BIOSYNTHESIS OF TITANIUM-SILICON DIOXIDE CORE SHELL FOR ENERGY DEVICE

***S. Thangeswari and B. Buddha kanya**

Department of Physics, St. Mary's College (Autonomous), Thoothukudi

Affiliated to Manonmanium Sundaranar University, Tirunelveli, Tamil Nadu, India

ABSTRACT

This work presents an explicated study on the biosynthesis and characterization of silica coated titanium oxide core by using *Bay Laurel* leaves extract. The resulting core TiO_2 and core shell TiO_2-SiO_2 were characterized by x-ray diffraction, scanning electron microscopy, energy dispersive spectroscopy and transmission electron microscopy. Additionally, Transmission electron microscopy exhibited that TiO_2 particles surfacewas surround by amorphous silica layer and the thickness of the amorphouslayer is estimated about 10–15 nm. The energy dispersive spectroscopy confirming the presence of elemental group in the prepared samples. X-ray diffraction data were used to find the size of the core is 26.27nm and core shell is 13.51 nm.Cyclic voltammetry analysis was used to demonstrate, the prepared core TiO_2 and core shell TiO_2-SiO_2 were efficient candidate for the energy storing devices.

KEYWORDS: Biosynthesis, Core Shell TiO_2-SiO_2,Cyclic voltammetry, Energy Device.

INTRODUCTION

The supercapacitor is also called an ultracapacitor. Compared with regular capacitors, it has higher capacitance values. It typically capacitorsstores 10 to 100 times energy per unit volume. A capacitor is a two-terminal electrical device that can store energy in the form of an electric charge. It consists of two electrical conductors that are separated by a distance. Super capacitors are classified in to three types. There are Electrostatic double layer capacitors, Pseudo-capacitors, Hybrid capacitors[1].

Core–shell type nanoparticles are a type of biphasic materials which have an inner core structure and an outer shell made of different components. These particles have been of interest as they can exhibit unique properties arising from the combination of core and shell material, geometry, and design[2].

Green synthesis of nanoparticles is becoming popular among researchers because it is a fast, cost-effective, environmentally friendly, and sustainable method.

Plant extracts play a crucial role in this process by acting as a capping agent, capturing metal ions in specific locations on the amylose helix. The texture of plant leaves and petals also influences the size of the nanoparticles and prevents them from clumping together, acting as a biotemplate [3].

In this study, the green synthesis of TiO-SiO_2 core shell using *Bay Laurel* leaves extract. Their structural features were compared by spectroscopic and microscopic techniques including XRD, SEM, EDX and TEM. Finally, the synthesized TiO2-SiO_2 were subjected to electrochemical investigations by cyclic voltammetry was determined.

MATERIALS AND METHODS

The materials used are titanium Tetraisopropoxide (TTIP), Tetraethyl orthosilicate (TEOS), ethanol and deionized (DI) water. These were purchased from Sigma Aldrich Pvt. Ltd, Tamil Nadu, India and all the chemicals were used as such without any further purification. The extracts of *Bay Laurel* was chosen for our green synthesis. This biomaterial is well known spices and easily available. Laurus nobilis was purchased from local market, Thoothukudi, Tamilnadu, India. After the purchase they were properly washed with DI water and naturally air- dried at room temperature to remove dust or any other contaminants.

The collected biomaterial was washed with double distilled water (DDW) several times to remove impurities. To prepare the aqueous green extract, 20 g *Bay Laurel* was mixed with 100 mL DDW taken in a 250 mL conical flask, and the mixture was kept in a boiling at 55°C for 30 min. The solution changed color from colorless to brownish color. Then, the mixture was cool down at room temperature and the obtained brownish color liquid was filtered using Whatman filter paper no. 41 for further use.

About 100 mL of 0.1 M $Ti[OCH(CH_3)_2]_4$ solution was taken in a 250 mL conical flask. The solution mixture was stirring to room temperature and centrifuged at 1000 rpm for 2 hours. Then, 20 ml of the filtered *Bay Laurel* extract was added drop by drop to the titanium solution while continuously stirring at 35°C for 1 hour. The resulting solution turned white in color. The obtained product was then calcinated

in a muffle furnace at 1000℃ for 1 hour. The resulting powder was collected, finely crushed, and stored in an airtight glass container for further experimentation.

Tetraethyl Orthosilicate (TEOS) (15 drops) and ethanol (50 mL) were mixed together and 50 mL of bio-extract was mixed to prepare a solution for coating of SiO_2. To the TOES solution, mechanically milled TiO_2 (1 g) NPs were added under stirred for 1 hour for dispersion. Followed by pH was monitored to achieve the requisite pH under stirring. The TOES solution and TiO_2 NPs were stirred which allowed to hydrolysis and condensation reaction to happen. Through hydrolysis and condensation, SiO_2 was coated to core TiO_2 NPs. After that the prepared core- shell TiO_2-SiO_2 NPs was washed four times, then isolated. The isolated TiO_2-SiO_2 NPs were dried under 100 ℃ for 3 h C in an oven, then kept under for 300 ℃ for 5 hours in a muffle furnace.

RESULTS AND DISCUSSION

Figure 1 presents the XRD pattern of the synthesized samples. It is observed that the well-defined TiO_2 core diffraction peaks 2θ at 25.6º, 37.9 º, 48.1º, 54.6º, 55.1º, 63.1º, 70.1º and 75.4º, which were assigned to the (101), (004), (200), (105), (211), (204) (116) and (215) crystal plane, respectively. This XRD characteristic pattern is consistent with the standard JCPDS values of anatase TiO_2 (JCPDS Card No. 21-1272) [4, 5]. As shown in Fig. 1b, the XRD patterns exhibited sharp diffraction peaks attributed to anatase of TiO_2/SiO_2 core shell. After adding SiO_2 the core peaks 2θ at 25.7º, 38.3 º, 48.5º, 54.9º, 55.3º, 63.2º, 70.2º and 75.6º, which were assigned to the (101), (004), (200), (105), (211), (204) (116) and (215) crystal plane. It is observed that the peaks value and intensity are slightly changed but same crystal plane. No peaks for SiO_2 can be observed, which indicates the metal content added during the synthesis process was too low or the metal has been well-dispersed at TiO_2 matrix in the form of small cluster. The average crystallites size (D) of the as-prepared sample is estimated using the following Scherrer's equation

$$D = k\lambda / \beta cos\theta \qquad (1)$$

where D is the crystallite size, k is a constant (=0.9, assuming that the particles are spherical), λ is the wavelength of the X-ray diffraction. β is the FWHM and θ is the angle of diffraction.

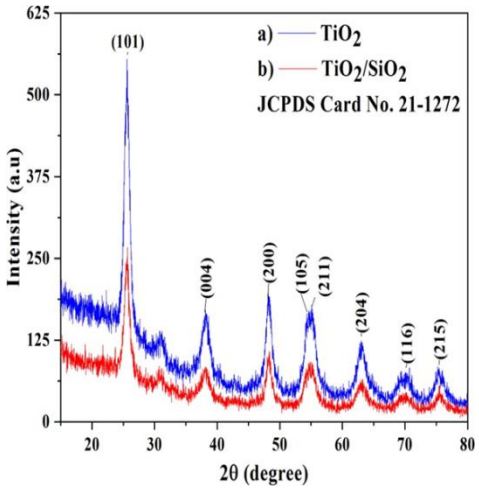


Figure1XRDpatternforTiO_2-SiO_2NPs

From the calculated crystallite size, it was found that the synthesized samples had small crystallite size with an average size of 26.3 nm and 13.5 nm for the core TiO_2 and core shell TiO_2/SiO_2, respectively. The other parameters were displayed in Table 1

Samples	Peaks (degree)	d-spacing (Å)	Size (nm)	Dislocation density(lines/m^2)	Microstrain
TiO_2	25.643	3.4739	40.579	0.6073	3.8478
	37.8787	2.3752	31.374	1.0159	3.4027
	48.1241	1.8907	12.998	5.919	6.5382
	54.642	1.6796	44.535	0.5042	1.6951
	55.0941	1.6669	11.155	8.036	6.7163
	63.078	1.4738	19.892	2.5272	3.3301
	70.0421	1.3433	12.077	6.8558	4.9993
	75.3684	1.2611	37.498	0.7112	1.5116
Averagesize: 26.27nm					
TiO_2/SiO_2	25.694	3.4671	15.216	4.3192	10.242
	38.156	2.3585	10.465	9.1303	10.13
	48.0938	1.8919	21.659	2.1318	3.9261
	54.9034	1.6722	16.717	3.5782	4.4961
	55.267	1.6621	6.6983	22.288	11.153

	63.1953	1.4713	12.668	6.2317	5.2205
	70.0735	1.3428	12.08	6.8531	4.9964
	75.4299	1.2602	12.503	6.397	4.5303
Averagesize: 13.51 nm					

Table1XRDcalculatedparameters

Figure 2 shows the SEM images of the prepared TiO_2NPs. The surface morphology of the TiO2 NPs was studied using scanning electron microscopy. The SEM images shows that the prepared TiO_2 NPs had a uniform spherical morphology. In general, the decrease in particle size is inversely proportional to the surface volume of the material. Similar trend was observed in figure 3

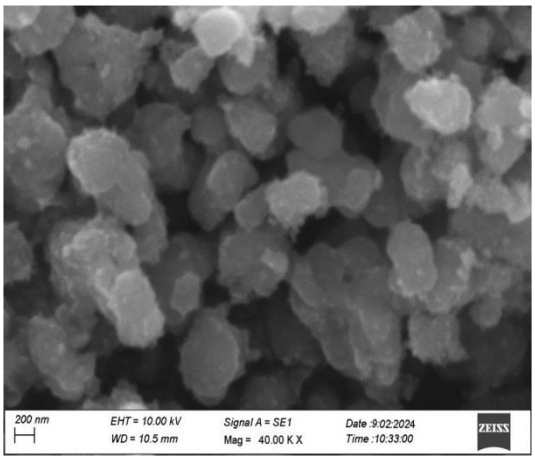


Figure2 SEM image of prepared TiO_2NPs

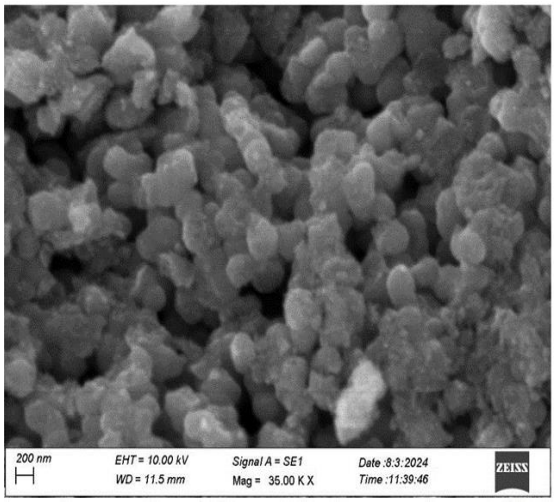


Figure3 SEM image of prepared SiO_2coated withTiO_2NPs

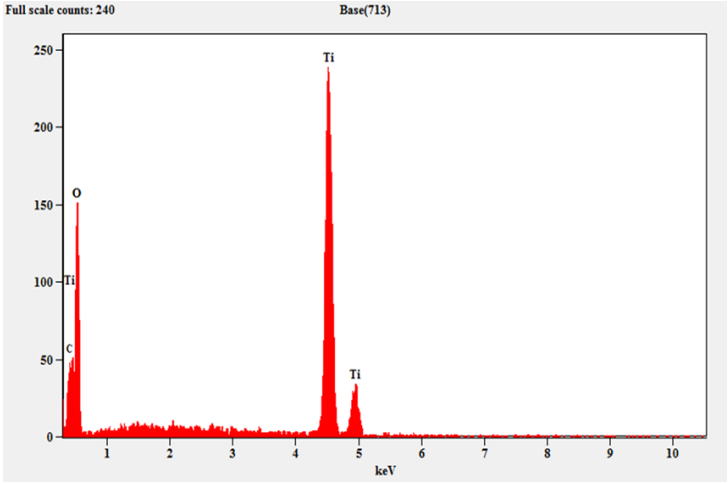


Figure 4 Energy Dispersive X-ray analysis (EDX) of TiO_2 Nano particles

EDX is performed to study the elemental compositions of TiO $_2$nanoparticles is shown in Figure4. The presence of significant peaks for Titanium (Ti) and oxygen (O) reveal the formation of Titanium Oxiden anoparticles. There are 2 peaks can be observed at about 4.5 and 5.0 keV, which corresponding to the binding energies of the titanium [6]. Thus, the formation ofTiO_2 nanoparticles is confirmed.

Element Line	*Weigh t%*	*Weight% Error*	*Atom %*
Ti K	40.05	---	66.67
C K	1.07	---	0.98
O K	58.88	±1.38	32.35
TiL	---	---	-
Total	100.00		100.00

Table2 The chemical composition of the TiO_2NPs

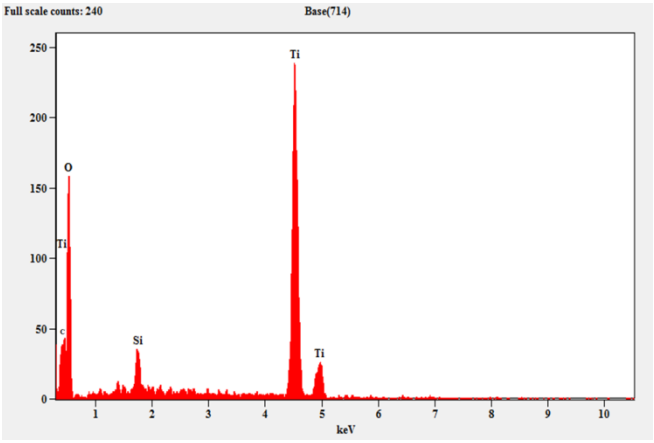


Figure 5 Energy Dispersive X-ray analysis (EDAX) of TiO_2 coated by SiO_2

Element Line	Weight %	Weight% Error	Atom %
OK	36.25	---	62.73
C K	2.70		2.20
SiK	2.74	±0.37	2.60
TiK	58.31	±1.38	32.47
Total	100.00		100.00

Table3 The chemical composition of the TiO_2NPs coated by SiO_2NPs

Besides, the inset table shows the major elemental component TiO_2 nanoparticles is oxygen (58.88%) and Titanium (40.05%). Carbon can be detected as well which the elemental compositions are 1.07%. This result proves that the presence of TiO_2 nanoparticles is verified. The similar trend was observed in figure 5. It is displayed that the addition Si obtained after completing the coating process. This result proved that the presence of TiO_2-SiO_2nanoparticles is verified.

Figure 6 shows that the TEM images of core-shell structured TiO_2-SiO_2nanoparticles. The comparison of these pictures shows that TiO_2 particles surfacewas surround by amorphous silica layer. The average diameter size of silica-coatedTiO_2 nanoparticles was determined as 20–50 nm. The thickness of the amorphouslayer is estimated about 10–15 nm.The densely continuous and uniform SiO_2coating layers formed with an average thickness of 5 nm. Core-shell structured TiO_2-SiO_2 nanoparticles of varying shell thicknesses were synthesized and confirmed through TEM examinations.

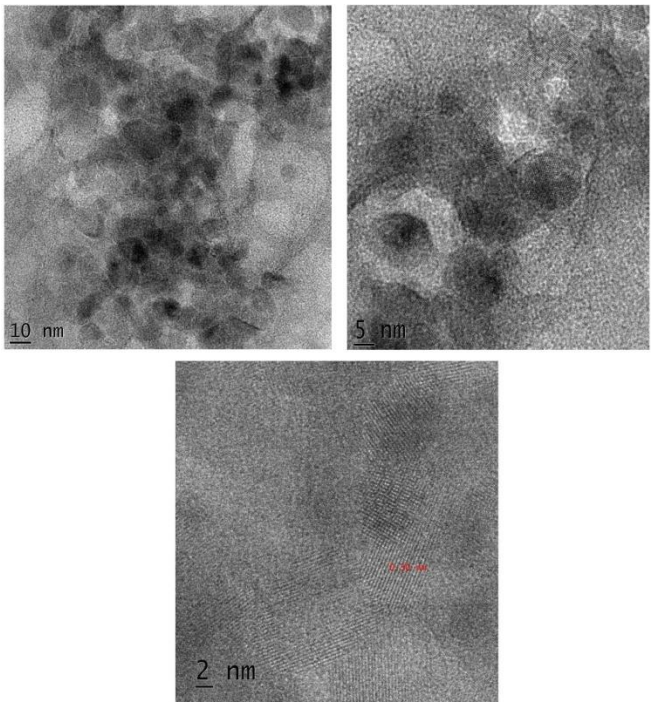


Figure 6 TEM images of prepared TiO_2Coated by SiO_2NPs

Electro chemical characterization was carried out using a three-electrode system. The working electrode was prepared by mixing 70% of active materials (inthiscase,TiO_2andTiO_2/SiO_2powder),20%ofacetyleneblackasconductive fillers, and 10% of poly tetra fluoro ethylene as a binder. The mixture was pasted on nickel foam (1 × 1 cm), which served as the current collector. The nickel foam was dried in an oven for 12 h at 353 K and then pressed to fabricate electrodes. A platinum wire was used as the counter electrode, and Ag/AgCl was used as the reference electrode. All measurements were recorded using 6M KOH as the electrolyte. Cyclic voltammetric (CV) measurements were recorded on the above- mentioned system within a range of −1.5 to +2 V at the scan rates of 10, 20, 30, 40, 50, 60, 80 and 100 mV/s

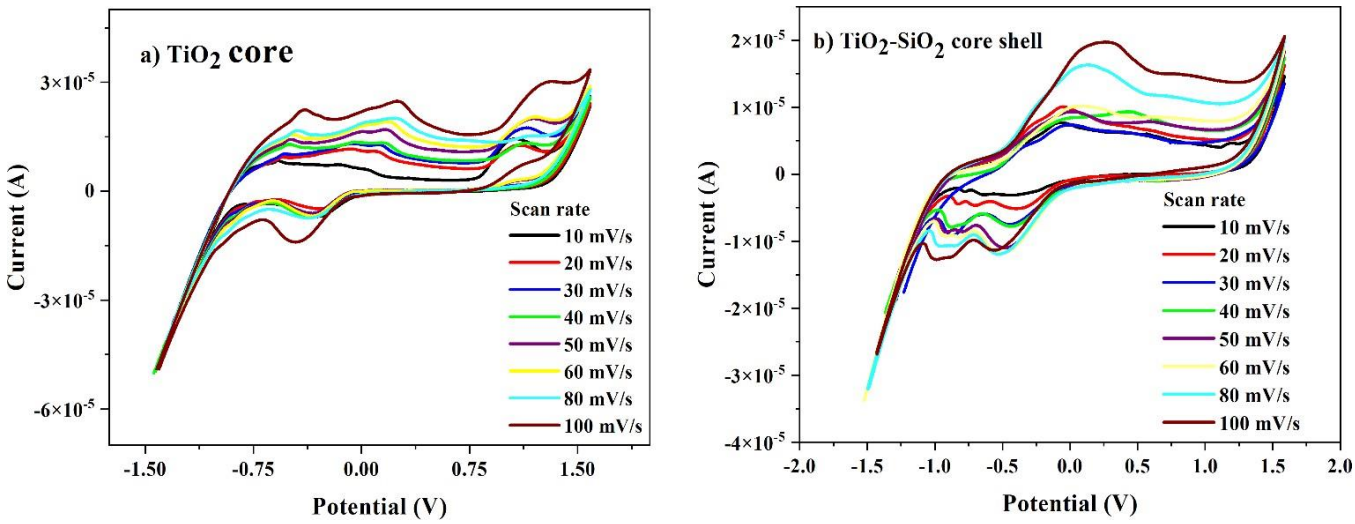
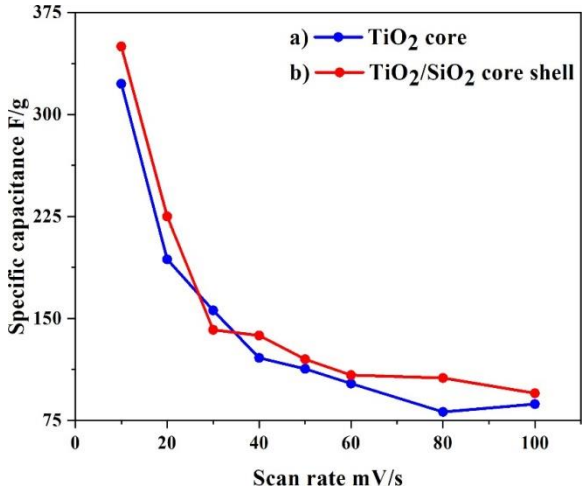


Figure 7 Cyclic Voltammetry Analysis of Prepared a) Titanium Oxide and b)Titanium Oxide coated by Silicon Oxide

Figure7 shows the electrochemical performance of TiO_2 and TiO_2-SiO_2 core shell as a super capacitor electrode. In Fig. 7, a pair of cathodic and anodic peaks in the CV curves can be clearly found due to its pseudo capacitance behavior, distinctly different from normal electric double layer capacitance with a rectangular CV shape. In inset of Fig. 4.7, the anodic peak current value show alinear relationship to the square root of the scanning rates, suggesting that the electrochemical reaction on the



electrode surface was a diffusion-controlled processs quare root of the scanning rates, suggesting that the electrochemical reaction on the electrode surface was a diffusion-controlled process

Figure 8 Spectrum of Scan rate vs Specific capacitance of prepared TiO_2-SiO_2nanoparticles

Figure8showsthespecificcapacitancedependentscanrateprofileforthesamples. The specific capacitance of the electrode might be calculated from thefollowing equation [7]

$$C_S = \frac{\int idV}{mXsX\Delta VXA} \quad (2)$$

where, ΔV is the voltage window, s is the constant scan rate (V s^{-1}), A is theaverage geometric area of the two electrodes (cm^2), and m is the combined mass oftheactivematerialonbothelectrodes(g).Thedevice'sarealandspecificcapacitancesascal culatedfrom the CV curvesspreadfrom323F g^{-1} to87Fg^{-1}forTiO_2and350Fg^{-1}to95Fg^{-1} withscanratesincreasingfrom10mVs^{-1} to100 V s−1. The decrease in capacitance with increasing scan rate is a common feature of Electric Double Layer Capacitors and is caused by the different time regimes of charge transport and ion diffusion for the varying scan rates. At lower scan rates, electrolytic ions have sufficient time to diffuse into the pores of the sample active layer, increasing the charge accumulation and thus the capacitance. At higher scanrates, charge accumulation is confined to the surface of the electrodes, decreasing the electrodes' capacitances obtained in table4 It is exhibited that the scan rate is increases and the specific capacitance values are decreased is shown infigure8.

Scan rate (mV/s)	**Potential(V)**		**Specificcapacitance(F/g)**	
	TiO_2	**TiO_2/SiO_2**	**TiO_2**	**TiO_2/SiO_2**
10	3.1	2	322.59	350
20	3.1	2	193.55	225
30	3.1	2	155.91	141.67
40	3.1	2	120.97	137.5
50	3.1	2	112.90	120
60	3.1	2	102.16	108.33
80	3.1	2	81.25	106.25
100	3.1	2	87.10	95

Table4 The calculated parameter for CV analysis

CONCLUSION

In this work, TiO_2 core and core TiO_2 coated by SiO_2 nanoparticles were synthesized successfully as biosynthesis method using *Bay laurel*. The optimal sample has been studied and established, and the crystal structure and pattern

calculated by powder XRD measurements. The elemental composition of TiO_2 core and core TiO_2 coated by SiO_2 have been verified by EDX. The energy level diagram for TiO_2 core and core TiO_2 coated by SiO_2 have been estimated based on electro chemistry techniques, using solid state prepared samples as the working electrode. In an extensive super capacitor device study, TiO_2 core and core TiO_2coated by SiO_2 have been employed as the active material in an EDLC device, and a simple and economical electrode fabrication process has been demonstrated. The titanium dioxide coated by silicon dioxide enhances the specific capacitance of the resulting material. These core exhibit improved capacitance values after coating material SiO_2 added to TiO_2. It is promoted that the prepared samples are efficientuseofpseudocapacitor.Greensynthesisopensupnewpossibilitiesfortheapplicatio n of nanoparticles in energy devices. From this analysis has proven that prepared nanoparticles based electrodes can be fabricated from the biometerial and integrated in low-cost, commercially-viable super capacitors for feature promising material energy storage capabilities.

REFERENCES

[1] Viviana Cigolotti, Matteo Genovese, Francesco Piraino, Petronilla Fragiacomo, 2023. Applications – Stationary|Stationary Energy Storage System: Overview. Reference Module in Chemistry, Molecular Sciences and Chemical Engineering.DOI:10.1016/B978-0-323-96022-9.00091-8

[2] Srdic V, Mojic B, Nikolic M, Ognjanovic S, 2013. Recent progress on synthesis of ceramics core/shell nanostructures. Processing and Application of Ceramics, 7(2), pg 45–62. DOI:10.2298/pac1302045s

[3] Green synthesis of nickel oxide nanoparticles using Acacia nilotica leaf extracts and investigation of their electrochemical and biological properties. Shabbir Hussain, Muazzam Ali Muazzam, Mahmood Ahmed, Muhammad Ahmad, Zeeshan Mustafa, Shahzad Murtaza, Jigar Ali, Muhammad Ibrar, Muhammad Shahid & Muhammad Imran. Journal of Taibah University for Science Volume 17, 2023 - Issue 1

[4] Kong, W., Liu, B., Ye, B., Yu, Z., Wang, H., Qian, G., & Wang, Z.(2011). An Experimental Study on the Shape Changes of TiO2 NanocrystalsSynthesized by Microemulsion-Solvothermal Method. Journal of Nanomaterials,2011, 1–6. doi:10.1155/2011/467083

[5] Zuas, O., & Budiman, H. (2013). Synthesis of Nanostructured Copper-dopedTitania and Its Properties. Nano-Micro Letters, 5(1), 26–33. doi:10.1007/bf03353728

[6] Zuas, O., & Budiman, H. (2013). Synthesis of Nanostructured Copper-dopedTitania and Its Properties. Nano-Micro Letters, 5(1), 26–33.doi:10.1007/bf03353728

[7] Adams,K.,González,A.F.,Mallows,J.,Li,T.,Thijssen,J.H.J.,&Robertson, N. (2019). Facile synthesis and characterization of $Bi_{13}S_{18}I_2$ films as astablesupercapacitorelectrodematerial.JournalofMaterialsChemistryA.doi:10.1039/c8ta11029h