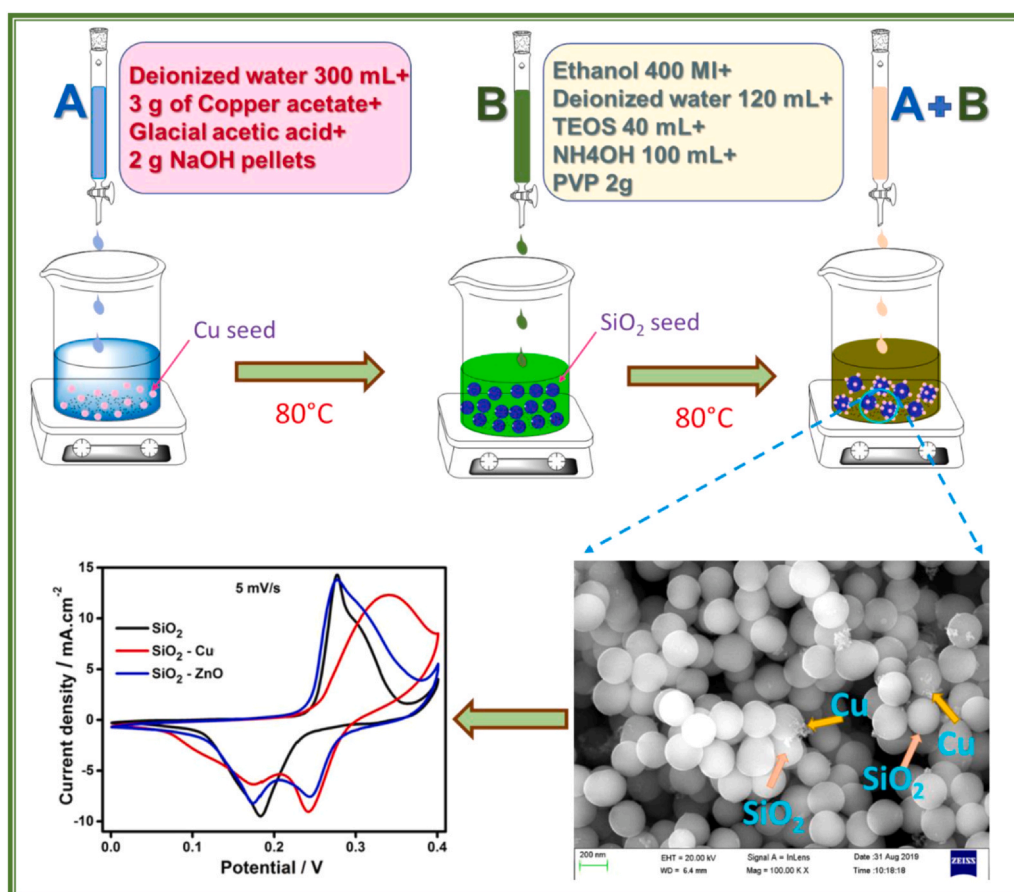
All chemicals were purchased analytical grade and used without further purification. Tetraethyl orthosilicate (TEOS), copper (II) acetate (Cu(CO₂CH₃)₂), zinc acetate dehydrates (Zn(CH₃COO)₂·2 H₂O), were purchased from Sigma Aldrich. Sodium hydroxide (NaOH), ammonium hydroxide (NH₄(OH)) and polyvinylpyrrolidone (PVP) were obtained from Nice Chemical Company were used as precursors. Glacial acetic acid and ethanol were purchased from Sisco Research Laboratories Pvt. Ltd. (SRL). All the glassware used in this work was acid washed. Ultrapure water was used for dilution and sample preparation.

2.2. Synthesis of SiO₂-Cu, and SiO₂-ZnO nanoparticles

The Cu and ZnO anchored SiO₂ were prepared by a facile sol-gel method as demonstrated in Scheme 1. The synthesis of SiO₂-Cu and SiO₂-ZnO has followed three sequential steps. In a typical synthesis of SiO₂-Cu, (A) 400 mL of ethanol and 120 mL of deionized water mixed in a 1 L beaker. Then 40 mL of TEOS was added slowly into above solution under stirring at 80 °C. Then, 2 g of PVP was added to the above mixture. Then about 100 mL of ammonium hydroxide was added into the above solution until the solution turned into gel form. (B), 3 g of copper acetate was separately dissolved in 300 mL deionized water under stirring at 100 °C. Then, 5 mL of glacial acetic acid solution was added to the above solution. Next, 2 g of NaOH pellets were directly added to the above mixture, subsequently the blue colour solution was turned into green and the dark colour. (C) Finally, the solution (B) was added onto the solution (A) drop by drop with continuous stirring. After 2 h stirring, the wet sample was washed with anhydrous ethanol and acetone for several times, and finally dried in a hot air oven at 160 °C for 2 h. For preparation of the SiO₂-ZnO, zinc acetate was used as precursor instead of copper (II) acetate following the same experimental procedure. The yield of the nanoparticles of was found to be 72.6%, 53.3%, 55.1% for pure SiO₂, SiO₂-Cu, and SiO₂-ZnO nanoparticles, respectively.

2.3. Fabrication of electrode for electrochemical studies

The electrochemical behaviour of the prepared samples was carried out using SP-300 electrochemical workstation in three cell



Scheme 1. Cu anchored SiO₂ preparation by sol-gel method (A) Cu precursor solution (B) SiO₂ precursor solution. Solution A and B mixed for prepare SiO₂-Cu nanoparticles.

electrode system. The electrochemical performances were exhibited using cyclic Voltammetry (CV), Galvanostatic Charging Discharging (GCD) and Electrochemical Impedance Spectroscopy (EIS) analysis with 3 M KOH electrolyte. The prepared SiO₂ nanocomposites were used as active materials for working electrode. Platinum wires and saturated calomel electrode (SCE) were taken as a counter and reference electrode, respectively, and a desired concentration of the sample was mixed with polyvinylidene fluoride (PVDF) which used as a binder and carbon black (super P) which used as conducting materials in 80:10:10 wt percentage, respectively. The electrode fabrication method has followed two steps: In the first step, a piece of Nickel Foam (NF) was immersed into diluted HCL solution for 10 mins after that, it was cleaned with deionized (DI) water and then the foam was sonicated using ethanol solution for 5 min to remove the outer layer of NiO from the NF surface. Subsequently, the cleaned NF was dried in oven at 60 °C and then measured weight of bare NF. The next step was to make slurry, a N-methyl-2-pyrrolidone (NMP) was used as solvent for the above mixer and grinded well and coated on NF. Next, the coated NF was dried at 100 °C for 4 h to confiscate any solvent present on the surface of coated NF. Then the modified electrode was again weighed to measure the weight different of the empty NF and coated NF. The calculated mass loading of catalyst was 2 mg. The specific capacitance (Sc) of the fabricated electrode was evaluated from CV data using the following Eq. (1).

$$Sc = \frac{1}{2} \frac{\int_{vi}^{vf} I(V) dV}{\nu \times m \times (\Delta v)} \quad (1)$$

Where, Sc represents the specific capacitance (F/g), ν denotes the scan rate (mV/s), m is mass of the active material (g), ΔV is the potential window (V), $\int I(V) dV$ denoted integrated area under the CV curve. In addition, the specific capacitance was calculated from GCD curves using discharge time (t_d) by the following relation (2).

$$Sc = \frac{I \times \Delta t}{m \times \Delta V} \quad (2)$$

Where Sc represents the specific capacitance (F/g), I denote the current density (A), Δt is the discharge time (s), ΔV represents the potential window (V) and m denotes mass (g) of the active materials. Finally, the specific capacitance of the modified electrode was determined using CV and CD data from electrochemical workstation.

2.4. Material characterisation

Crystal structure of the synthesised nanoparticles was confirmed by X-ray diffraction (XRD) using a powder diffractometer (PAN Analytical X'pert PRO Model X-ray diffractometer) with monochromatic Cu-K α radiation ($\lambda = 1.5418$ Å). The morphology and surface of the samples was characterised using field emission scanning electron microscope (FE-SEM) equipped with elemental dispersive X-ray spectroscopy (EDX) (FE-SEM-Zeiss Ultra 55 with Oxford EDX instrument). Size and structure of the samples was determined using transmission electron microscopy (TEM, JEM 2100 F) with an acceleration voltage of 200 kV. A Raman spectrum of synthesised samples was studied using Renishaw Raman Spectrometer equipped with

laser source of wavelength 514 nm. UV-Vis diffuse reflectance spectrometer was used to study optical behaviour of the samples, the UV-vis spectra were recorded between 200 and 800 nm range using a UV/Vis-NIR double beam spectrophotometer (VARIAN, Cary 5000).

3. Results and discussion

3.1. X-ray diffraction

The as-synthesised SiO_2 nanoparticles were characterised by powder X-ray diffraction (XRD). Fig. 1(a) shows XRD pattern of the pure SiO_2 , Cu and ZnO nanoparticles anchored SiO_2 microspheres. A broad peak of an amorphous nature with the equivalent Bragg angle between in the range of $2\theta = 15\text{--}30^\circ$ was recorded for all the three samples [34,35], which is replication of disorder graphitic plane (0 0 2). Martinez et al. [36] synthesised a similar amorphous SiO_2 microstructure by the sol-gel procedure, subjected it to thermal treatment, and then analysed it using the Rietveld refinement. The XRD spectrum of $\text{SiO}_2\text{-Cu}$ shows the diffraction peaks (2θ) at 43.36° , 51.08° , and 72.71° are attributed to the (1 1 1), (2 0 0), and (2 2 0) planes of Cu, respectively, which can be indexed undisputedly to cubic Cu (JCPDS No. 04-0836) [37]. The presence of the peaks at 32.07° , 34.76° , 36.61° , 47.91° , 57.03° , 63.12° and 68.22° corresponds to (1 0 0), (0 0 2), (1 0 1), (1 0 2), (1 1 0), (1 0 3) and (1 1 2) planes are clearly confirmed hexagonal structure of ZnO [38]. The strong diffraction peaks presence along with SiO_2 is clearly indicates that the hexagonal ZnO were anchored on the SiO_2 surface.

In order to investigate optical properties, UV-visible spectra were measured for the powder samples of pure SiO_2 , Cu and ZnO anchored SiO_2 nanoparticles. The obtained UV-visible absorption spectra and corresponding bang gap curve (Tauc plot) of the samples are shown in Fig. 1(b, c), respectively. Absorption peak edge of the Cu and ZnO anchored SiO_2 is significantly red shifted compared to the pure SiO_2 as displayed in the Fig. 1(b). The significant red shift associated with the well-defined microsphere thus shifting the plasmon resonance away from the interband transition of Cu material, leading to sharper plasmon bands. The band gap of the nanoparticles was determined using Tauc plots. The obtained band gap value (Fig. 1c) of 3.58 eV, 2.39 eV and 3.24 eV corresponding to pure, Cu and ZnO anchored SiO_2 nanoparticles. The obtained is clearly showed that the Cu anchored SiO_2 has very narrow band gap than other samples. The decreasing band gap is may be due to increasing the size of the microstructure.

3.2. Raman spectroscopy

Raman spectroscopy is a sensitive probe to analyse the vibrations, local atomic arrangements of the material and used to characterise the structural information. In general, four membered ring structures (D1-D4) were observed for SiO_2 samples. A small peak observed at around 490 cm^{-1} attributed to D1; A broad peak (D2) near 440 cm^{-1} corresponded to symmetric vibrations of oxygen atoms; Two other peaks at 290 and 350 cm^{-1} were attributed to D3 and D4 bands. For $\text{SiO}_2\text{-Cu}$, the characteristic Cu peaks were found at 276, 326 and 625 cm^{-1} which corresponding to A_g , B_{1g} , and B_{2g} mode, respectively [39]. Another peak was found at 500 cm^{-1} is related to Cu [40]. Raman shift observed for pure at 437 cm^{-1} , corresponding to high frequency mode of wurtzite structure from C_{6v} symmetry group [41,42]. The structural defects in ZnO are represented by the peak at 582 cm^{-1} which is assigned to E_g mode. The peak centred around 380 cm^{-1} and a small shoulder peak at 410 cm^{-1} are due to A_g mode and E_g mode frequencies, respectively [43].

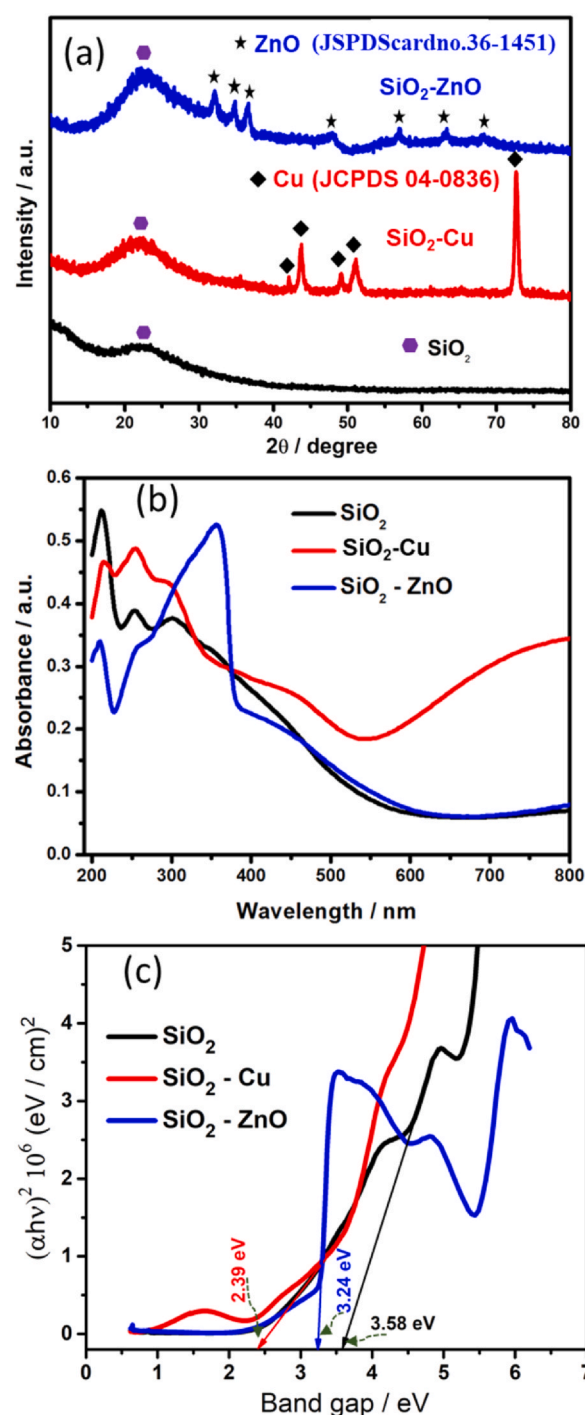


Fig. 1. (a) XRD pattern (b) UV-visible absorption spectra of pure SiO_2 , $\text{SiO}_2\text{-Cu}$ and $\text{SiO}_2\text{-ZnO}$ nanoparticles.

In the SiO_2 sample, out of the four vibrations, two major peaks of D1 and D4 were observed at 482 and 340 cm^{-1} which confirms the formation of SiO_2 shown in Fig. 2. The D2 peak (440 cm^{-1}) of SiO_2 , corresponding to the planar threefold $[\text{SiO}_3]^{2-}$ rings was not found in Raman spectrum [44]. In case of Cu anchored SiO_2 sample, a sharp peak with high intensity observed at 490 cm^{-1} was probably a blend of two different peaks: one for D1 band of SiO_2 (at 482 cm^{-1} in Fig. 2)

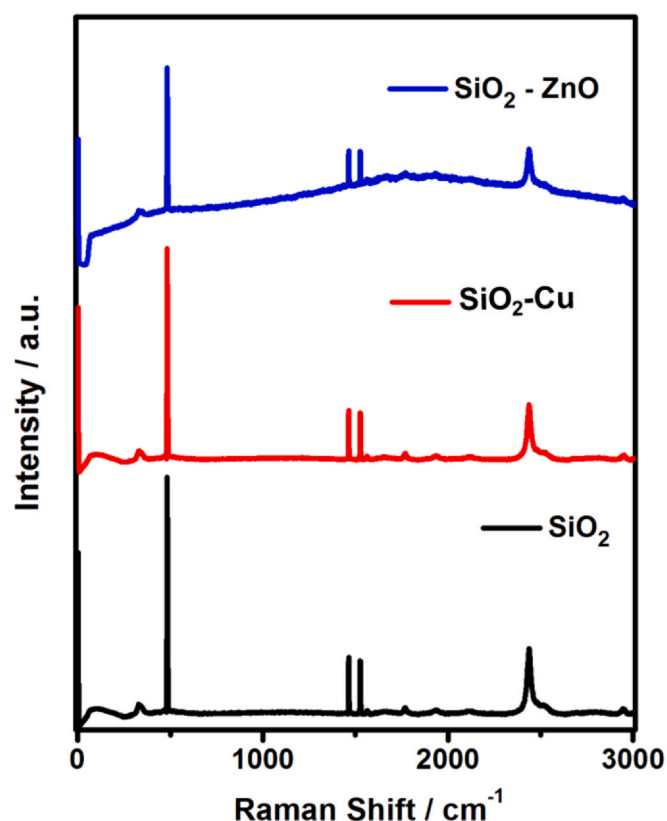


Fig. 2. Laser Raman spectra of pure SiO₂, SiO₂-Cu and SiO₂-ZnO nanoparticles.

and the other for B_{2u} mode of Cu (at 500 cm⁻¹ in Fig. 2). In case of SiO₂-ZnO sample, the obtained bands are similar to SiO₂ sample. The characteristic peak for ZnO is not observed in vibrational spectra. The Raman-active mode of ZnO appears at 470 cm⁻¹ [45]. However, two bands are overlapped by the intense band of bending vibration (D1) at 482 cm⁻¹. So that it could not distinguish the characterised vibrations of ZnO in the Raman spectrum of SiO₂-ZnO nanoparticles.

Fig. 3(a) showed the Raman spectra of the SiO₂ samples and corresponding mapping in Fig. S1(a) shows 6 different positions of sample. The positions are shown in the micrograph as dots (1–6). Fig. 3(b) showed the Raman spectra of the Cu anchored SiO₂ sample and same mapping of the samples shown in Fig. S1(b) with 6 different positions of sample and the positions are marked by dots. Fig. 3(c) showed the Raman spectra of the SiO₂-ZnO sample with 6 different positions as shown in Fig. S1(c) and the positions were marked by dots. The identical spectrum obtained at different place of the sample indicates high purity and the composition of the elements are uniformly distributed along with the sample.

3.3. Microscopy study

The FESEM images (Fig. 4a–f) shows that surface morphology of the pure SiO₂ and SiO₂ anchored with tiny Cu, ZnO nanoparticles, respectively. Especially, the Fig. 4(a–b) illustrates that very unique size and shape of pure SiO₂. To check the surface decoration on SiO₂ with Cu nanoparticles, maximum 100,000× magnification was used to operating scanning electron microscopy and exhibiting very bright uniform, monodisperse and smooth surface were found Fig. 4(c–d). Similarly, in Fig. 4(e–f) shows there is a explode growth of ZnO nanoparticles on the surface of pure SiO₂ [46–48]. This kind of

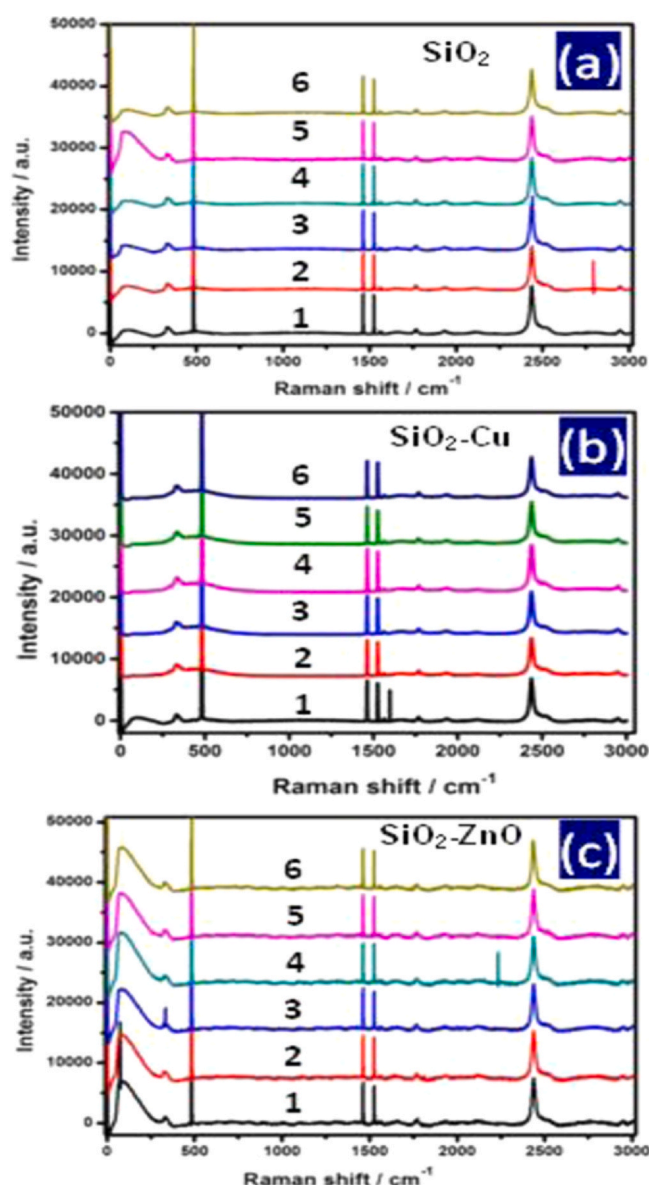


Fig. 3. Laser Raman spectra of pure (a) SiO₂, (b) SiO₂-Cu and (c) SiO₂-ZnO samples at different places.

mesopores anchored structures helps to fast ions transport in energy devices [49,50].

TEM analysis of SiO₂ nanoparticles are shown in Fig. 5(a–d). The SiO₂ prepared by sol-gel method shows like O-Si-O network structure, which are self-assembled in the tripod shape. The Selected area diffraction pattern (SAED) Fig. 5(c) (inset) denotes the ring pattern of amorphous silica oxide matrix. From the different magnification images at different places, it confirms the average particles size about 15 nm. Fig. 6(a–d) shows TEM images of SiO₂ anchored Cu nanoparticles. The TEM images are clearly shows that very much uniform pores existing in SiO₂-Cu microsphere. The cheaper and one step process demonstrated that the proposed chemical method is able to achieve perfect and agglomerations free SiO₂ based mono-dispersed microstructure. Especially, uniform pores, large surface area, thin pore walls and mesoporous structure are more advantages in diverse energy applications, particularly in supercapacitors, fuel

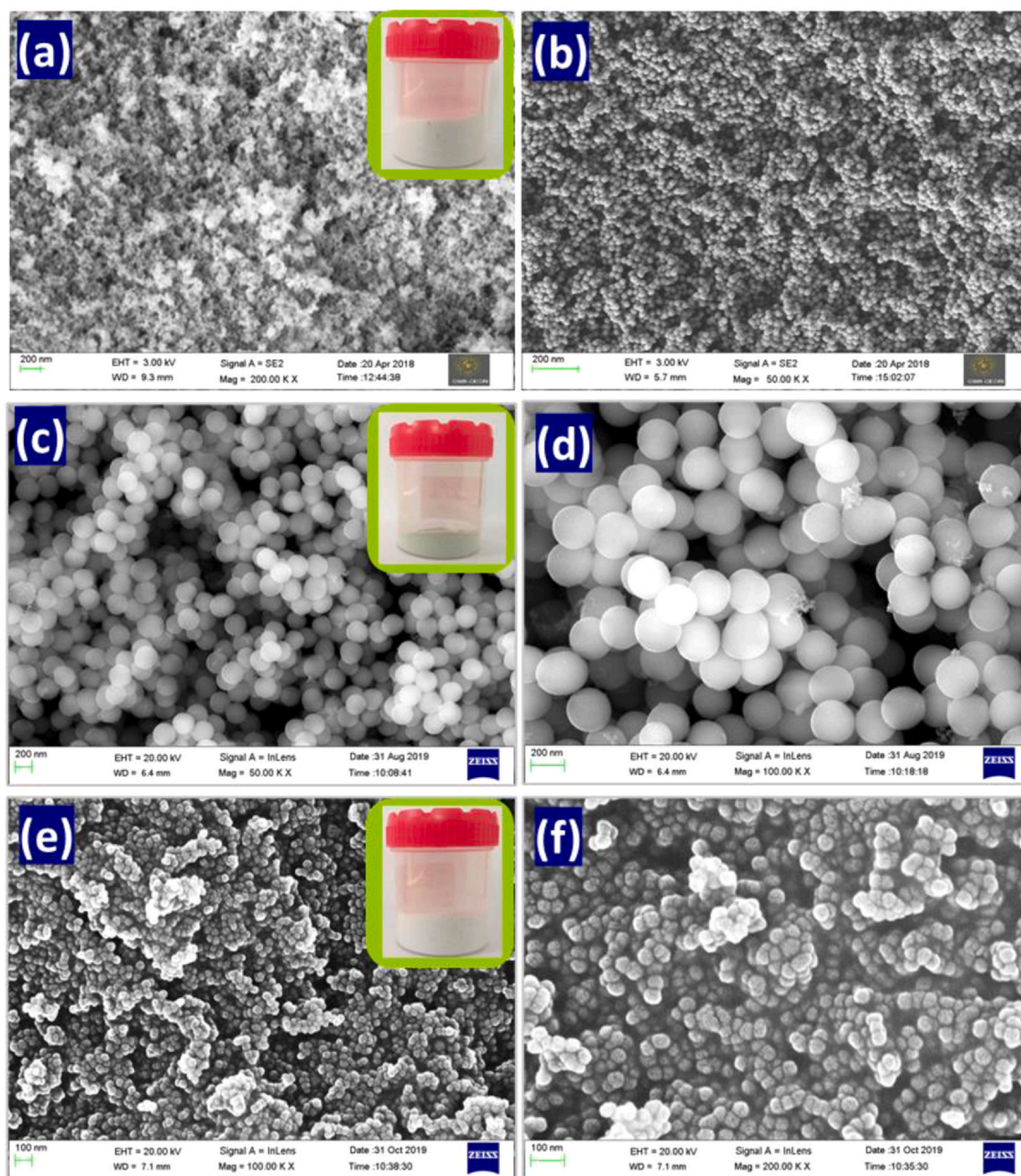


Fig. 4. FESEM images of pure (a-b) SiO_2 , (c-d) $\text{SiO}_2\text{-Cu}$ and (e-f) $\text{SiO}_2\text{-ZnO}$ with different magnifications.

cells, rechargeable batteries, and solar cell [51,52]. The uniform mesochannels can help transport ions/electrons, which is highly essential and will exhibit excellent storage properties.

Further the Fig. 6(a-d) shows that the morphology of $\text{SiO}_2\text{-Cu}$ catalyst sphere closely depends on synthesising condition and decoration amount of Cu nanoparticles. The TEM figures reveal that tiny Cu nanoparticles anchored with SiO_2 has good dispersity compared to pure silica sample, and present with different degrees of aggregation. Moreover, the amount of Cu caused the mutual adhesion between SiO_2 sphere accumulated of the Cu surface and influenced as catalysts [46]. The ZnO embedded silica pore structure are shown in Fig. 7(a-d). Nearly monodisperse nanoparticles are clearly

identified in Fig. 7(a & b). The size of ZnO nanoparticles very small and average size of 5 nm and agglomeration free identical particles can be seen the TEM images. Compare to others work, we achieved moderately well and much reduced particles sizes [47].

3.4. X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) was employed to acquire information about the surface composition and chemical state of the samples. Fig. 8(a) shows XPS survey spectrum of Cu anchored SiO_2 nanoparticles with the existence of Si 2s, Si 2p, Cu 2p, O 1s, and C 1s elements. Fig. 8(b) depicts high resolution spectrum Si 2p, it shows

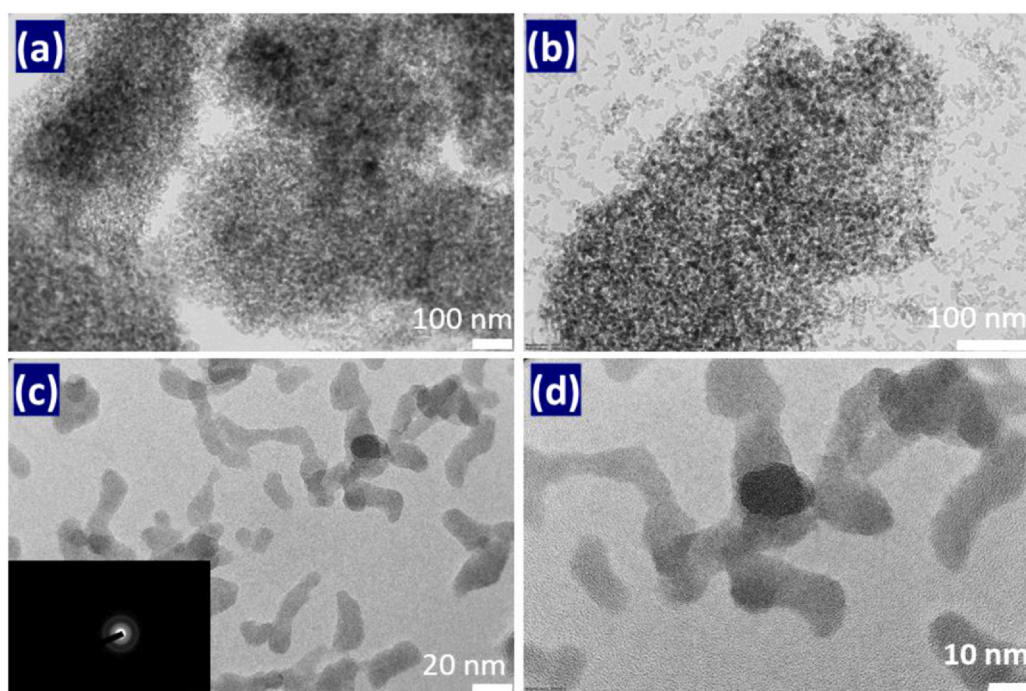


Fig. 5. TEM images of pure (a-d) SiO_2 nanoparticles with different magnifications and SAED pattern of the corresponding sample (inset of image).

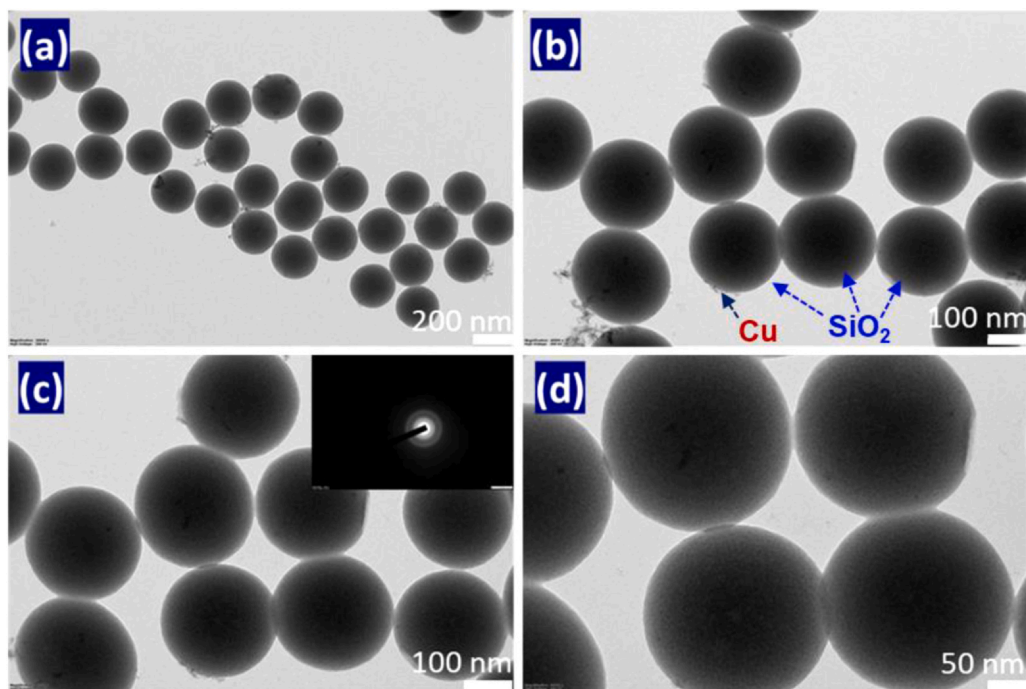


Fig. 6. TEM images of pure (a-d) SiO_2 -Cu nanoparticles with different magnifications and SAED pattern of the corresponding sample (inset of image).

strong doublet peaks with the binding energy of 100.8 eV and 103.3 eV corresponding to Si $2p_{3/2}$ and Si $2p_{1/2}$, respectively [53]. Fig. 8(c) present a high-resolution spectrum of Cu 2p peak centred at 934.2 eV which assigned to the Cu $2p_{3/2}$, along with the strong peak, two satellite peaks showed at 932.1 eV and 936.4 eV [54], it confirms

that presence of metallic Cu on the surface of SiO_2 as confirmed in both FE-SEM and HR-TEM study. This is in good agreement with the results of reported literature [55]. Fig. 8(d) displays a high-resolution O 1s spectrum has binding energy at 530.1 eV and 532.3 eV due to the metal-oxide and metal-hydroxide, respectively [14]. Fig. 8(e)

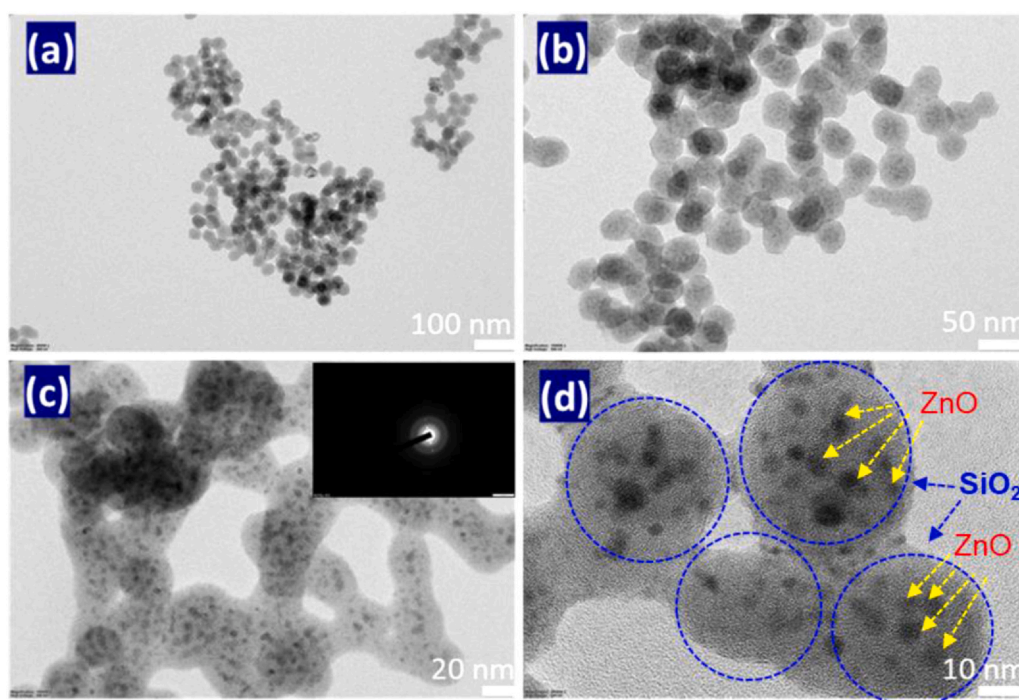


Fig. 7. TEM images of pure (a-d) SiO₂-ZnO nanoparticles with different magnifications and SAED pattern of the corresponding sample (inset of image).

depicts a high-resolution C 1s spectrum exhibit a binding energy peaks located at 283.3, 285.1 eV and 287 eV which attributed to C-C, C-O-C and O-C=O, respectively [56].

The XPS analyses were also carried out to investigate compositional information of the ZnO anchored SiO₂. Fig. 9(a) shows a complete survey spectrum of ZnO anchored SiO₂ nanoparticles in the presents of Si 2s, Si 2p, Zn 2p, O 1s, and C1s elements. As seen in Fig. 9(b), strong peaks appeared at 100.5 eV and 102.1 eV corresponds to Si 2p_{3/2} and Si 2p_{1/2}, and a satellite peak at 100.5 eV due to SiO₂ oxidation state [53]. The high-resolution Zn 2p spectrum display in Fig. 9(c) which demonstrates a peak centred at 1021.8 eV, which can be assigned to Zn 2p_{3/2}. A small shift is observed compared to pure ZnO [57]. The corresponding satellite peaks appeared at 1015, 1016.8, 1019.3, 1023.4 eV, and 1025.3 eV due to the ZnO 2p_{3/2} oxidation state, respectively [58]. This shift suggests a change in the binding state of Zn ions which can be induced by the formation of Zn-O-Si cross linking bonds at the interface between ZnO and SiO₂ matrix in ZnO anchored SiO₂ nanoparticles. A high-resolution peak showed at 531.6 eV and 533 eV (Fig. 9d) is due to metal-oxide and metal-hydroxide of ZnO and SiO₂ nanocrystals [14]. Fig. 9(e) a show the high-resolution C 1s spectra has a strong peak at 283.5 eV, 285.7 eV and 288 eV which assigned to C-C, C-O-C and O-C=O, respectively [56]. Since the electro negativity difference between the anchored particles (Cu and ZnO) with Si is less than 0.4, it is unable to formation ionic or covalent interaction. Therefore, the Cu and ZnO may be anchored with SiO₂ with physically adsorption.

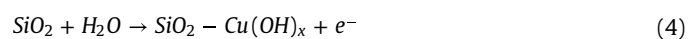
3.5. Electrochemical studies

3.5.1. Cyclic voltammetry and Galvanostatic charge discharge

Electrochemical behaviours such as CV, GCD and EIS of microsphere SiO₂, Cu and ZnO anchored SiO₂ were studied using three-electrode system. Fig. S2 (a & b) shows comparison of CV curves of all the samples tested at 5 and 100 mV/s. The CV analysis is clearly

demonstrating that significant peak shape changes observed for Cu and ZnO anchored SiO₂ microsphere [59]. An additional peak appeared along with SiO₂ characteristic peak, it ascribed due to plasmonic resonance of metal and synergetic effect metal oxides. It showed large area in CV curve of SiO₂-Cu indicates that the sample has superior capacitive behaviour than the pure SiO₂ and SiO₂-ZnO nanoparticles at lower scan rates [60,61]. However, at the higher scan rate, the CV area was reduced for SiO₂-Cu compared to the SiO₂-ZnO. The decreasing CV area at higher scan rate which may be due to redox behaviour of the metal Cu (the metal ion may allow for the cations can only adhere to the outer surface of the electrode). For comparison purpose, the GCD profile tested at 4 mA g⁻¹ is displayed in Fig. S2(c). It is observed that the SiO₂-Cu sample showed increased discharge time, it indicates high storage and discharge capacity of the sample. The obtained result is well correlated with the CV profile.

Fig. 10(a-c) depicts the CV curves of the SiO₂ and its composites, measured at the scan rates of 3, 5, 10, 15, 20, 25, 30, 40, 50, 60, 80 and 100 mV/s in the potential range of 0–0.4 V. The similar potential window for the aqueous electrolyte has been reported by several research groups [62–66]. All the CV curves exhibited the pair of oxidation and reduction peaks which represent redox peaks on the surface of the electrode and electrolyte. It was observed that the peak current position of the CV curves is shifted towards right (oxidation trend) and shifted towards left (Reduction trend) with the increase of scan rates. This is mainly due to the polarisation occurred at the electrode surface. In the process of KOH reaction, according to the redox properties of SiO₂, SiO₂-Cu and SiO₂-ZnO [67–69], the following reactions can be achieved,



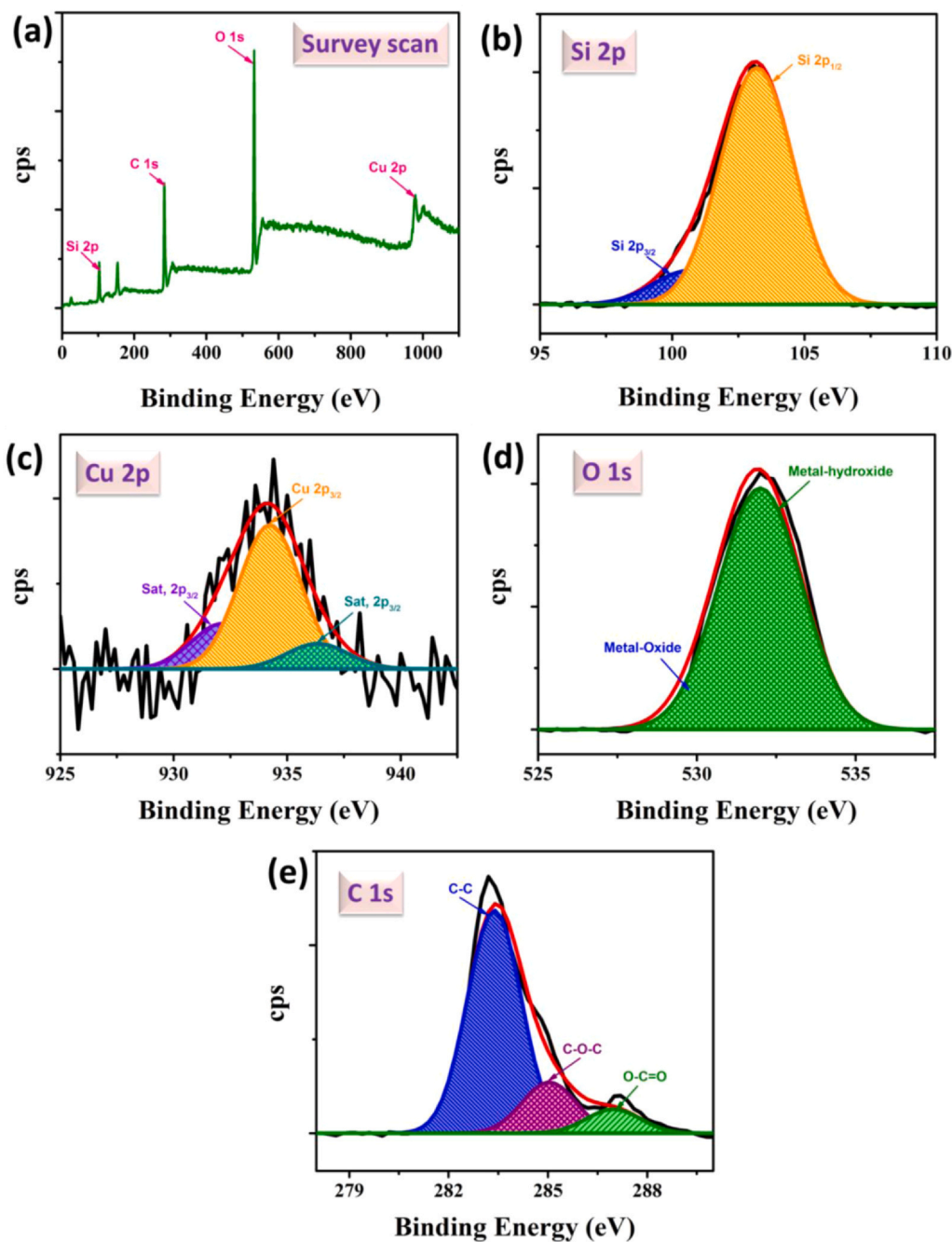
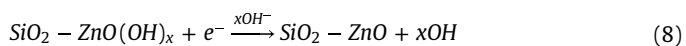
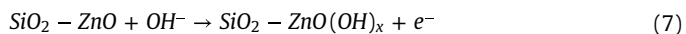
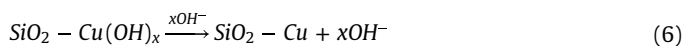
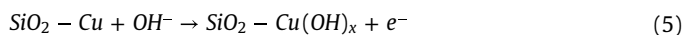


Fig. 8. XPS spectra of Cu anchored SiO₂ nanoparticles. (a) survey spectrum (b-e) high resolution spectra of Si 2p, Cu 2p, O 1s and C 1s, respectively.



In addition, the variation in peak potential separation indicates the quasi-reversible nature of the active materials in an alkaline medium (3 M KOH). Fig. 10(b, c) illustrate the shapes of the CV

curves were clearly related to the interaction of Cu and ZnO with SiO₂. But the multiple peaks at different potentials correspond to the formation of SiO₂ anchored Cu and ZnO species with different oxidation states [70,71]. This was because of the nanometal and metal oxide crystals with larger specific surface area in the electrode material generate more electrochemical reactions and large number of electric charges was stored in the electrode. The CV area was increased with increasing scan rate of the samples. The increase in peak current with increase of scan rate is due to diffusion-controlled electron transfer process in the electrochemical reaction. The CV result showed maximum specific capacitance of 206.02, 305 and

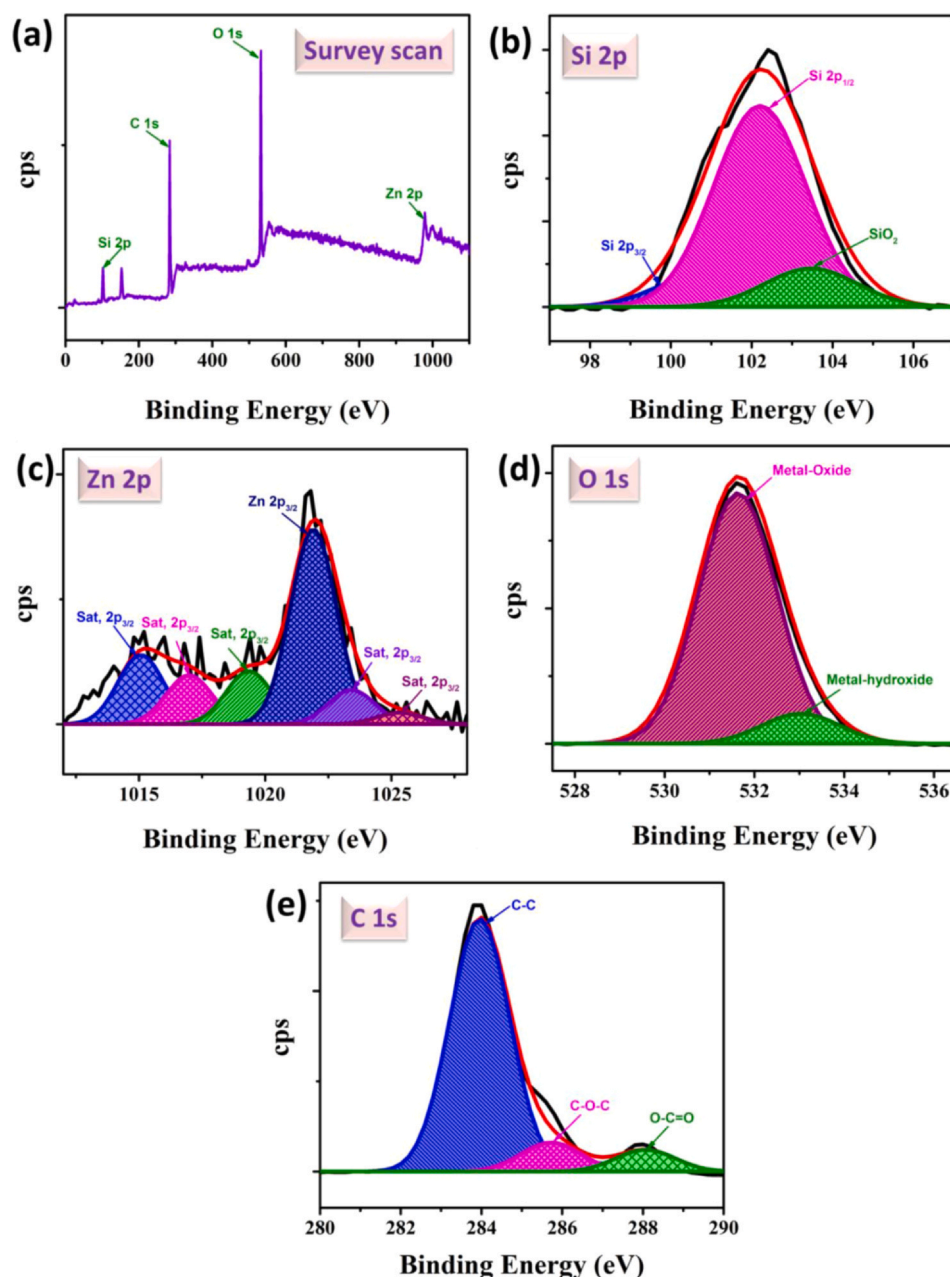


Fig. 9. XPS spectra of ZnO anchored SiO₂ nanoparticles. (a) survey spectrum (b-e) high resolution spectra of Si 2p, Zn 2p, O 1s and C 1s, respectively.

283.89 F g⁻¹ for SiO₂, SiO₂-Cu and SiO₂-ZnO, respectively at scan rate of 3 mV/s. The observed redox peaks in CV curves confirms the existence of pseudocapacitive behaviour which may occur due to the presence of Cu and ZnO with SiO₂ microsphere. Moreover, the SiO₂-Cu shows a larger area of CV curves than pure SiO₂ and SiO₂-ZnO, as a result higher specific capacitance values achieved the Cu anchored SiO₂.

GCD profile tested at various current densities for all three samples (SiO₂, SiO₂-Cu and SiO₂-ZnO) at potential range of 0–0.4 V are displayed in Fig. 10(d-f). It has been shown that the energy storage mechanism of the electrode material was a typical Faraday storage mechanism which is evidenced from CV and GCD studies.

The specific capacitance decreased with the increase of current density because the REDOX reaction rate was relatively slow at high current density [72]. The as-prepared samples delivered as high as specific capacitance of 164, 423 and 227.5 F g⁻¹ for SiO₂, Cu and ZnO anchored SiO₂ at current density of 4 mA g⁻¹, respectively. The obtained result demonstrated high specific capacitance value compared to the reported literature as presented in Table 1. This proved that the SiO₂-Cu showed the high specific capacitance than pure SiO₂ and SiO₂-ZnO samples. Moreover, the current density of the Cu anchored SiO₂ electrode is clearly shows higher discharge time than that of the ZnO anchored SiO₂ electrode. This is mainly attributed to the enlarged surface area and the increased ionic transport from SiO₂

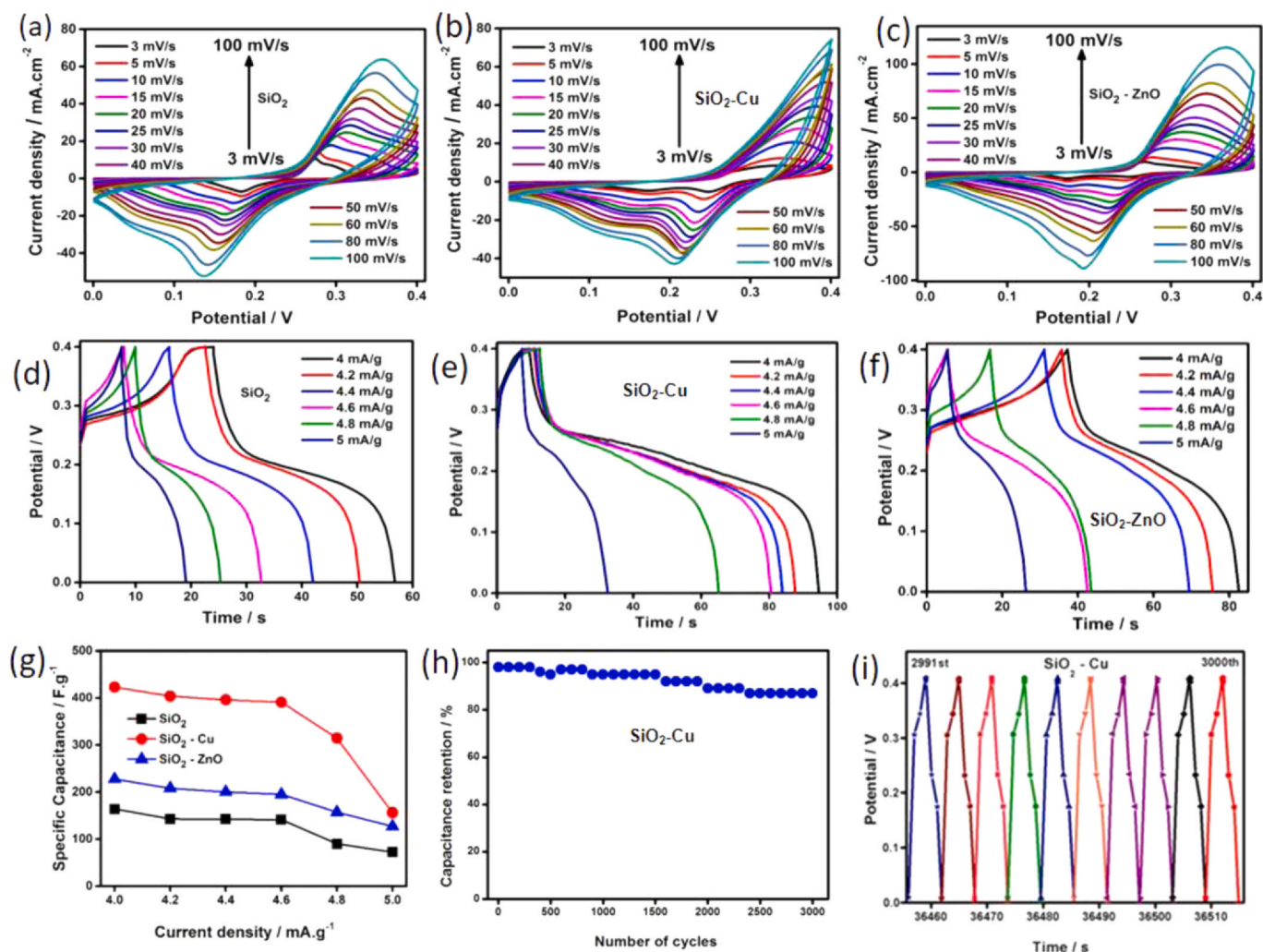


Fig. 10. (a-c) CV curves of SiO₂, SiO₂-Cu and SiO₂-ZnO electrodes for different scan rate at 3 M KOH electrolyte solution, (d-f) Charge-discharge curves of SiO₂, SiO₂-Cu and SiO₂-ZnO electrodes. (g) Specific capacitance calculated from GCD (h) Capacitance retention of SiO₂-Cu nanoparticles for 3000 cycles (i) Charge-discharge stability of SiO₂-Cu nanoparticles for last 10 cycles.

Table 1

Comparison of the specific capacitance of Cu and ZnO anchored SiO₂ electrodes with other reported SiO₂-based materials.

Electrode material	Electrolyte	Specific capacitance/F g ⁻¹	Capacitance performance	Ref.
GPE+SiO ₂	EMISF	58	91% of capacitance after 900 cycles	[5]
SiO ₂ /Carbon	1 M KOH	260	97% of retention after 5000 cycles	[13]
SiO ₂ microsphere	–	298	91.53% after 1000 cycles	[19]
Cu nanowire/SiO ₂ electrode deposition	Cu ₂ O-SiO ₂	550	73% capacitance retention after 900 cycles	[29]
SiO ₂ -Cu	3 M KOH	316	88.3% of the capacitance retention after 3000 cycles	This Work

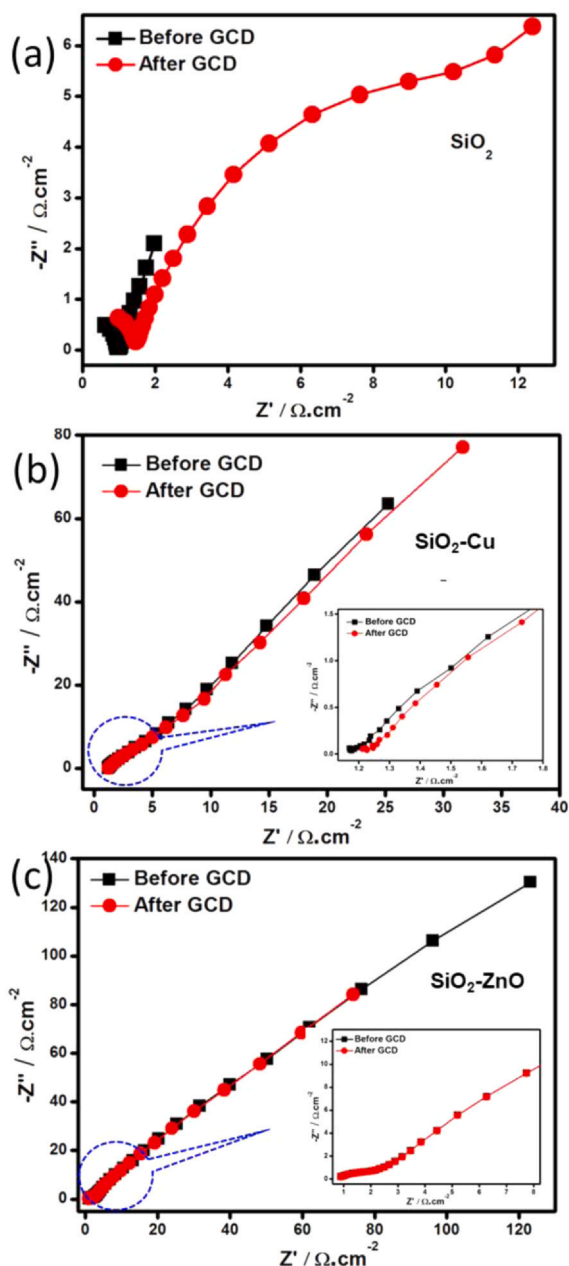
electrode to the inner layers via the Cu species [39]. On the other hand, the increasing specific capacitance for the SiO₂-Cu may be due to characteristic of the metal with segregated particles permits better permeation of the electrolyte ions at lower current [73,74]. Fig. 10(g-i) depicts over all specific capacitance of all the samples calculated from GCD data, cycling stability of SiO₂-Cu and last 10 cycles of CD, respectively [75–77]. The cycling stability study shows good capacitance retention of SiO₂-Cu [29]. Moreover, these samples delivered 86.3% capacitance retention after 3000 cycles at 5 mA g⁻¹ current density. The comparative study of aqueous supercapacitor positive electrodes [78–83] shown in Table 2.

3.6. Electrochemical Impedance Spectroscopy (EIS)

Electrochemical impedance is also an important analysis to find the frequency response at the electrode/electrolyte interface and its profile between imaginary components (z'') of its impedance against real component (z'), resistivity [35]. Nyquist plots of the samples are shown in Fig. 11(a-c). The curve showed in Fig. 11(a-c) recorded at 100 kHz to 1 Hz before and after GCD analysis, respectively. The EIS spectra of the samples showed semicircle (inset figure) at high frequency followed by linear spike at low frequency; the inclined linear spike indicating the partial diffusion or surface redox reaction of the samples. In the high

Table 2
Aqueous supercapacitor positive electrodes.

Electrode	Potential (V)	Electrolyte	SC (F g^{-1})	Energy density (Wh kg^{-1})	Power density (W kg^{-1})	Ref.
ZnO/N-OHPC	0.1–0.5 (vs SCE)	6 M KOH	250	–	–	[1]
CeO ₂ @NiO	0–0.45 (vs SCE)	1 M KOH	317	11	750	[20]
NiO/CuO	0–0.4 (vs SCE)	6 M KOH	280	–	–	[78]
NiO-3 Nanoflakes	0–0.45 (vs Ag/AgCl)	2 M KOH	401	–	–	[79]
NiO-4 Nanoflakes	0–0.45 (vs Ag/AgCl)	2 M KOH	240	–	–	[79]
NiO-5 Nanoflakes	0–0.45 (vs Ag/AgCl)	2 M KOH	206	–	–	[79]
3D nickel foam/UGF/CNTs/NiO	0–0.45 (vs SCE)	6 M KOH	575.6	–	–	[80]
NiO/NF	0–0.4 (vs SCE)	5 M KOH	235	–	–	[81]
3D Ni@NiO core shell	0–0.4 (vs SCE)	3 M HCL	2 F cm^{-2}	1.06 mWh cm^3	0.42 W cm^3	[82]
CeO ₂ /G	0–0.5 (vs SCE)	3 M KOH	208	–	–	[83]
SiO ₂ -Cu	0–0.4 (vs SCE)	3 M KOH	305	–	–	This work

**Fig. 11.** (a–c) Nyquist plot of SiO₂, SiO₂-Cu and SiO₂-ZnO electrodes, respectively.

frequency region, the intersection with the real axis (z') represents the equivalent resistance of electrolyte (R_s), while the diameter of the semicircle in high frequency range corresponds to the charge transfer resistance (R_{ct}) at the electrode–electrolyte interface. From the Fig. 11(b) the semicircle for SiO₂-Cu is smaller than that of other samples such as pure SiO₂ and SiO₂-ZnO at the high frequency range and it also shows the low contact resistance at the active material interface and low combination resistance of ionic resistance electrolyte. It clearly indicates good charge transfer which is important for charge storage and electronic conductivity. In the low frequency range, Warburg impedance corresponds to the SiO₂-Cu straight line slope is steeper than the pure SiO₂ and SiO₂-ZnO indicating shorter ion diffusion between electrode surface and electrolyte.

4. Conclusions

In summary, we have prepared Cu and ZnO anchored SiO₂ nanoparticles using industrial-scale adoptable facile sol-gel method. The synthesised nanoparticles showed highly uniform size with good crystal quality. The Cu and ZnO anchored silica showed excellent supercapacitor performance at 3 M KOH. Because of the good conductivity and strong synergistic effect between Cu and ZnO with SiO₂, the silica-based electrode exhibits high discharge specific capacitance of 423 F g^{-1} and 227.5 F g^{-1} at current density of 4 mA g^{-1} , respectively. The specific capacitance value for Cu and ZnO anchored silica showed considerably higher than those of all the previously reported SiO₂-based supercapacitor electrodes even some other metal oxides-based electrode materials. In addition, the supercapacitor showed high cycling stability (3000 cycles). From this study, it can be anticipated that high-performance with low-cost metal and metal oxides anchored SiO₂ supporting nanoparticles for electrode materials in energy storage devices such as supercapacitors, batteries, may be fabricated through rationally designing the structure of SiO₂ based nanoparticles.

CRediT authorship contribution statement

Narthana Kandhasamy: Methodology, Formal analysis, Writing – review & editing, Supervision. **Gopal Ramalingam:** Methodology, Formal analysis, Writing – review & editing. **Govindhasamy Murugadoss:** Methodology, Formal analysis, Writing – original draft, Writing – review & editing, Supervision. **Manavalan Rajesh Kumar:** Validation, Formal analysis, Supervision. **Gunasekaran Manibalan:** Methodology, Investigation. **Hamad Al-Lohedane:** Formal analysis. **Hemraj M. Yadav:** Formal analysis, Validation.

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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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jallcom.2021.161489.

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