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Synthesis of Carbon Nano Sheet by Using Cobalt Nano Catalyst and Its Analysis

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ABSTRACT

We report here simple method of preparation of Carbon nano sheets by chemical vapour deposition (CVD) technique. Decomposition of M oil(carbon source) was carried out over finely dispersed Co as a catalyst. Scanning electron microscope (SEM) image revels that the Carbon nano sheets formed around10~ 20 nm in width. For the synthesis of carbon nano sheet synthesis of cobalt catalyst is important step, a simple solution combustion synthesis of Cobalt oxide (Co_3O_4) nano particles was carried out by using glycine as a fuel and Cobalt nitrate hexahydrate ($Co(NO_3)_2.6H_2O$) as an oxidizer and it's reduction to cobalt nano particles by using hydrogen gas. The morphological structural properties of nano particles were investigated by scanning electron microscopy (SEM), Fourier transform infrared (FT-IR). The synthesized Co particles have a crystalline size of ~ 20 nm. The agglomeration of fine particles with particle size in the range of 30~40 nm is seen by SEM images. The FTIR shows absorption band for CoO at ~ 484 Cm^{-1} and 484 Cm^{-1}. The FT-IR spectrum is shows absorption band at ~ 466 cm^{-1} for Co nano particles. These cobalt nano particles are used as catalyst for the synthesis of carbon nano sheets. Synthesised carbon nano sheet material was analysed by XRD and SEM technique, which can be used in different fields like catalysis supercpacitors, fuel cell etc.

Key words: Solution combustion, Cobalt oxide, Glycine, CVD, M-Oil (carbon source), Carbon nano sheet

I. INTRODUCTION

Nanoparticales of transition metals like Ni, Co, Fe etc. have been studied by several scientists in the last few years. Nanoparticles of transition metals are getting continuous importance for various application such as catalysts [1] [2] super capacitors, gas sensors electrochromic devices [3] [4] [5] [6] [7] magnetic materials [8] rechargeable batteries [9]solar energy absorber [10] pigment for ceramics[11] biosensors, fuel cell [12] Several researchers have prepared CoO by different method like sol-gel [13] surfactant-mediated synthesis [14] thermal decomposition, solution combustion synthesis [15] [16] polymer combustion route [18] and so on. However to the best and most commonly used laboratory synthesis is solution combustion method (SCS) [19]. In solution combustion method different combination of fuels and oxidizers are used; oxidizers like metal nitrate, metal chloride metal sulphates etc, and fuel like glycine, urea, citric acid, oxalic acid, glucose, sucrose, aniline are used. Current report is solution combustion synthesis using Cobalt nitrate hexahydrate as an oxidizer and glycine as a fuel. The prepared CoO is reduced to Co nanoparticles by using H_2 gas. Several methods were used for the perpration of carbon nao particles like arc discharge [20] laser ablation [21] etc. but most widely used method is chemical vapour deposition (CVD) [22] [23]. Prepared CoO and Co were analysed by FTIR and SEM. carbon nano sheet were analysed by SEM and XRD.

II. METHODS AND MATERIAL

Synthesis of Cobalt oxide and Co nano particles

Very small particles of metals such as Ni, Co, Fe are known for their catalytic role in growth of CNT [24] [25]. Co catalyst was prepared by thermal decomposition method. Cobalt nitrate hexahydrate and glycine were mixed at fixed 1:1 molar ratio in 25ml distilled water and stir for 10 minutes. The solution was then kept in pre heated muffle furnace at 350^0C at the flash point of glycine. The decomposition of glycine is highly exothermic and large amounts of ammonia and carbon dioxide are liberated and fine Cobalt oxide was obtained. Here NO_3^- in metal nitrate act as oxidizer and an organic compound that has carboxylate and/or amine (i.e. glycine) act as fuel. This is an autocatalytic and self-propagating reaction utilizing exothermic redox decomposition of fuel and oxidizer. Residual energy of combustion (reaction enthalpy) is used to crystallize the particle. The explosive gas blows off and material resulting into ultra-fine crystallite powder.

$Co(NO_3)_2.6H_2O + NH_2CONH_2 \rightarrow Co_3O_4(s)+8H_2O(g) + CO_2(g) + 2N_2(g) + O_2$. [26]

Cobalt oxide produced in grind with hand pastle to get fine powder. cobalt oxide obtained after grinding is blackish in colour (Figure 1A). After sonication and drying cobalt oxide was reduced in furnace by H_2 at 600^oC for 2h yielding a very fine metal nano particle (Figure1B). These Co particles were characterized by SEM and FT-IR.

Figure 1 A. Co_3O_4 Nanoparticles

Figure 1B. Co Nanoparticles

Synthesis of carbon nano sheet

Co nano particles was used as catalyst to grow CNTs by CVD [27] [28]. In CVD unit two furnaces with heating zones were used. The precursor M oil was kept in quartz boat in furnace - A and catalyst powder of Co catalyst was kept in the quartz boat in furnace – B (Figure 2). Carrier gas H_2 was allowed to flow into the quartz tube with a fixed flow rate (6ml/min) [29]. After 15 min of flow, furnace-B was switched on to reach the desired temperature 750^oC. When the desired temperature was reached the oil was heated in furnace-A to 400^oC so as to vaporize the oil. Temperature of furnace B was also maintained at this pyrolyzing temperature for 2.5h to insure maximum deposition. At the end of the desired time the furnaces was switched off and allowed to cool at room temperature.

Carbon material formed inside the quartz boat was collected and purified by treating with 50% HCl for 24 h, in order to separate the carbon nano sheet from catalyst [28]. After that carbon material were filtered of and finally washed with distilled water to neutral pH and dried in an air at $400^{0}C$ to remove amorphous carbon. This Carbon material was characterized by SEM, XRD and FTIR.

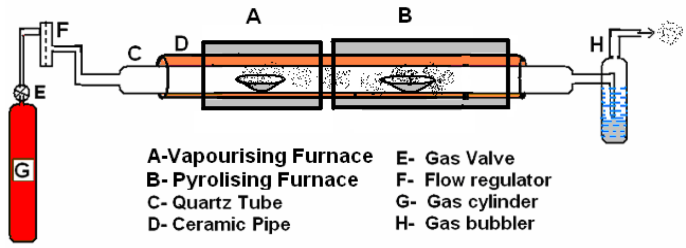

Figure 2. Schematic diagram of CVD setup

III. RESULTS AND DISCUSSION

SEM and FTIR Study of Cobalt particles

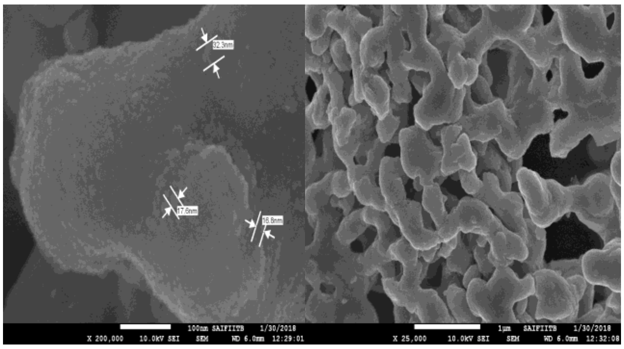

Figure 3. SEM images for Co Nanoparticles

SEM images confirmed that Co nano particles are in the range of 15-35 nm. At low magnification Co particles shows agglomerated bud of large size, Presences of voids are also observed under in the structure under low magnification, but under high magnification round shape particles present in close vicinity.

FTIR Study of CoO and Co particles

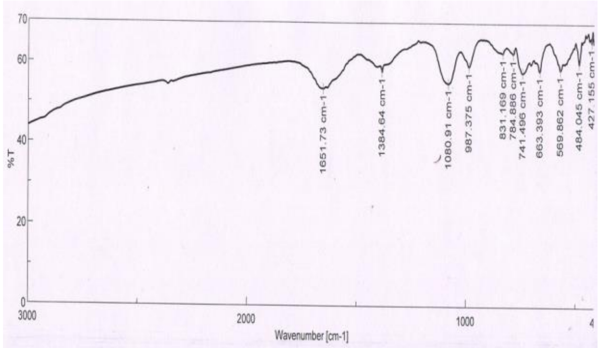

Figure 4A. FTIR spectrum for CoO

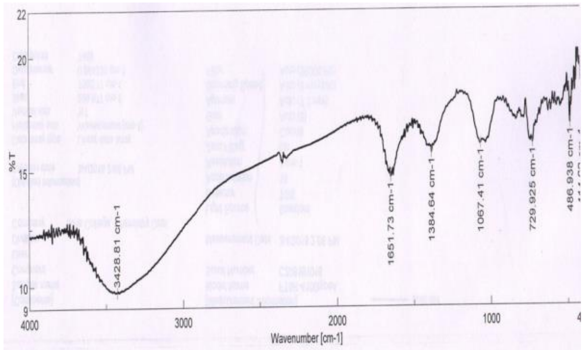

Figure 4B. FTIR spectrum for Co

FT-IR sprctra of CoO (Figure 4A) shows two characteristic peak appering at 484 cm^{-1} and 663 cm^{-1} correspond to the metal oxygen stretching vibration modes of CoO. Absence of Peak around 3600 cm^{-1} confirms that there is absence of –OH group. These two peaks disappear and and new peak appeared at 466 cm^{-1} which was indicate presence of Co particles (Figure 4B).

SEM and XRD Study of carbon nano sheet

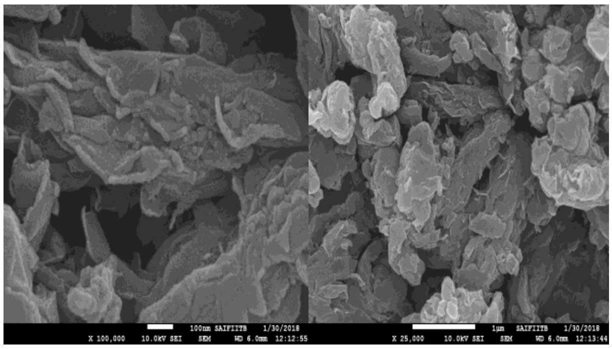

Figure 5. SEM Images for carbon nano sheet

SEM images (Figure 5). confirmed that carbon sheets of arronud 5-10 nm width are present. SEM images are s under low magnification shows sheets are agglomerated one over other, but under high magnification sheets can be distinctly observed. The agglomerated sheet can be separated by better sonication.

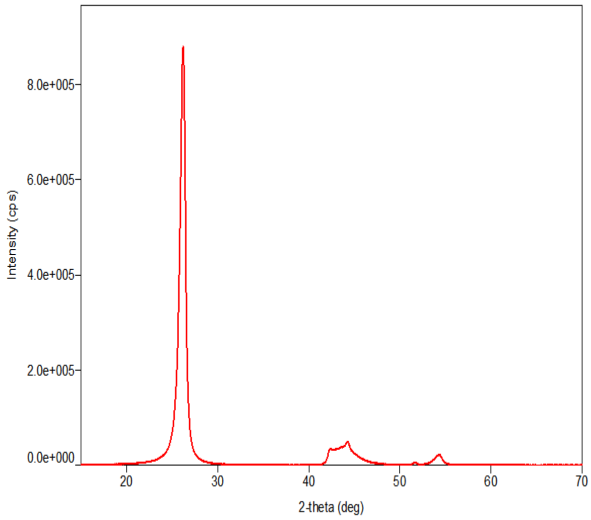

Figure 6. XRD of carbon nano sheet

XRD peak at 2θ = 26.21, 42.36, 44.27, 51.71, 54.30 corresponding to carbon nano sheet shown in (Figure 6). The crystalline size 'D' was obtained the measurement of broadening of diffraction lines and application of the Debye-Sheerer equation $D = 0.94\lambda/\beta½COS\theta$ .Where λ is wavelength of XRD radiation β is the full width at half maximum of the peak corresponding to the plane. θ is the angle obtained from 2θ value corresponding to the XRD pattern. From the equation average crystalline size found is 2.51 nm.

IV. CONCLUSION

Co nanoparticles were successfully synthesized by solution combustion method by using glycine as fuel with good yield 8-10%. The synthesized Nanoparticles are agglomerated, homogeneous in size and ranging in between 15-35 nm. We observed that Co nanoparticles agglomeraes very fast. These Co nano particles used as catalyst for the synthesis of carbon nano sheet by CVD method using M oil as carbon source The prepared carbo nano sheet are of 5-10nm in width. Therefore it is expected to have such high surface area, carbon nano material will be suitable for potential application in supercapacitors, biosensors, electrochromic devices, etc. In further investigation we are using synthesized carobn nano sheet for the supercapcitor application.

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