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# Cobalt oxide nanopowder synthesis using cellulose assisted combustion technique

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ABSTRACT

Cobalt oxides nanopowders were prepared using novel cellulose assisted combustion synthesis and solution combustion synthesis techniques. The synthesis conditions were optimized to produce high surface area cobalt oxide nanopowders. Effect of precursors ratio on product properties (such as crystalline structure, nanoparticle size, surface area etc.) were studied and compared for the two methods. Thermodynamic calculations along with TGA/DTA studies were used to understand the synthesis mechanism leading to cobalt oxide formation. The synthesized nanopowders were characterized using various materials characterization techniques such as XRD, SEM and TEM.



## 1. Introduction

Nanoparticles in the dimension of 1–100 nm possess unique properties that attract wide attention due to the application in various fields of studies. Its application in industry and science includes catalyst, optics, electronics energy storage, conversion devices and biomedical science [1–5]. Cobalt oxide is technologically important and widely used in applications such as gas sensor, heterogeneous catalyst, lithium ion batteries, data storage, pigments, fuel cells etc. [6–14], due to being a semiconductor material and providing unique tuning ability for its physical and chemical properties [15]. Various physical and chemical techniques (such as thermal method, precipitation methods, pyrolysis process, sonochemical method, polyol method, microwave irradiation, sol-gel process, combustion method etc.) have been reported for the synthesis of different morphological structures of cobalt nanoparticles [16–20]. In this article we report the use of combustion based techniques (e.g. Solution Combustion Synthesis (SCS), and cellulose assisted combustion synthesis (CACS) also known as Impregnated Layer Combustion Synthesis (ILCS)) to synthesize cobalt oxide nanopowders. Solution based combustion synthesis techniques are reported to have numerous advantages; such as these techniques are simple, economic and produce highly crystalline materials in a single step [21–29], without requiring post synthesis separation and further calcination as needed in other methods (e.g. colloidal synthesis, co-precipitation etc.). Solution based combustion synthesis techniques [30,31] require water soluble precursors (metal nitrates and a reducing agent) to make an aqueous phase homogeneous solution to be combusted. Essentially, the synthesis process proceeds via a redox reaction taking place during the combustion of oxidizing agent (metal precursor, usually nitrates) and reducing agent (fuels e.g. glycine) [32,33]. The stoichiometric equilibrium reaction between the cobalt nitrate and glycine, used in this study, can be described by the following equation deduced from general combustion synthesis equation reported elsewhere [31–34].

$$Co(NO_3)_2+\left(\frac{10}{9}\varphi\right)NH_2CH_2COOH+\frac{10}{4}(\varphi-1)O_2 \downarrow CoO(s)+\left(\frac{20}{9}\varphi\right)CO_2(g)+\frac{25}{9}\varphi H_2O(g)+\left(\frac{5\varphi+9}{9}\right)N_2(g) \quad (1)$$

The parameter $\varphi$ indicates the glycine to cobalt nitrate ratio, which is the critical parameter in the system and defined in a way that $\varphi=1$ represents stoichiometric condition, whereas $\varphi>1$ ($<1$) implies fuel rich (lean) condition. The stoichiometric condition requires no external oxygen to complete the combustion, while fuel rich case requires extra oxygen supply and fuel lean condition means the system has more oxygen than required. Initial

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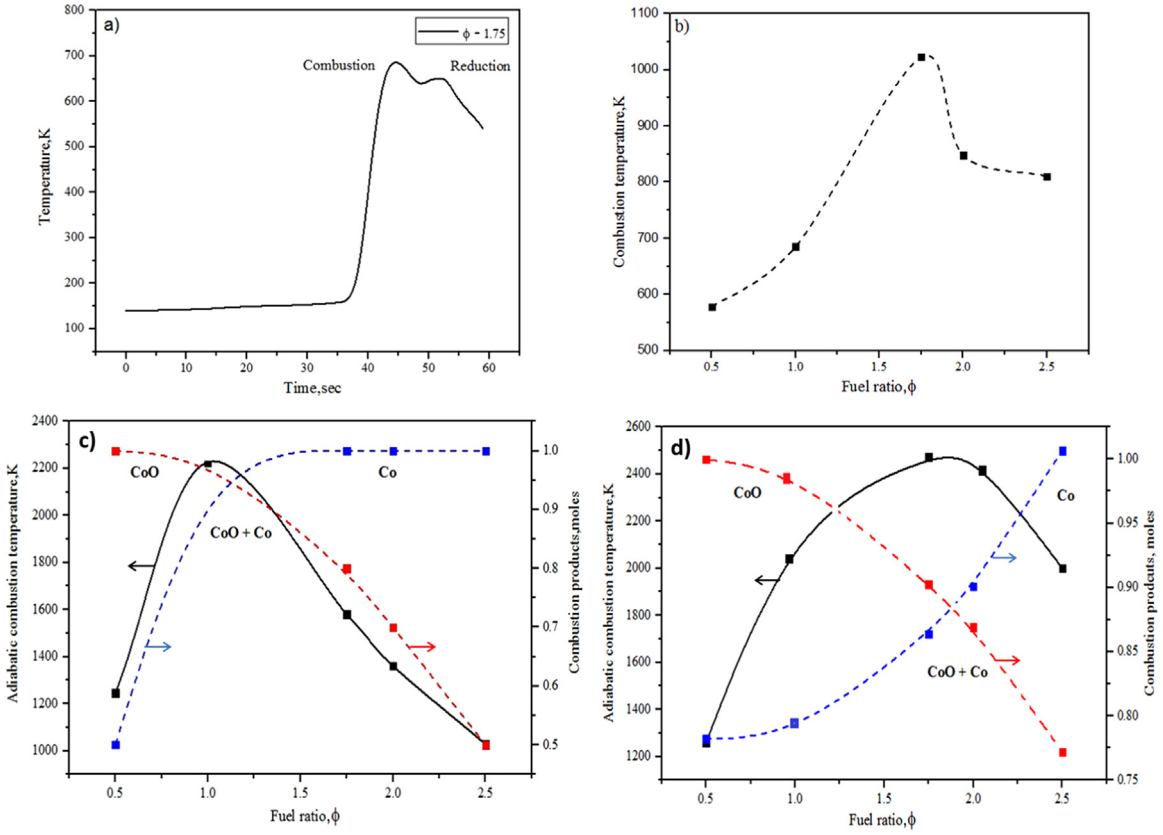


**Fig. 1.** (a) Temperature profile of SCS in cobalt nitrate glycine system with $\varphi = 1.75$, (b) combustion temperature in SCS wrt. fuel ratio ($\varphi$). Thermodynamic calculation of adiabatic combustion temperature with $\varphi$ value under (c) inert condition (d) oxygen rich environment.

investigations on metal nitrate and glycine systems indicate that $HNO_3$ and $NH_3$ are released during decomposition of metal nitrate glycine respectively, and the reaction between these two compounds is the source of combustion energy required for crystalline materials synthesis [31,32]. The amount of fuel in the reactive mixture is reported to determine the oxidation state, particle size, surface area etc. of the final product obtained. At a higher value of $\varphi$, the reactive medium generates $H_2$ rich reducing environment to convert metal oxide to metallic form [31,32]. Based on the Eq. (1), the parameter $\varphi$ also affects the total gas phase products, enthalpy of combustion; which are translated into solid product porosity and change in adiabatic combustion temperature affecting the size of the synthesized nanoparticles. Recently another technique was introduced where the homogeneous solution is deposited as a thin layer on the surface of a substrate [23,33–37]. The general form of this technique, known as Impregnated Layer Combustion Synthesis (ILCS) includes a wide range of active and inert substrates (e.g. cellulose paper, carbon sheet, metal oxides etc.) [23,33–37], whereas in this manuscript we mainly focus on the technique using cellulose as an impregnation substrate, known as Cellulose Assisted Combustion Synthesis (CACS) [33–35]. Cellulose not only acts as a substrate holding the reactive solution, it also acts as an active combustible material providing energy in weekly exothermic systems. A thin layer is expected to increase the heat transfer area facilitating the post-combustion cooling of synthesized products resulting in smaller particles due to control in the sintering process. This method also provides a mean to transform the conventionally batch synthesis method into a continuous mode of synthesis for a large scale production [30]. A number of studies have been conducted on SCS reporting thermodynamic analysis, effect of fuel content on synthesized products, and reaction pathway leading to final product formation [31,32,36], whereas similar studies are lacking in case of the novel CACS method. Initial work mainly focused on understanding the combustion flame propagation, ignition characteristics and catalytic performance of the synthesized materials [34,35]. Our previous work on cellulose assisted synthesis focused on understanding the reaction pathway using TGA DTA analysis on CuNi system [33], and this work follows up on the previous findings and reports the results of thermodynamic equilibrium analysis to understand the effect of cellulose content on combustion temperature and product properties on a model system of cobalt oxide, and compares the results with same products synthesized by SCS method.

## 2. Experimental

Cobalt oxide was synthesized from an aqueous solution of cobalt nitrate ($Co(NO_3)_2{\cdot}6H_2O$) and glycine ($C_2H_5NO_2$) using SCS and CACS method of synthesis. The amounts of precursors were calculated based on the synthesis of 1.5 g of product in the final stage using the stoichiometric Eq. (1). The precursors were dissolved in a 75 ml of water and kept there for 1 h to obtain a homogenous mixture of solution. In SCS method, the resulted solution is placed in a hot plate heater (Barnstead Thermolyne, model no: sp 46925) and heated upto its self-ignition temperature, which lead to the evaporation of water and combustion of the active mixture resulting in metal oxide synthesis. In case of CACS, a cellulose paper is dipped in the solution containing cobalt nitrate and glycine to absorb the liquid until it gets saturated. Thereafter the paper is removed from the solution and dried in open atmospheric air for 24 h. The dried cellulose paper is then ignited at one end by a hot wire to initiate the combustion process resulting in the final product.

The temperature-time profile for SCS was recorded using a high speed data logger (Daq 3005 personal board, Omega).