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Preparation and characterization of bioactive silica derived from Rice husk supported TiO_2 and cobalt nanocomposite via sol – gel route

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Abstract

In the present study, amorphous silica nano particles were taken from low cost rice husk by carrying out an acid treatment by the process of heat treatment. Silicon precursor was obtained in the form of sodium silicate rice husk ash. Sodium silicate solution was obtained by direct silica extraction from rice husk via solvent extraction method without adding any template. The target nano composite (RHS/TiO_2/Co) was formed by embedding the cobalt nanoparticles into SiO_2/TiO_2. The prepared samples were characterized by XRD,FTIR, SEM/EDS, TG-DTA,UV and TEM. The cobalt was found to isomorphouslysubstitute in the silica matrix. A good dispersion of cobalt nanoparticles was evidenced by X-ray diffraction. Scanning electron microscopy confirmed the formation of well dispersed and spherical cobalt nanoparticles. During TGA analysis, it was observed that, mass trace suddenly goes backwards along the abscissa and then continues forward normally. This technique provided an environmentally friendly production process for conversion of waste rice husk to high performance materials.

1. Introduction:

Increased environmental consciousness has motivated research into the effective utilization of agricultural byproducts. Rice husk is an important agricultural waste that abundantly produced globally every year. Due to its high silicon content, rice husk has become a Source for preparation of elementary silicon and a number of silicon compounds, especially silica (sodium silicate) [1], silicon carbide [2] and silicon nitride [3]. Silica is the major inorganic constituent of the rice husk, which by carrying out an acid chemical treatment followed by the process of burning; it is possible to extract high-surface area amorphous silica. Recently, Adam et al. managed to incorporate various types of transition metals into rice husk silica and reported their catalytic potentials in the oxidation, acylation and benzylation reactions [4–6]. Among knowntransition metals, cobalt undoubtedly has gained wide interestin numerous catalytic studies. For example, cobaltnanoparticles supported on silica in steam reforming ethanol, $CoFe_2O_4$ and Co_3O_4nanocrystals as heterogeneous catalystfor cyclohexane oxidation and also methane combustion. Owing to its broad applications, various methodshave been employed by researchers to produce unique Co orCo bimetallic nanoparticles which includes thermal decomposition,pulsed laser irradiation chemical vaporcondensation (CVD) [7], co-precipitation, reversedmicelle technique reduction of cobalt chloride andthermolysis [8]. Most recently, a ferromagnetic cobaltnanoparticle between 35-200 nm size range was successfullysynthesized by a modified polyol technique [9]. Additionally,cobalt nanoparticles were synthesized by reverse microemulsionconsisting of either neutral or ionic surfactants[10]. Furthermore, Fu and co-workers [11] have developedspherical core cobalt/silica nanoparticles by activated plasmaevaporation of the metal. However, most of these existingprocedures are expensive, complicated, time consuming andinvolves organic solvents. For instance, thermal decompositionmethodology requires long period of calcination and hightemperature as reported by Yang *et al.*, [12].Silica is an inert support material with a high surface area.It has been widely used in ceramics and electronics. Rice husk, an abundantly available agricultural wastehas emerged as an ideal source of high grade amorphoussilica. Many studies have been reported on the use of silicafrom rice husk as a catalyst support.Sol-gel processis claimed to be a simple and effective synthesis pathwayfor the production of nanomagnetite, silica nanotubesand nanocomposites [13].Thus, this study a simple and sol – gel route to synthesize cobalt nano particles supported on rice husk silica/TiO_2 with unique morphology and structural properties.

1.2 Materials

All the chemicals used were analytical grade. Titanium isopropoxide ($Ti(OC_3H_7)_4$ 97%) was used as a precursor of titania and Cobalt nitride($Co(NO_3)_2.6H_2O$ as dopant sources. Other materials used were nitric acid and sodium hydroxide pellets. Rice husk gathered from agriculture department, AnnamalaiUniverrsity. All the chemicals used directly without further purification. Methanol and distilled water were used as a solvent in sol – gel process.

1.3. Characterization

Powder X-ray diffraction pattern was obtained from aRigakuminiflex diffract meter for 2ɵ values from 10^0 to 90^0 using Cukα target at wavelength of $\lambda = 1.5406A^0$. The FTIR analysis was carried out in a Perkin Elmer Spectrum 1000 using the KBr pellet method. The UV-Vis spectra were recorded with a Hitachi, UV3501 spectrometer. Scanning electron microscopy (SEM), (JEOl – JSM – 6360LV) was used to record the morphology of the prepared materials and the elemental analysis was carried out by energy dispersive analysis (EDX) and Treated rice husk ash TGA and DTA analysis were performed in thermo gravimetric equipment (Pyris7, Perkin – Elmer).

2. Experimental Procedures

2.1. Preparation of Rice Husk Ash

Preparation of rice husk ash is done by cleaned and washed with distilled water. The cleaned 100 gm rice husk was shocked in 500 ml of 3M HNO_3 and the mixture was stirred for 3 hours at 80^0C temperature. After the reflux, the solids are washed with de ionized water until neutral (acid free) and dried at a temperature of 120^0C overnight. Rice husk that have been dried and then calcined at temperature of 700^0C for 5 hours.

2.2. Preparation of silica gel nano particles

5g rice husk ash was mixed with 250mL of 1N sodium hydroxide aqueous solution. The mixture was refluxed for 3h at 110^0C. The solution was filtered and stored in a refrigerator for further usage [14]. A 5ml sample of sodium silicate solution was taken from the stock solution and poured into

15ml distilled water at a time and stirred for a specific time. The pH of the solution was adjusted to 10-12 by drop wise addition of hydrochloric acid under stirring speed to form silica gel. The time want for gelation is approximately within five minutes after sol solution was neutralized. Agitation was continued for another one hour to obtain wet gel nano particles. The prepared gel was aged at 700^{0}C for3h under finalized condition. Distilled water, NaCl and other impurities were separated from the gel by solvent exchange with dilute and pure methanol in 4-5 times. The dilute methanol (75%) was used to avoid any structural shrinkage during the solvent exchange. Completely, methanol exchange was done six times and aged at 700^{0}C. The total time of aging was 52 h. The wet gels were then dried [15]. The final product labeled at RH-Silca.

$$SiO_2\ (Ash) + 2NaOH \longrightarrow Na_2SiO_3 + H_2O \quad \text{----------------} (1)$$

$$Na_2SiO_3 + H_2SO_4 \longrightarrow SiO_2 + Na_2SO_4 + H_2O \quad \text{---------------} (2)$$

During the addition of sulphuric acid, Si-OH formed and condensed to form siloxane bond as shown below

$$Si-OH + HO-Si \longrightarrow Si-O-Si + H_2O \quad \text{----------------} (3)$$

2.3 Synthesis of RHS doped Titania:

The synthesis of titania – silica nano composites was prepared by sol – gel method. The molar ratio of silica to titania sols was 0.5:0.02. The Stock solution was added to titania solution while stirring for 5 hr until a gel was formed. The gel was aged for 24 hrs and then rinsed with water followed by heating at 150^{0}C for 5 hrs. Finally the solution was filtered at whatmann filter paper and dried was kept at oven. The final product was labeled at RHS-TiO_2.

2.4 Synthesis of RHS/TiO_2/Co nano composites:

The preparation of RHS/TiO_2nano composites doped nickel by using sol – gel technique. The Stock solution was added to titania (0.5:0.02) solution while stirring for 30 minutes and immediately added to cobalt solution(varying concentrations are 0.5,1.0,1.5%) within a fraction of time the gel was formed. The wet gel was dried kept at hot air oven. The finally product labelled RHS/TiO_2/Co

2.5. Phase Investigation and structural analysis:

The X-ray spectra and characteristic absorption peak of RHS have been acquired and displayed in Fig 4.2.1 (a), the sample is entirely amorphous as pointed out by the featureless diffract grams and the appearance of a scatter maximum at $2\theta = 23^0$ characteristic for amorphous silica [16]. This pattern exhibits a very broad line and no defined peaks due to crystallinity were encountered. On the figure 1(a) are also described the theoretical postures of the main reflexion of the phase cristobalite (SiO_2) and graphite (C) and no peaks were discovered in these postures. The results obtained conceded to conclude that the ash produced has an amorphous structure.

2.5.1. RHS doped TiO_2

In Fig 4.2.1 (b) RHS doped with TiO_2 (1:1) agrees the presence of peak $2\theta = 25.28^0$ corresponding to (101) plane and it is the characteristic peak of anatase (JCPDS 21-1272). Strong diffraction peaks at 25^0 and 48^0 indicating TiO_2 in the anatase structure. There is no any spurious diffraction peak found in the sample. The peak intensity of the sample reflects that the formations of nanoparticles are crystalline. Amorphous disclosed a broad pattern with low intensity. Silica can exhibit the formation anatase by impeding direct contact between TiO_2 particles forming the Ti – O – Si binding [16]. The diffract gram clearly suggesting that only anatase phase has been formed. The use of TiO_2 in the silica matrix of 50% will reduce the anatase phase and forming amorphous $TiO_2 – SiO_2$ [17].

2.5.2 Cobalt doped RHS/TiO_2

In Fig 4.2.1 (c-e) RHS- TiO_2 doped cobalt (0.5, 1.0 and 1.5 % wt) respectively. The peak relatively (311) plane and the corresponding angle $2\theta = 35.41^0$ (JCPDS 43 – 1003) was used for finding the particle size of the formed oxide; an average dimension 38nm was calculated. The presence of $Co_3 O_4$ and CoO can be further analysed from XRD spectra.

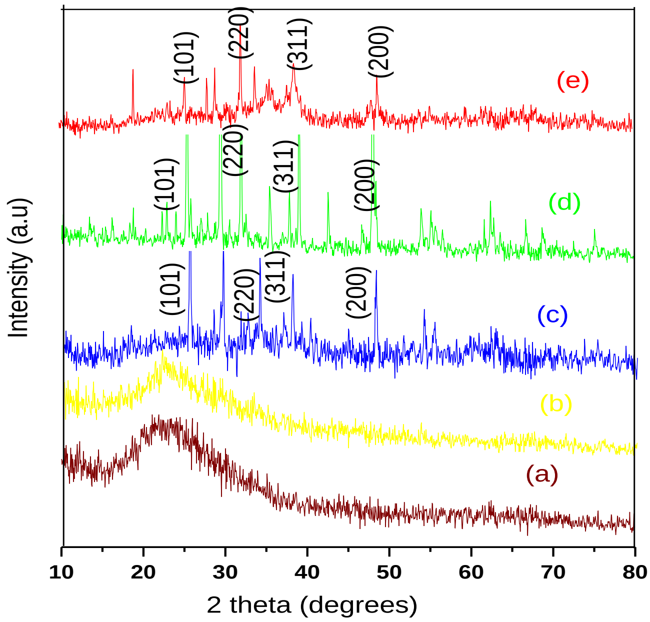

Fig 1 XRD pattern of a) RHS b) RHS/TiO_2 c) RHS/TiO_2/0.5 Co d) RHS/TiO_2/1.0 Co e) RHS/TiO_2/1.5 Co

Moreover, it is worth nothing that the amorphous structure of silica present in our sample remained and no peaks corresponding to the transition metal oxides are also observed. This implies that cobalt is still well dispersed in the titania – silica framework [18]. Smaller co particles undetected in the XRD may also lead to untraceable crystalline peaks. Reflections corresponding to Co could not be observed which could be due to the overlap with other signals or broadening of the XRD peak.

Table.1. Particle size and Dislocation density of the Nano Composites

Sample Name	Particle size (Debye) nm	Particle size (W-H plot) nm	Strain Unit less	Dislocation Density (m^2)
RHS	50.42	69.32	0.002	0.638 X 10^{-15}
RHS/TiO_2	22.04	54.32	0.002	0.541 X 10^{-15}
RHS/TiO_2/0.5% Co	43.84	78.78	0.001	0.176 X 10^{-15}
RHS/TiO_2/1.0% Co	39.02	54.34	0.002	0.471 X 10^{-15}
RHS/TiO_2/1.5% Co	38.03	27.73	0.005	0.919 X 10^{-15}

This is in agreement with titania promoted silica assisted cobalt catalyst subjected to air drying out 150^{0}C which showed decomposition of cobalt nitrate into intermediate cobalt silicate phase and finally the product was labelled at RHS–TiO_2 –Co.

2.6. Spectral studies:

Fig 4.2.2 (a) shows an FTIR spectrum at RHS. A broad band in the range of 3362 cm^{-1} is due to the stretching vibration of the O – H band. This band is due to silanol groups (Si – OH) and the adsorbed water bound to the surface. The weak band 1642 cm^{-1} is assigned to H – O – H bending vibrations mode where also represented due to the adsorption of water in air when FTIR samples disk were prepared in an atmospheric pressure. Also, there is a tiny dip in the spectra at 2354 cm^{-1} due to the presence of atmospheric CO_2. These peaks are trapped in the matrix of silica surface. The predominant peak at 1383 cm^{-1} is due to silaxone bonds (Si – O – Si). The adsorption bands between 474 and 993 cm^{-1} are because of silica structures and other peaks observed in the range of 1247 and 2764 cm^{-1} are because of impurities such as carbonate and sodium groups. The peaks between 1055 and 711 cm^{-1} indicates the vibration modes of Si – O – Si network. A most intense band at 1110 cm^{-1} and a peak 765 cm^{-1} are due to asymmetric and symmetric stretching mode at Si – O – Si. The bending vibration of Si – O is shown by strong band at 475 cm^{-1}. The vibration of oxygen atoms joined with the adjacent atoms in the asymmetric stretching vibrations of Si – OH bond appeared at 1150 cm^{-1} [19].

2.6.1. RHS doped TiO_2

In Fig 4.2.2 (b) the presence of some weak transmittance bands between 3362 &3467 and at a 1634 are seen, which are gradually decreased with TiO_2 doping concentrations. An intense band at 606 and 852 cm^{-1} is seen which is attributed to different vibrational modes of TiO_2. The intense band below 1343 cm^{-1} is due to Ti – O – Ti vibrations. The shift in lower wave numbers and sharpening of the Ti – O – Ti band width increase of TiO_2 concentration could be attributed to the decrease of particle size. The band 835 cm^{-1} are mainly ascribed to Ti- O and Ti – O – O bonds. According to the FTIR spectrum, the sample containing SiO_2:TiO_2 equal to 50:50 obviously shows the presence of Ti – O – Si bonding.

2.6.3. Cobalt doped RHS/TiO_2

In fig 4.2.2(c-e) Cobalt doped with RHS/TiO_2 (0.5, 1.0 & 1.5%wt) respectively. The band at 990 cm^{-1} RHS disappeared after introducing cobalt into silica framework. The change in intensity with increasing Co concentration indirectly substitution of cobalt ions in the silica framework. Replacement of Si with Co results in a decrease in the intensity of the 990 cm-1 band showing the replacement of the Si – O – H groups with Si – O – Co groups.inset spectrum fig 6(a) clearly demonstrates band at 646 cm^{-1} for RHS – Co which is absent in RHS. The 646 cm^{-1} is described to spinel type Co – O bond corresponding to Co_3O_4. It confirms the M- O stretching vibration in which Co^{2+} is tetra hedrally coordinated. The nitrate group has six normal vibrations that are IR active.

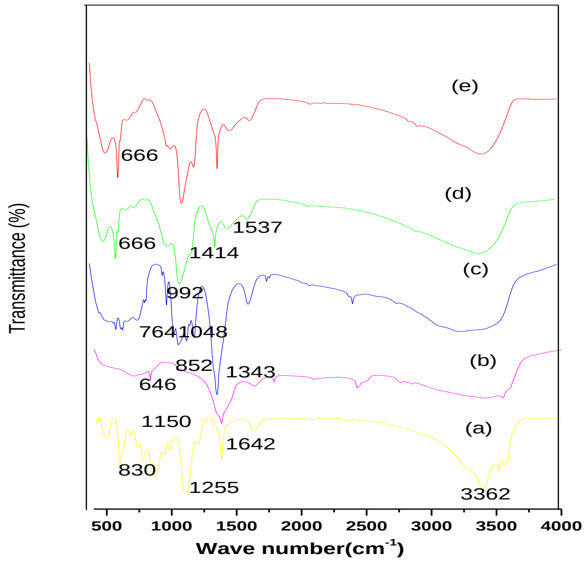

Fig4.2.2. FTIR spectra of a) RHS b) RHS/TiO_2 c) RHS/TiO_2/0.5 Co d) RHS/TiO_2/1.0 Co e) RHS/TiO_2/1.5 co

These are the anti symmetric stretching, out of plane bending, anti symmetric in plane bending and the symmetric in plane bending observed at 1519, 1362, 1045, 825, 780 and 646 cm^{-1} respectively [20]. Meanwhile, unobvious peaks in the range 400 – 1500 cm^{-1} attributed to the anatase phase are found in this sample. No significant differences weredifferences were observed at the spectra which repeatedly confirm the formation of cobalt nano particles

2.7. Thermal Studies:

In this experiment with linear heating at 10^0C/min, the TG curve are analysed the gas of sample with decomposition from atmosphere as shown in fig (4.2.3). The TG spectra observed that in the 200^0C to 280^0C. The initial weight loss should be decomposition of CoO(OH) according to the equation

$$12\ CoO(OH) \longrightarrow 4Co_3O_4 + O_2 + 6H_2O \quad (1)$$

$$2Co_3O_4 \longrightarrow 6\ CoO + O_2 \quad (2)$$

Above 600^0C, the weight remained constant confirming the complete decomposition of the RHS/TiO_2/Co nano composites [21].

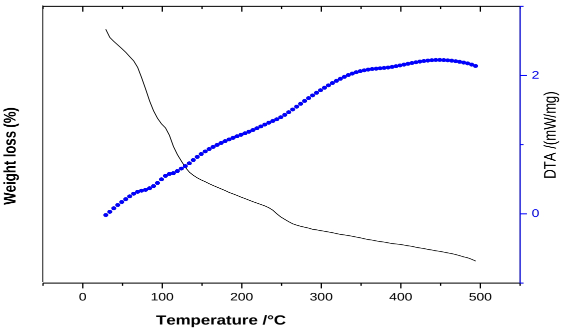

Fig.3. TG/DTA curve RHS/TiO_2/Co

2.8. Morphology Studies:

Fig 4.2.4 (A) & (B) exhibits the SEM and EDX analysis Rice husk silica. In SEM image, RHA particles are polygonal shape with different sizes. A strong intensity of Si in the EDS spectrum is confirmed the silica at higher weight percentage Fig 4.2.4 (C) & (D) show SEM characterization of titania – rice husk silica. The images had small grains without clear boundaries.The forming competition between silica and titaniaanatase phase, can cause the agglomeration [22]. Silica in amorphous phase prevents the formation of grain boundaries of titania and silica. It reveals that the presence of Ti, O and Si are the only elementary species in the sample [23].The surface morphological features of synthesized Nickel doped RHS/TiO_2 nano composites were studied by SEM in Fig 4.2.4 (E) & (F).The instrumental parameters, accelerating voltage, spot size magnification and working distances are indicated on SEM images.The observed SEM images exhibits that the particles are spherical and are polycrystalline. This infers that the addition of cobalt does not affect the crystal structure which confirms the incorporation of cobalt in to Ti lattice site. While increasing the doping concentration the particle size was

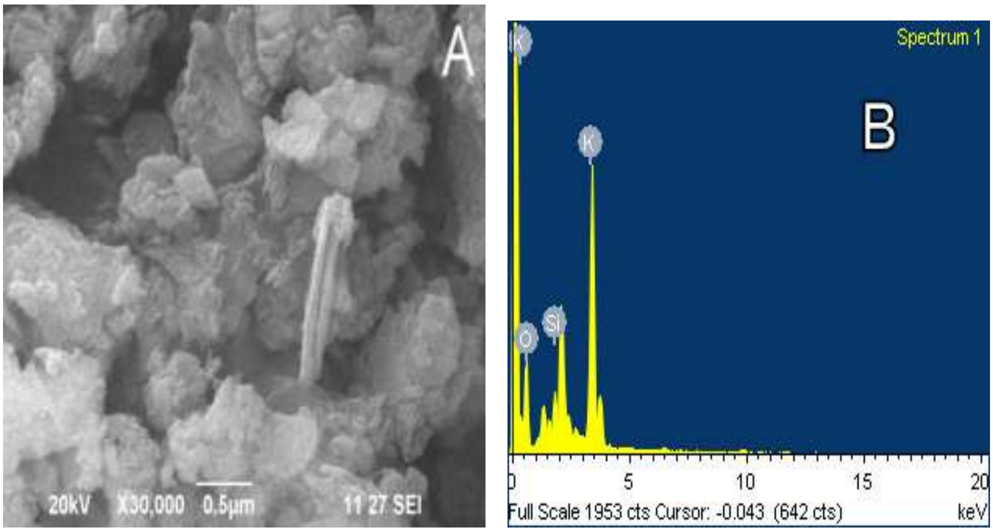

Fig 4 (A) SEM image of RHS **(B) EDS spectrum of RHS**

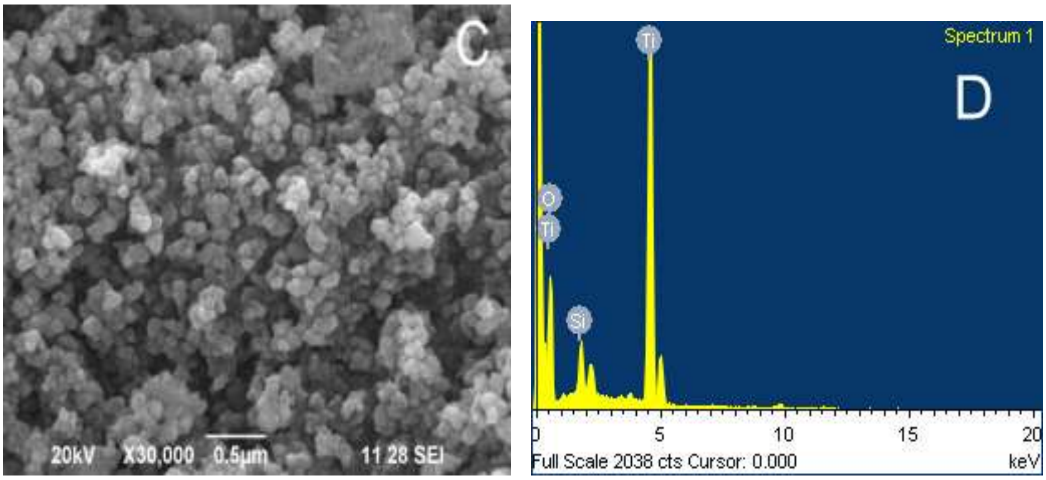

Fig 4(C) SEM image of RHS/TiO_2 **(D) EDS spectrum RHS/TiO_2**

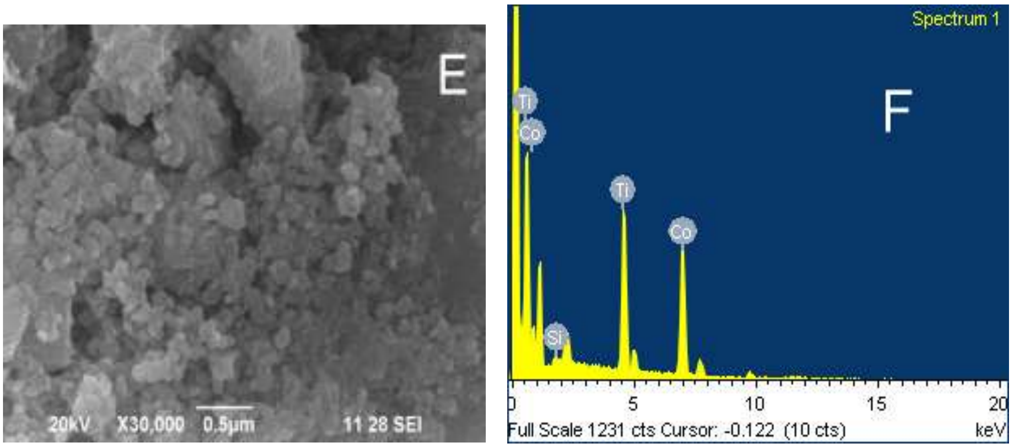

Fig 4(E) SEM image of RHS/TiO_2/Co **(F) EDS spectrum RHS/TiO_2/Co**

Considerably reduced and aggregated. The EDX spectrum for RHS/TiO_2 and 1.5%Co nano composites are shown in Fig 16 (b). The figure reveals that the presences of Ti, O, Si and Co are the only elementary species in the sample. Moreover, no additional peaks were observed (30).

2.9. Optical Studies:

Fig (4.2.5) exhibits the relation between absorbance and wavelength for cobalt doped RHS/TiO_2. It can be obtained that the absorbance increases with wavelength in the range of 550 nm and then followed suddenly slow at higher wavelengths. The spectrum exhibits high transmittance in the visible and infrared regions and absorption edge is sharp in the visible region [24]. The DR UV – Vis spectroscopy was known to be a sensitive probe for the identification and characterization of metal ion concentration and its existence in the framework and/or in the extra framework position of metal containing nano composites. Fig shows two bands with the maxima near and nm attributed to the O^{2-} Ti^{4+}.

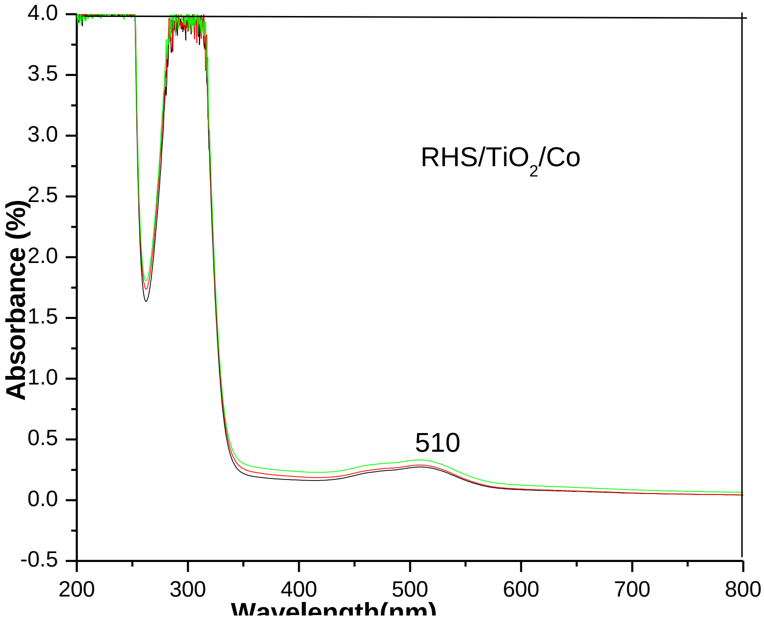

Fig.5 UV – Vis spectrum RHS/TiO_2/Co

Conclusion:

Cobalt nano particles were synthesized via simple sol – gel route under mild conditions. This simple approach resulted in the successful generation of spherical and polycrystalline cobalt nano particles. The characterization of FTIR and XRD reveals the presence of CoO, Co3O4 and Co – silicate hydroxide in the material. Characteristic peaks for cobalt and cobalt oxide were not present in the XRD patterns for Co – doped Rice husk silica /TiO_2nano composites, indicating that the doped copper was well distributed and amorphous. UV absorption for the 0.5, 1.0 and 1.5 wt% Co - doped Rice husk silica /$TiO_2$was observed at 485,490 and 510nm.

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