Transition Hausmannite Nanoparticles Embedded on Uniform Carbon Micro Spheres Synthesis for Electrochemical Examination

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Abstract*—Carbon spheres wrapped by maghemite nanoparticles were synthesized through facile hydrothermal method. The structural parameters were analyzed through powder x-ray diffraction analysis. Functional groups were analyzed by Fourier transform infrared spectroscopic analysis. The prepared carbon spheres wrapped by maghemite nanoparticles morphology were investigated using scanning electron microscopic analysis. The elemental composition and distribution of elements were examined by energy dispersive spectroscopic technique with mapping. Redox property, charge discharge mechanism was done through cyclic voltammetry and galvanostatic charge-discharge studies.

***Keywords*—Maghemite nanoparticles, carbon spheres, hydrothermal, SEM, cyclic voltammetry, charge-discharge.**

I. INTRODUCTION

In past few decades, nanotechnology has been great interest in vast area of applications for developing the nanosized materials. This can be achieved through various preparation techniques. Depending upon the size of nanomaterials their properties varies that are different from the macroscopic particles which lead to unique applications. This type of changes might be due to surface-volume ratio and quantum confinement effects [1-5].

The extraordinary physical and chemical properties of carbon spheres have attracted many researchers working in various areas. In recent days, the modifications in surface such as coating/wrapping inside and outside nanoparticles were of much interest. Many properties like optical, electronic, catalytic, and magnetic can be enhanced by wrapping the metal oxide nanoparticles onto the surface of carbon spheres. This makes the optics, electronics, catalysis and magnetism fields much wide with greater improvements [6-8].

Among various transition metal oxides, the iron oxide nanoparticles are magnetic inorganic material. It has many polymorphic structures in which the magnetite, maghemite and hematite are frequently formed. It has its own unique properties in various applications such as electrochemistry, electronics and magnetism, etc. Particularly, maghemite nanoparticles have wide variety of applications such as sensing, batteries, wastewater treatment, dye dehydration, catalysis, supercapacitors, etc [1, 9-11].

In this work, we have prepared carbon sphere wrapped by maghemite nanoparticles through hydrothermal route. Herein, iron (III) chloride and glucose has taken as starting material and have shown the electrochemically active nature of the prepared material.

II. EXPERIMENTAL SECTION

A. Materials

Iron (III) chloride hexa hydrate $Fe(Cl)_2.6H_2O$ was employed to prepare the maghemite nanoparticles and glucose for the carbon spheres and NaOH pellates. The chemicals with analytical grade were bought from Sisco Research Laboratories Pvt. Ltd., Mumbai, India. Maximum purity of about 99% was employed. De-ionized (DI) water was used as solvent for throughout reaction. KOH, PVDF, and NMP were purchased from Sigma Aldrich Pvt. Ltd for electrochemical studies.

III. EXPERIMENTAL SECTION

Revised Manuscript Received on December 09, 2019.

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A. Materials

In order to prepare the sample, Glucose, $MnCl_2$, NaOH and ethanol were purchased from Sisco Research Laboratories Pvt. Ltd., Mumbai, India. Analytical grade chemicals with high purity of 99% were used. Ultra-pure Millipore deionized (DI) water was used as a solvent for whole reaction. To do the electrochemical test, activated carbon (AC), potassium hydroxide (KOH), N-methyl-2-pyrrolidinone (C_5H_9NO, NMP) and polyvinylidene fluoride ($(-(C_2H_2F_2)_n-)$, PVDF) were used and it obtained from Sigma-Aldrich (Mumbai).

B. Materials characterization

4 g of glucose were disolved in 30 ml de-ionized water and stirred for 10 min. The transperent solution was transferred into 50 ml Teflon-lined autoclave and maintain temperature at 180 °C for 8 h. Then allowed to room temp. the black pricipate was collected and dispersed under ultrasonic treatment for 10 min. the product was recollect using centrifuged with 6000 RPM and washed several times with deionized water and ethanol. Finally, the prepared sample was dried at 80 °C for 12hrs in a vacuum oven [12].

C. Synthesis of carbon sphere wrapped by maghemite nanoparticles and modified electrode preparation

The maghemite (Fe_2O_3) nanoparticles wrapped on surface of carbon spheres were prepared by hydrothermal method. 0.1 M of was dissolved in 120 ml DI water. Separately, 0.1M of $Fe(Cl)_2.6H_2O$, 0.5g of carbon spheres and 0.1 M (0.4 g) of NaOH pellets were dispersed in DI water 50, 50 and 15 ml respectively. This three solutions were stirred up to 20 min. to make a homogeneous dispersity. This two precursors (Fe(Cl)$_2$.6H2O) and NaOH were drop by drop added in to dispersed carbon spheres solution and instantly, Fe_2O_3 precipitation were formed on the surface of carbon spheres. The reaction mixture was allowed to stir up to 3 h then transferred to teflon lined autoclave and maintained at 100 °C for 10 h. The final product was washed several times with DI water and ethanol. The product was recollecting with centrifuged at 6000 RPM and dried the final product at 80 °C for 12 h in a vacuum oven [12].

The modified electrode material was prepared by employing doctor blade technique. Fe_2O_3 NPs, conductive carbon with polyvinylidene fluoride as binder in the ratio of 85:15:5, respectively. The mixture was grounded N-methyl-pyrrolidone as a solvent to make a slurry and it was coated on the surface of the Ni-foil (1×1 cm^2) and dried in an oven at 80 °C for 5 h.

D. Characterization techniques

The synthesized carbon sphere wrapped by maghemite (Fe_2O_3) nanoparticles were characterized using X-ray diffraction analysis, the structure of crystal formed were confirmed by X-ray diffraction analysis (XRD) by Bruker X-ray diffractometer (D8 advance ECO) with monochromatic wavelength range 1.5406 Å and Cu-K_α radiation source. Scanning Electron Microscope (SEM) with Energy Dispersive Spectroscopy (EDS) and mapping was used to observe the morphology, elemental distribution of carbon sphere wrapped nanoparticles using ZEISS-EVO 18 Research, Japan, and sample Fourier transform infrared spectrometer (FTIR) was employed using a Shimadzu (IR Tracer-100) spectrophotometer within the range of 4000–400 cm^{-1} using KBr pellet system. Electrochemical workstation with three electrode system (CH instrument 6008E) was used to investigate the redox nature and impedance analysis.

IV. RESULTS AND DISCUSSION

A. X-ray diffraction-structural analysis

Fig.1. shows a XRD pattern of carbon sphere wrapped by maghemite (Fe_2O_3) nanoparticles. The sharp edges and broadening of peaks implies that the prepared material were nano-crystallized with small size in nanoscale range. 30.12°, 35.67°, 43.36°, 53.84°, 57.29°, 62.64°, 71.42°, and 74.52° were the diffracted peaks matched well with JCPDS number 39-1346. These diffracted peaks were indexed to the hkl planes (220), (311), (400), (422), (511), (440), (620), and (533) respectively [13, 14 & 15]. It confirmed the prepared nanoparticles were cubic structure of Fe_2O_3 nanocrystals. The broadened line was influenced by crystallite size of the prepared nanoparticles. The crystallite size was determined from Scherrer formula given in equation (1) and hence calculated the average grain size were found to be ~22 nm.

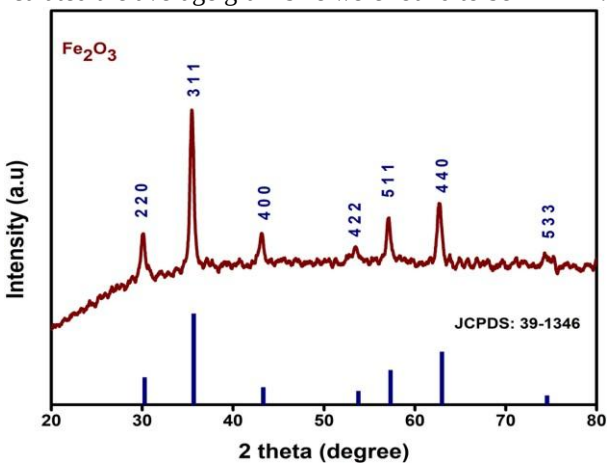

Fig. 1. XRD pattern of prepared carbon sphere wrapped by maghemite nanoparticels

B. FTIR spectral studies.

The FTIR spectrum of prepared material was shown in Fig. 2. The spectral range was fixed between 4000-400 cm^{-1}.

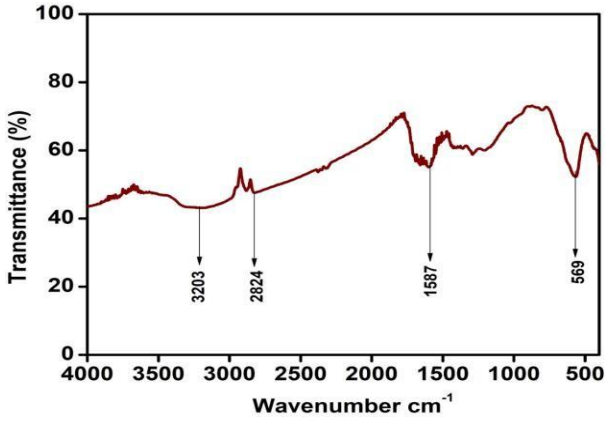

Fig. 2.FTIR spectrum of carbon sphere wrapped by maghemite nanoparticles

The stretching vibration of Fe-O was found in 569 cm^{-1}. The strong peak near 1587 cm^{-1} indicated presence of C=O. C≡C bond vibrations were observed in the peak 2824 cm^{-1}. The broad peak at 3203 cm^{-1} shows the O-H bond formation which might be due to the absorption from the surrounding as it contains mesoporous structure.

C. SEM- Morphological studies.

It was evident from the name that the prepared carbon spheres wrapped by maghemite nanoparticles were observed to be in sphere morphology. The smooth surface with the maghemite nanoparticles wrapping were evident from lower magnifications.

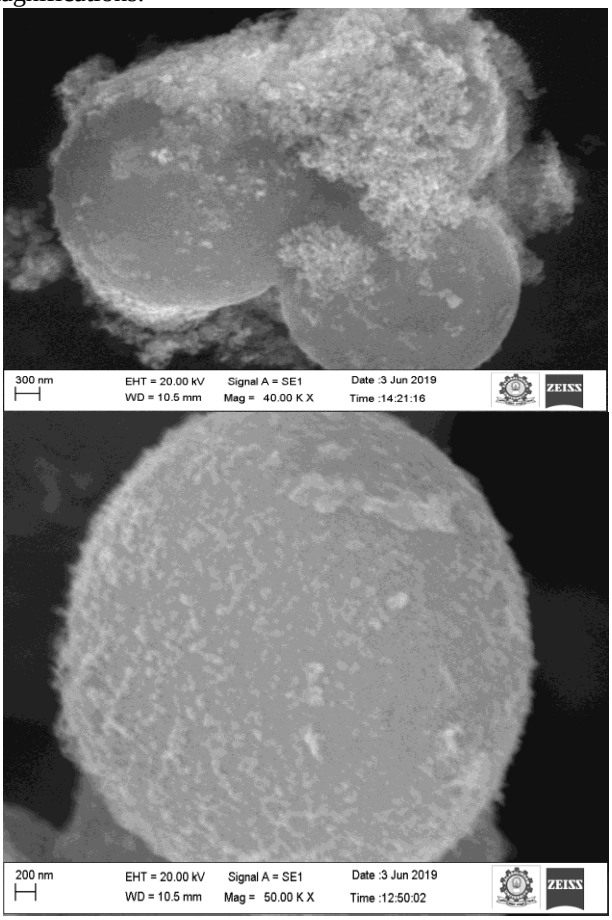

Fig. 3.SEM images of maghemite nanoparticles wrapped carbon sphere

In higher magnification of around 200 nm the maghemite nanoparticles wrapping on the surface of the carbon sphere were clearly observed [12].

D. EDS with mapping analysis

A spectrum recorded explains the purity of the prepared carbon sphere wrapped by maghemite nanoparticles. EDS spectrum with mapping images were shown in Fig. 4. The weight percentage was shown as inset in the Fig. 4. The mapping images clearly indicated that prepared carbon sphere wrapped by maghemite nanoparticles were even in distribution.

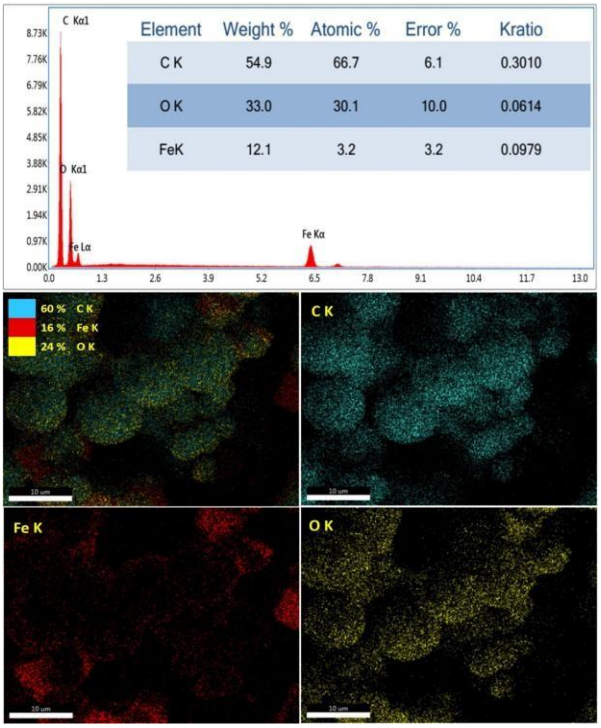

Fig. 4.EDS spectrum and mapping of prepared carbon sphere wrapped by maghemite nanoparticles

E. Electrochemical and Cyclic voltammetry analysis

The redox property of the prepared carbon sphere wrapped by maghemite nanoparticles were investigated by cyclic voltammetry studies. Fig. 5. reveals the CV graph of prepared nanoparticles with different scan rate. The potential window was fixed between 0.2 to 0.6 V. A pair of redox peaks for various scan rates implies the pseudocapacitance nature. As the characteristic peaks were observed in both cathodic and anodic region, the prepared material has been confirmed to have the capacitance nature [1, 12 &15].

F. Chronopotentiometric analysis

The galvnostatic charge-discharge curve of the prepared maghemite nanoparticles wrapped carbon sphere were shown in Fig. 6. The potential window was fixed to 0 to 0.5V. The curve was recorded with the current 0.5 mA/Cm^2. It states that the specific capacitance and storage capacity of material [10-12, 16].

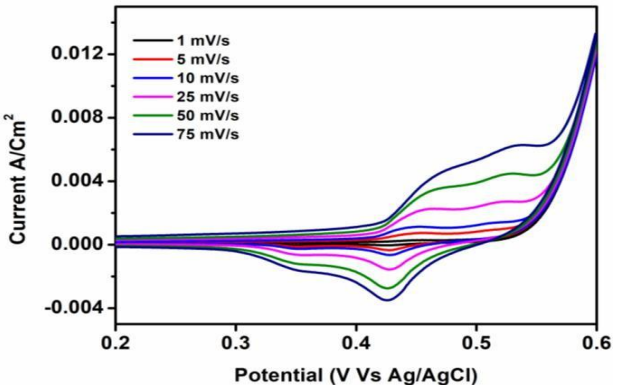

Fig. 5.CV graph of carbon sphere wrapped by maghemite nanopaticles

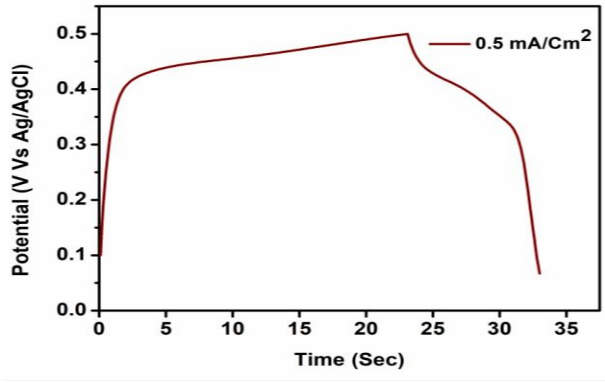

Fig. 6.GCD curve of carbon sphere wrapped by maghemite nanopaticles.

V. CONCLUSION

In summary, The carbon sphere wrapped maghemite nanoparticles were successfully prepared by effective hydrothermal method. The XRD pattern shows that the prepared mag material was cubic structure with grain size of nm. The carbon-carbon bond vibrations and metal oxide vibrations were confirmed in FTIR spectrum. These results have been co-ordinated with the EDS spectrum as the atomic and elemental weight percentage was almost same with the elemental compositions. The morphology of the prepared nanoparticles was found to have spheres shape with the maghemite nanoparticles wrapped on the surface. This was in corresponded with the mapping images as the distribution of nanoparticles were even. The redox behaviour was investigated and found to have two pair of redox peaks in anodic and cathodic region. The charge-discharge process states that the prepared material could be a pesudocapacitive material with good energy storage property.

ACKNOWLEDGMENT

The author P.D and all co-authors are very grateful to IRC, Kalasalingam Academy Research and Education (KARE) for providing and facilities.

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