

Journal Pre-proof

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PII: S0925-8388(20)30716-7

DOI: <https://doi.org/10.1016/j.jallcom.2020.154353>

Reference: JALCOM 154353

To appear in: *Journal of Alloys and Compounds*

Received Date: 13 November 2019

Revised Date: 11 February 2020

Accepted Date: 13 February 2020

Please cite this article as: S.-R. Yan, T. Gholami, O. Amiri, M. Salavati-Niasari, S. Seifi, M. Amiri, M. Sabet, L.K. Foong, Effect of adding TiO₂, SiO₂ and graphene on of electrochemical hydrogen storage performance and coulombic efficiency of CoAl₂O₄ spinel, *Journal of Alloys and Compounds* (2020), doi: <https://doi.org/10.1016/j.jallcom.2020.154353>.

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Shu-Rong Yan: Formal analysis. **Tahereh Gholami:** Software, Writing - Original Draft. **Omid Amiri:** Visualization. **Masoud Salavati-Niasari:** Writing - Review & Editing. Conceptualization, Supervision, Project administration. **Soodabe Seifi:** Resources. **Mahnaz Amiri:** Investigation. **Mohammad Sabet:** Data Curation. **Loke Kok Foong:** Validation, Methodology,

Effect of adding TiO₂, SiO₂ and graphene on of electrochemical hydrogen storage performance and Coulombic efficiency of CoAl₂O₄ Spinel

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Abstract

One of the famous blue pigments is cobalt aluminate which has a normal spinel that in this work has been synthesized with thermal decomposition technique via the help of olive leaf extract as a precipitation agent. Furthermore, CoAl₂O₄/SiO₂, CoAl₂O₄/TiO₂ and CoAl₂O₄/graphene nanocomposites were prepared besides the pure one. To investigate the structure and composition of products, X-ray diffraction (XRD) pattern and Fourier transform infrared (FT-IR) analysis were served. Also, the morphologies of products were studied by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) and the effect of different nucleation and growth conditions of the products were investigated. The hydrogen storage ability of the pure CoAl₂O₄

nanostructures was investigated and to increase the hydrogen storage capacity, different CoAl_2O_4 nanocomposites were prepared and studied. The maximum discharge capacity and Coulombic efficiencies are 2800 mAh/g and 62% that related to $\text{CoAl}_2\text{O}_4/\text{TiO}_2$ composition and CoAl_2O_4 , respectively.

Keywords: Nanostructures; Cobalt aluminate; Hydrogen storage; Composition; Coulombic efficiency.

1. Introduction

One of the environmentally fuels that can be used for many energy converters is hydrogen [1]. In recent years many attention is served for using nanomaterials for hydrogen storage [2-4]. Today, the decreasing of negative effects of fossil fuels have been attracted the most interest of scientists and they try to find the alternation of them [5]. On the other hand, because of the width application of hydrogen in the development of clean energy, hydrogen studied in several papers in the last decade [6]. In contrast to fossil fuels, hydrogen has several advantages such as eco-friendly, clean energy, recycle ability, safety and inexpensive [7]. Due to specific properties in comparison to bulk material, nanomaterial has great performance in the hydrogen storage field. One of the binary oxide compounds that are composed of cobalt and aluminum oxides is cobalt aluminate. Cobalt aluminate is the most famous intermediate aluminum metal [8]. Because of the specific properties of cobalt aluminate, it used a pigment industry and called Tenard's blue [9]. The CoAl_2O_4 spinel nanostructure due to having high thermal resistance, electrical, optical and catalyst properties have wide applications in the various field [10]. In recent years it was widely used for coloration of rubber, glass, ceramic, fiber and so on [11]. Besides this unique property, it has significant optical [12], catalysis [13], and magnetic [14] properties and can be used in optical devices. Up to now there are many afford to the synthesis of cobalt aluminate with different methods such as coprecipitation [15], sol-gel [16], ultrasonic hydrothermal [17], combustion [18], microwave [19] and solid-state methods [20]. In order hand, in 1990, due to increasing in chemical material pollution and a bad environmental effect of them, green chemistry appearance [21]. Green chemistry is defined as a technique that leads to the design of chemical produce and process that decrease or remove toxic material from the environment [22]. Synthesis of nanomaterials with the

help of chemical routes is required three kinds of reagents; a metal precursor, a reducing agent, and a surfactant or capping agent. By reducing each chemical reagent and replace with green materials, we can reduce the chemical synthesis hazardous [23]. Using a green plant extract instead of toxic agents is a method to synthesize nanomaterials. In this viewpoint, the enlargement of novel approaches for metal oxide nanoparticle synthesis utilizing different sources like plants, algae, fungus, bacteria and others can be deliberated as today's main challenges. These routes are using non-toxic, environmentally friendly, benign reagents. Among the green chemistry approaches, the utilize of extracts of plant from leaves, roots, seeds, fruits or flowers are a particular attentiveness route, since the plants contain a diversity of chemical components, such as amino acids, carbohydrates, vitamins, flavonoids, etc. that can act as chelating /reducing/ capping agents. These routes can coordinate the ions of the metal to form precursors of the polynuclear complex that lead to nanoparticles with narrow size distribution and high stability by thermal decomposition method. An overview of the literature indicates that there are a few investigations on the production of nanoparticles of cobalt aluminate using Sesame indium L leaves extract [24], Tamarind fruit extract [25], *Opuntia dillenii* extract [26], and Aloe Vera leaf extract [27].

In this work, we used olive leaf extract as a precipitation agent for the synthesis of CoAl_2O_4 nanostructures. Also, preparation CoAl_2O_4 via green chemistry has been used as hydrogen storage material and to the improvement of the capacity TiO_2 , SiO_2 and graphene have been applied. Graphene, TiO_2 and SiO_2 have been used to improve the performance of electrochemical hydrogen storage of the host. Graphene, a single-layer planar carbon sheet, has a special structure with superior physical characteristics that can communicate the ability of hydrogen absorption into the host materials. It is an inexpensive, chemically inert and low weight material. The chief advantage of using graphene in energy storage is the application of graphene by electrical, electrochemical, and chemical devices [28]. Nanoparticles of TiO_2 have desirable photocatalytic and redox ability. These nanoparticles can catalyst water decomposition and progress the reduction/oxidation of hydrogen atom. As an example, the lecture reported that

MWCNTs coated with TiO_2 can storage more hydrogen than the pure MWCNTs [29]. According to the reported researches, the physicochemical properties of SiO_2 nanoparticles can impressively improve hydrogen storage of the host materials characteristics [30].

The products were investigated by different analyses such as XRD, SEM, TEM and FT-IR that all of them confirmed the synthesis of pure CoAl_2O_4 and nanocomposites with nano dimension. Furthermore, to study the porosity of the products, BET analysis was served.

2. Experimental

2.1 Materials and physical measurements

All chemical reagents in our experiments were used in analytical grade without further purification. X-ray diffraction (XRD) patterns were recorded by a Rigaku D-max C III, X-ray diffract meter using Ni-filtered Cu Ka radiation. Elemental analyses were obtained from the Carlo ERBA Model EA 1108 analyzer. Scanning electron microscopy (SEM) images were obtained on Philips XL-30ESEM equipped with energy-dispersive X-ray spectroscopy. Fourier transform infrared (FT-IR) spectra were recorded on Shimadzu Varian 4300 spectrophotometer in KBr pellets. The N_2 adsorption/desorption analysis (BET) was performed at -196°C using an automated gas adsorption analyzer (Tristar 3000, Micromeritics). The pore size distribution was calculated from the desorption branch of the isotherm by the Barrett, Joyner and Halenda (BJH) method. The transmission electron microscope (TEM) image was obtained on a Philips EM208 transmission electron microscope with an accelerating voltage of 200 kV.

2.2 . Preparation of olive leaf extract

To prepare olive leaf extract, dried and chopped powders of olive leaf were prepared by grinding. The powders prepared in 100 ml ethanol were refluxed on a magnetic stirrer at 50°C for 72 hours. The solution obtained with smooth filter paper and the green solution was used in the preparation of spinel nanostructures.

2.3. Synthesis of CoAl_2O_4 (Co) nanostructure

A mixed solution of metal nitrates was prepared by dissolving $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in water with the molar ratio of $\text{Co}^{2+}/\text{Al}^{3+}=1:2$. Separately 20 ml Olive leaf extract was added. The previous reaction mixture subsequent heating at 80 °C with continuous stirring for 1 h on a hot plate allows the ions to react. The solution was evaporated on a hot plate above 120°C for dehydration and continued until the powder was obtained and then samples finally calcined at 800 °C for 5h.

2.4. Synthesis of $\text{CoAl}_2\text{O}_4/\text{TiO}_2$ (CT) nanostructure

Tetraethyl orthotitanate (1mol) and acid chloric 37% (0.5ml) were dissolved in 10 ml of ethanol and stirred for 1h. Then this solution was added to a beaker containing a mixture $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and Olive leaf extract. The solution is heated at 80 °C for 1h and 120°C until powder was obtained and then samples finally calcined at 800 °C for 5h.

2.5. Synthesis of $\text{CoAl}_2\text{O}_4/\text{SiO}_2$ (CS) nanostructure

The CS was synthesized with a reaction between $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and TEOS (tetraethyl orthosilicate) with the molar ratio of 1:2:1 in the presence of Olive leaf extract as a precipitating agent. The TEOS was dissolved in suitable amounts of water and methanol under ultrasonic and a few amounts of ethylenediamine (catalyst) was added and sonication continued for 15 min. Then this mixture was added to solution containing $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and green tea extract. The product was heated at 80 °C for 1h and 120 °C until the powder was obtained. The resulting powder was then calcinated at 800 °C for 5 h.

2.5. Synthesis of graphene (GR) from graphene oxide (GO)

In this work, the used GO was prepared by a modified Hummers method from natural graphite [31] and reduced through the described method in previous work [32].

2.6. Preparation of CoAl_2O_4 /Graphene (CG) sample

The CG was synthesized via a pregraphenization technique. Briefly, 0.1 g from Co added into the black suspension of GR (Co: GR: 1:1) and stirred for 30 min at 90°C. Finally, the beaker containing the above mixture was put in a household microwave oven (Haier, 2450 MHz, 750 W) for 15 min and then cooled to room temperature naturally. The black precipitation centrifuged and washed with distilled water and absolute alcohol, and dried at 100°C for 12 h in a vacuum dryer.

2.7. Electrochemical systems

Chronopotentiometry technique was employed to measure the hydrogen storage capacity of the electrodes. The charge and discharge cycles were performed by a three-electrode system. The Cu-samples, Ag/AgCl and Pt electrodes are used as the working, reference and counter electrodes, respectively. The electrolyte was 6 M KOH aqueous solution. In this system, the potential difference was measured between the working and the reference electrodes, and a constant current was applied between the working and counter electrodes. To make an electrode of samples, copper foam of nano-size porosities was used as a substrate for the samples. To organize an electrode of samples, 0.1 g samples was homogeneously dispersed in 5 ml ethanol for 30 min. Then, a pure copper plate (1*2 cm²) is coated by a thin layer of sample at 80 °C (ethanol was evaporated and only sample adheres to the Cu plate surface). Then, prepared plates were emerged in 20 ml ethanol (to draw off unstable sample) and then were dried. The electrode was weighted before the coating in high precision scale with a resolution of 0.01 mg in order to measure the weight of the sample after coating. The difference between weight of working electrode before and after of coating is equal to mass of sample that was coated on working electrode.[33]

3. Results and discussion

It can be observed (Fig 1a) the product is composed of Co with cubic phase ($a=b=c=8.1066 \text{ \AA}$). The peaks located at 19.39, 31.61, 37.17, 45.15, 55.97, 59.67, 65.57, 74.40 and 77.62 are related to (220), (311), (400), (422), (511), (440), (620) and (533) Miller indices, respectively that belong to Co product with JCPDS NO= 82-2252. The crystallite size of the Co sample was calculated 23.65 nm, via the Scherrer equation ($d=0.9K/\beta\cos\theta$) [34].

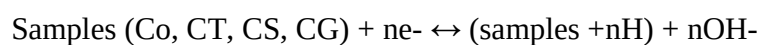
Fig 1. b shows the XRD pattern of $\text{CoAl}_2\text{O}_4/\text{TiO}_2$ (CT). It can be seen that the product is composed of two materials; one of them is CoAl_2O_4 with a cubic phase and the other one is TiO_2 with anatase and rutile phase. The other pattern is related to $\text{CoAl}_2\text{O}_4/\text{SiO}_2$ nanocomposite that due to the amorphous structure of SiO_2 it shows only the CoAl_2O_4 miller indices with cubic phase (fig 1 c). The final pattern is related to $\text{CoAl}_2\text{O}_4/\text{graphene}$ nanocomposite (fig 1 d). It can be observed that the pattern shows a peak located at 28° that belongs to the graphene structure. The other peaks are related to CoAl_2O_4 nanostructure with phase. It can be concluded that all nanomaterials such as pure CoAl_2O_4 and its nanocomposites with TiO_2 , SiO_2 and graphene structure were synthesized successfully.

Fig 2. Shows the FT-IR spectra of the synthesized products. Fig 2a shown the FT-IR spectra Co Sample. The vibration peaks located at 546 cm^{-1} and 667 cm^{-1} are related to lattice vibrations of Co-O_4 and Al-O_6 that confirm the synthesis of cobalt aluminate. The peaks are seen at 1630 cm^{-1} and 3431 cm^{-1} are belonging to stretching and bending vibrations of O-H bonding of the water molecules adsorbed on the surfaces of the nanoparticles. In fact, due to the high activate surface of the synthesized nanostructures, they can adsorb water molecules on their huge surface. The small peak located at 2853 cm^{-1} and 2923 cm^{-1} are related to symmetric and asymmetric of C-H bond that can be attributed to olive leaf extract remaining on the product surface [35, 36]. As can be seen in Fig. 2b, d and c, besides the CoAl_2O_4 peaks there are some peaks related to the TiO_2 , SiO_2 and graphene structures. The broad peak located at 950 cm^{-1} is due to the lattice vibration of Ti-O-Ti. The vibrations at 517 cm^{-1} and 669 cm^{-1} are belonging to Ti-O bond vibration [37, 38]. In the FT-IR spectra of the CS product (Fig. 2c), there are three peaks located at 476 cm^{-1} , 556 cm^{-1} and 667 cm^{-1} that are related to stretching and bending vibrations of Si-O bond. The peaks at 556 cm^{-1} and 667 cm^{-1} are due to symmetric and asymmetric vibrations of O-Si-O bond. Furthermore, a peak located at 476 cm^{-1} belongs to the bending vibration of O-Si-O bond [39, 40]. FT-IR spectra of CG is shown in Fig. 2d. The symmetric and asymmetric vibrations of C-H bond have appeared at 2850 cm^{-1} and

2924 cm^{-1} . Also the peaks located at 1122 cm^{-1} and 1627 cm^{-1} are related to stretching vibrations of C-O and C=C bonds [41].

The product size and morphology were studied by SEM images. As shown in Fig. 3 a pure CoAl_2O_4 shows sphere like besides cubic like nanostructures that can be attributed to different reasons such as nucleation and growth conditions. By synthesis of $\text{CoAl}_2\text{O}_4/\text{TiO}_2$ nanocomposite and presence of TiO_2 besides the CoAl_2O_4 nanostructure, the nucleation and growth conditions were changed and hence some aggregated nanoparticles were achieved. The aggregation is mainly due to the high surface energy of the synthesized nanostructures. There is no significant difference between $\text{CoAl}_2\text{O}_4/\text{TiO}_2$ and $\text{CoAl}_2\text{O}_4/\text{SiO}_2$ nanocomposites. However, the little difference is due to the difference between nucleation and growth conditions of TiO_2 and SiO_2 . The morphology of $\text{CoAl}_2\text{O}_4/\text{TiO}_2$ and $\text{CoAl}_2\text{O}_4/\text{SiO}_2$ nanocomposites are nanoparticles. Nanoparticles of $\text{CoAl}_2\text{O}_4/\text{SiO}_2$ nanocomposites are configured as bullets structure due to the special conditions of nucleation and growth, but these bullets are not seen in the morphology of the $\text{CoAl}_2\text{O}_4/\text{TiO}_2$ nanocomposite. The SEM images of $\text{CoAl}_2\text{O}_4/\text{graphene}$ nanocomposite is shown in Fig.3d. it can be observed that the product is composed of both zero and two-dimension nanomaterials that can be attributed to graphene and CoAl_2O_4 nanostructures. The SEM results showed the synthesis of CoAl_2O_4 nanocomposite changes the nucleation and growth conditions of the synthesis procedure that can affect the product morphology, directly.

Performance of the Co, CT, CS, CG samples in electrochemical hydrogen storage under constant current (1mA) were inspected by the galvanostatic technique in 6 M KOH aqueous medium. In the charging process, atoms of hydrogen are formed through the electrochemical decomposition of aqueous alkaline that these atoms move in the solution to the working electrode, then absorbed by prepared samples [42]. The atoms of hydrogen come out from the working electrode (process charging) [43]. The reaction of charge and discharge is displayed below:



It must be mentioned that the mechanism of storage in the electrode of prepared samples is physical adsorption. Adsorption/ desorption of atoms of hydrogen is done at ambient temperature and pressure. According to the previous lecture, the weak Van Der Waals bond is created between the hydrogen atom and material surface in physical adsorption. Instead, due to the strong chemical bond between the hydrogen atom and material surface needs to high pressure and temperature for hydrogen desorption in chemical absorption [44]

Fig 4 shows the discharge process curve of sample electrodes. The discharge capacity of Co electrode increased gradually from 150 mAh/g in the first cycle to 1750 mAh/g after 15 cycles (Fig 4 a). As you can see in Fig 4a, hydrogen storage discharge capacity from the 13th cycle to the 15th is almost constant. To improve hydrogen storage capacity was prepared composite CoAl₂O₄ spinel with TiO₂, SiO₂ and. Graphene. The addition of titanium dioxide to CoAl₂O₄ and the preparation of CoAl₂O₄/TiO₂ composition, the discharge capacity increased to 2800mAh/g after 15 cycles (Fig 4 b). The discharge capacity changes are very slow from the 9th to the 15th. Also, discharge capacity achieves 2000 mAh/g and 2700mAh/g by adding SiO₂ and graphene to CoAl₂O₄, respectively (Fig 4 c, d). the discharge capacity of the CT electrode is higher than the repeated charge and discharge cycle of sample electrodes has led to increasing discharge capacity. In the discharge curve, two obvious plateau of potential appears that indicates two different hydrogen adsorption sites [45].

To compare hydrogen storage performance, the coulombic efficiency of Co, CT, CS and CG, were calculated. The Coulombic efficiency is calculated using equation 1 which is a value less than 100, approximately [46].

$$\frac{Q_d(\text{discharge capacity})}{Q_c(\text{charge capacity})} \times 100 \quad (1)$$

Fig 5 shows the charge capacity curve of samples in the 15th cycle. The coulombic efficiency obtained 62% ($\frac{1750}{2800} \times 100$), 39% ($\frac{2800}{7100} \times 100$), 47% ($\frac{2000}{4200} \times 100$) and 27% ($\frac{2700}{10000} \times 100$) for Co, CT, CS and CG electrodes after 15 cycle, respectively. The Co electrode has coulombic efficiency higher than other electrodes. So it's a

better candidate for hydrogen storage. The production CoAl_2O_4 composition with TiO_2 , SiO_2 and graphene increased but the Coulombic efficiency decreased. Material is a suitable candidate for hydrogen storage which has to charge time minimum and discharge time maximum and has high coulombic efficiency [47].

The N_2 adsorption/desorption profile and pore size distribution of Co and CT electrodes (maximum discharge capacity relative to CS, CG samples) shown in Fig 6a, b, respectively. The Co and CT according to the IUPAC classification are type III isotherm with H3 hysteresis loop [48] (Fig 6 a).

Type III isotherm is typically found on solids containing agglomerates or aggregates of particles that form slit-shaped pores (edged or plates particles like cubes), with an irregular shape and/or size [49-55]. SEM images confirm Fig 5 a, b confirms the type of hysteresis of Co, CT samples.

As shown in Fig 6 b, the size pore is 1-100 nm, which confirms the presence of meso- and macropores in Co and CT samples. The mean pore diameter was reported 16.73 nm for Co and 11.27nm for CT sample. Also, the BET analysis showed 28.32 and 27.15 m^2/g specific surface areas for Co and CT samples, respectively.

To study more about the product size and morphology, TEM analysis was used. Fig 7 shows the TEM image of CT sample. The observations confirmed the SEM results and approved the product is composed of very tiny particles with less than 30 nm diameter aggregated together.

4. Conclusion

In summary

- The Co, CT, CS, CG samples were synthesized using a non-toxic and natural precipitating agent.
- . The XRD results showed the products have high purity and are well crystallized.
- The product size and morphology were investigated by SEM images and the results showed the difference among the pure CoAl_2O_4 and nanocomposites is due to difference in nucleation and growth conditions
- The discharge capacity of CoAl_2O_4 spinel was evaluated and improved by using TiO_2 , SiO_2 and graphene.
- The use of TiO_2 , SiO_2 and graphene with CoAl_2O_4 lead to reduces Coulombic efficiency.

- The Co and CT have maximum Coulombic efficiency (62%) and discharge capacity (2800mAh/g) after 15 cycles charge/discharge under ± 1 mA, respectively.
- The size pore of Co and CT sample are 1-100 nm which confirms the presence of meso- and macropores.

Acknowledgments

Authors are grateful to the council of Iran National Science Foundation (97017837) and University of Kashan for supporting this work by Grant No (159271/1290). Also we acknowledge for Bilingual Teaching Programme of Hainan University (hndsyk 201909); the Key project of the National Social Science Foundation of the year 2018 (18AJY013); the 2017 National Social Science foundation project (17CJY072); the 2018 planning project of philosophy and social science of zhejiang province (18NDJC086YB); the 2018 Fujian Social Science Planning Project (FJ2018B067); The Planning Fund Project of Humanities and Social Sciences Research of the Ministry of Education in 2019 (19YJA790102)

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Figure captions

Fig.1. XRD patterns of (a) Co, b) CT, c) CS, d) CG samples.

Fig 2. FT-IR spectra of (a) Co, b) CT, c) CS, d) CG samples.

Fig 3. SEM images of (a) Co, b) CT, c) CS, d) CG samples.

Fig 4 Discharge capacity curve of (a) Co, b) CT, c) CS, d) CG electrodes 15 cycle under 1 mA current.

Fig 5. Charge capacity curves of sample electrodes in the 15 cycle under 1mA current.

Fig 6. (a) N₂ adsorption/desorption isotherms. (b) Pore size distribution of Co and CT samples.

Fig 7. TEM image at different scales of CT sample.

Schmeme1. Schematic flow chart for the synthesis of (a) CoAl₂O₄/TiO₂, (b)CoAl₂O₄/SiO₂ and (c) CoAl₂O₄/Graphen nanocomposite.

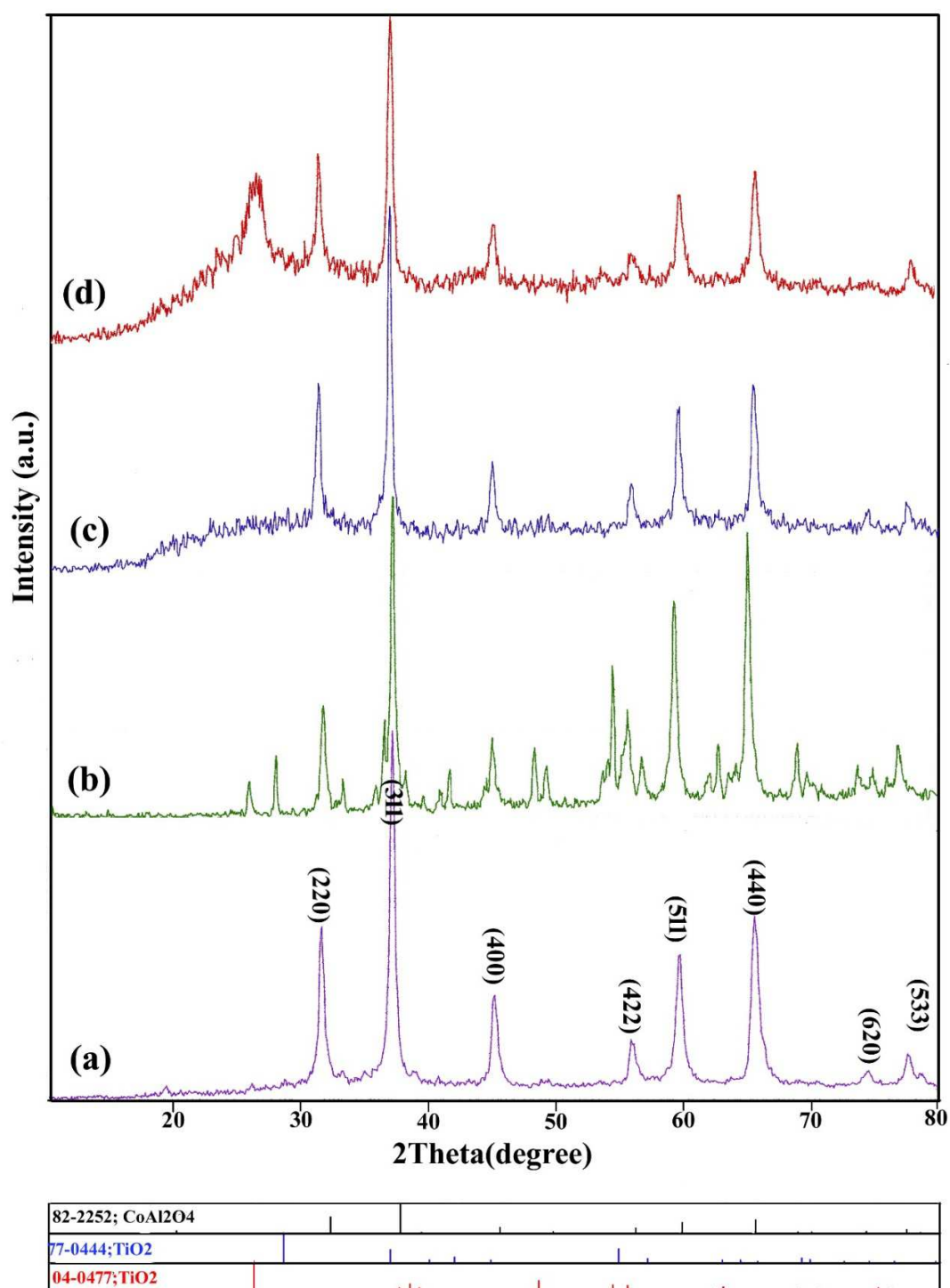


Fig.1

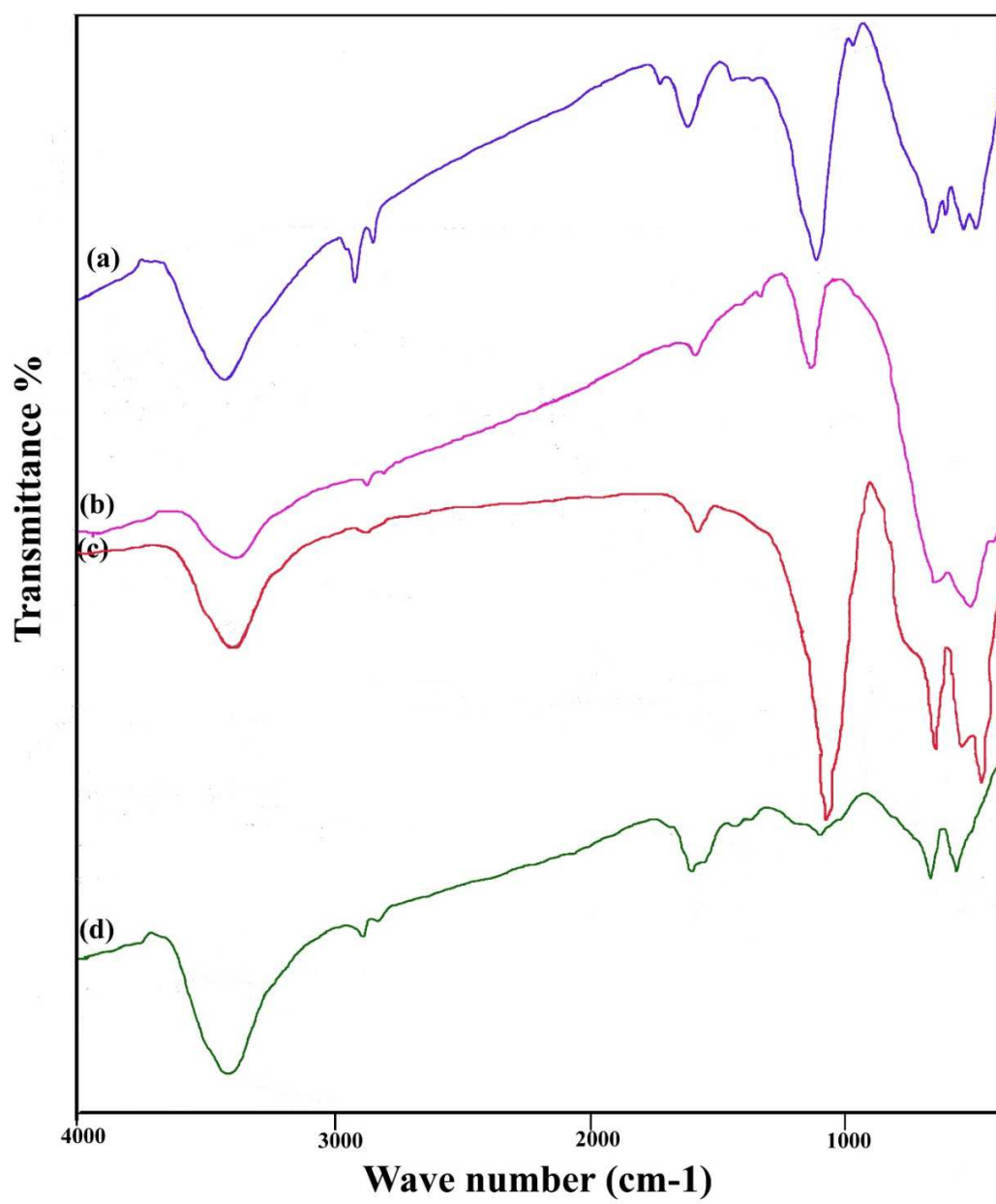


Fig.2

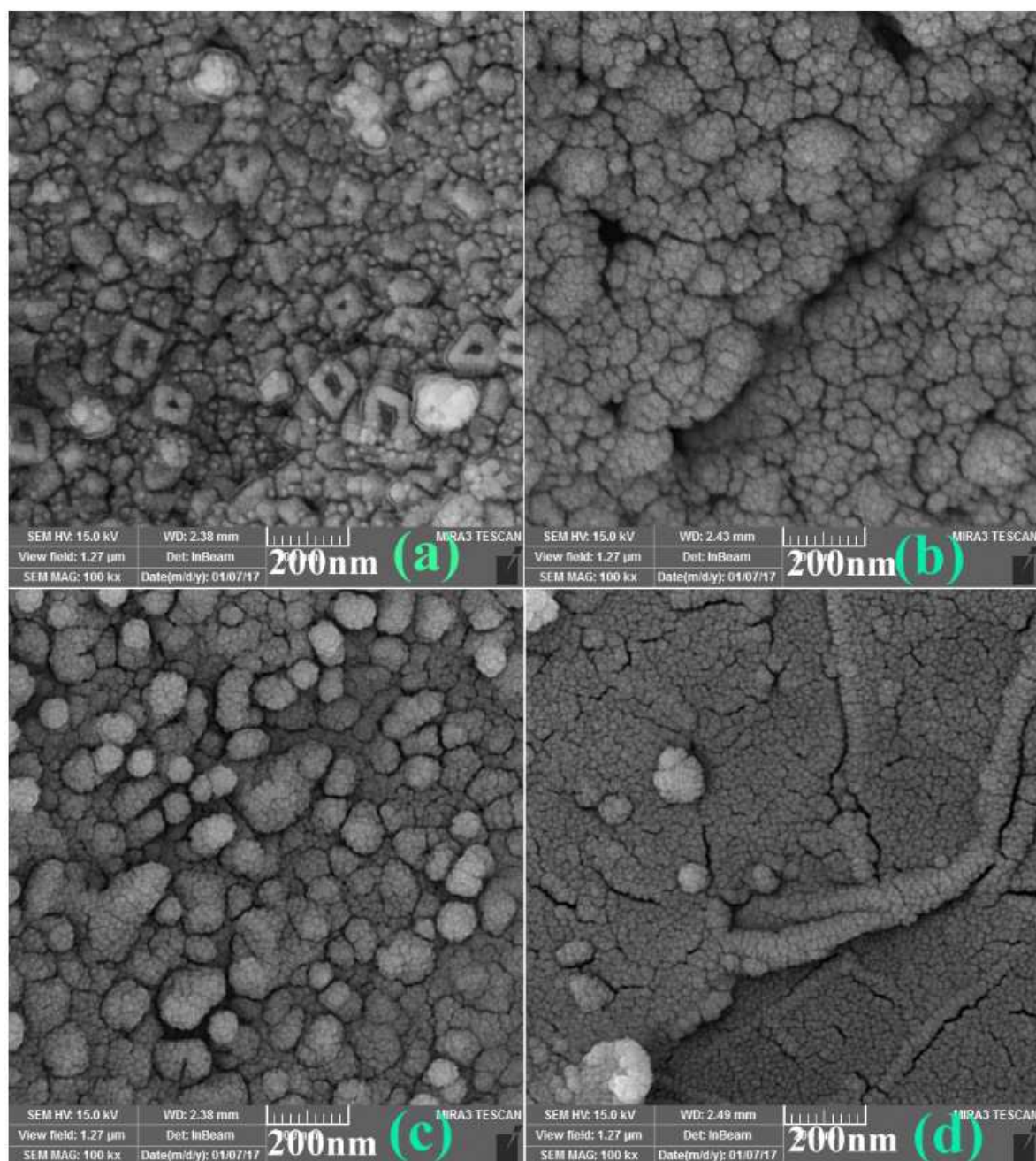


Fig. 3

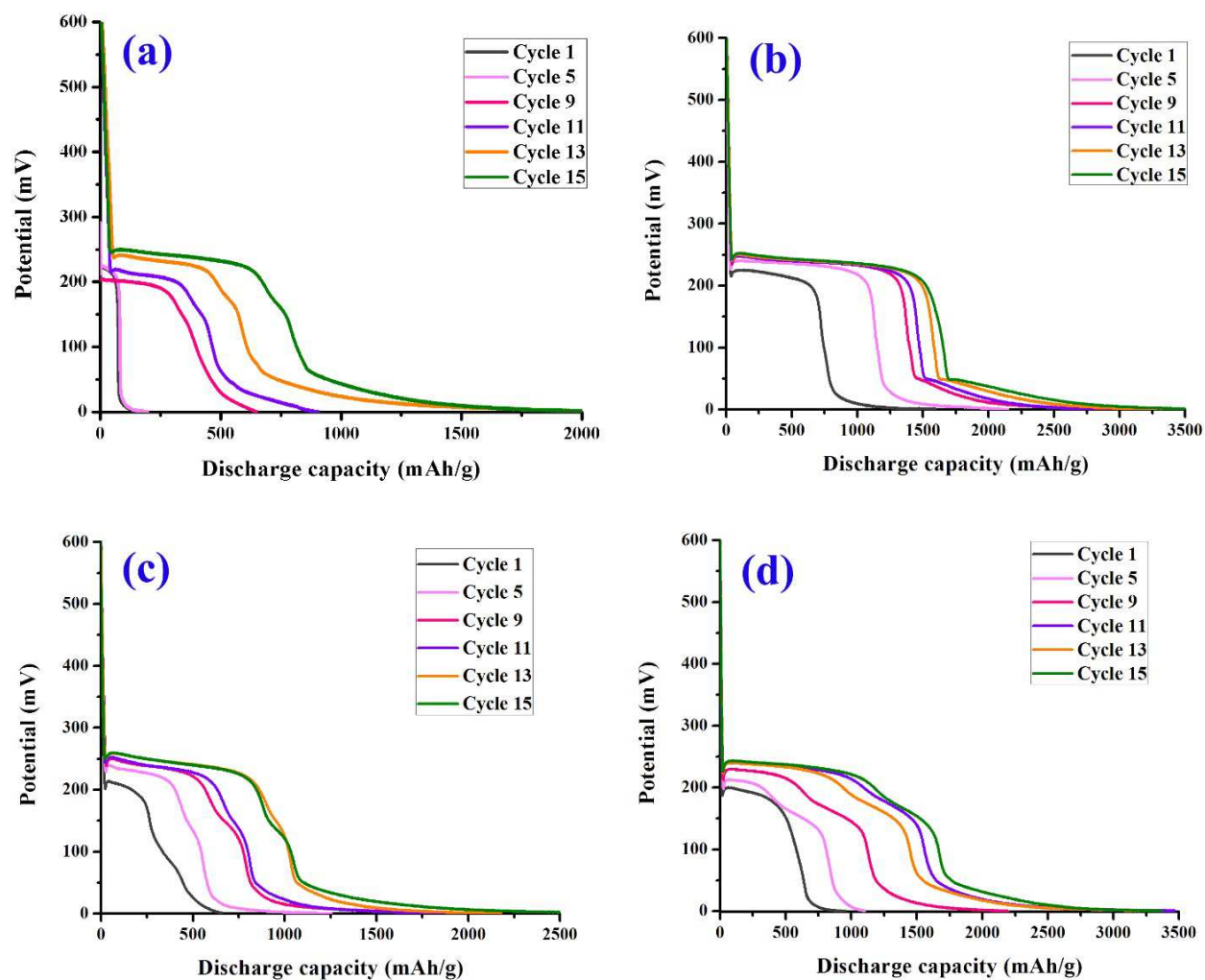


Fig. 4

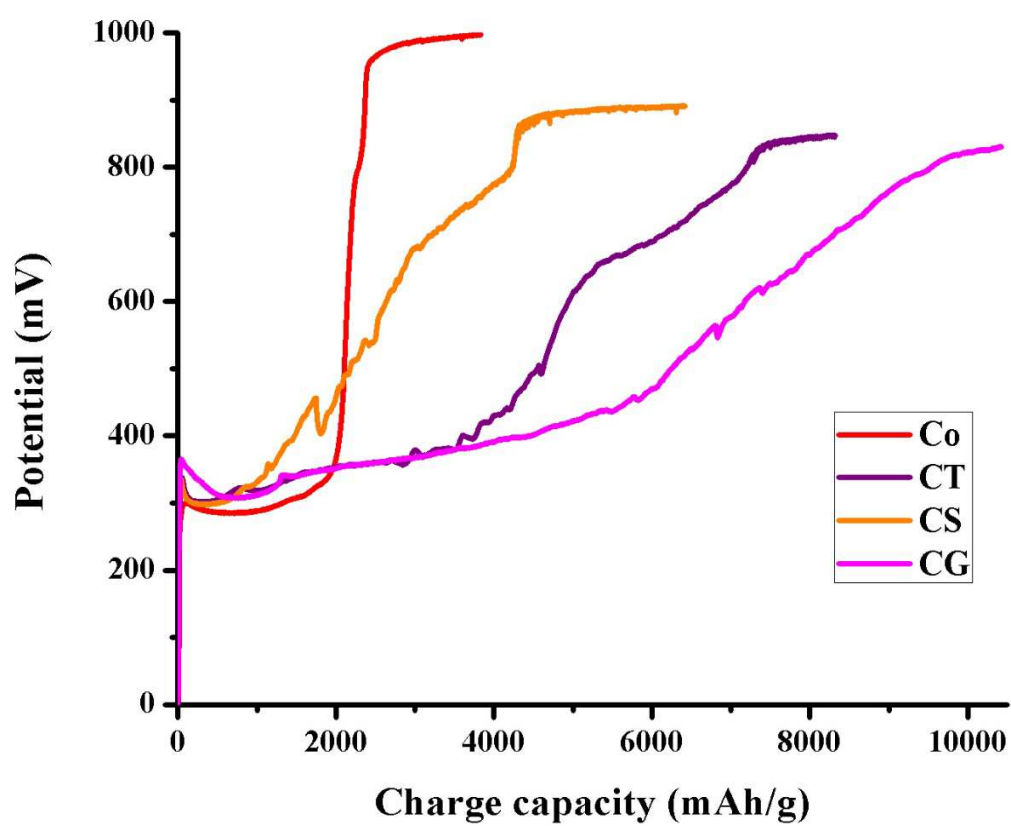


Fig. 5

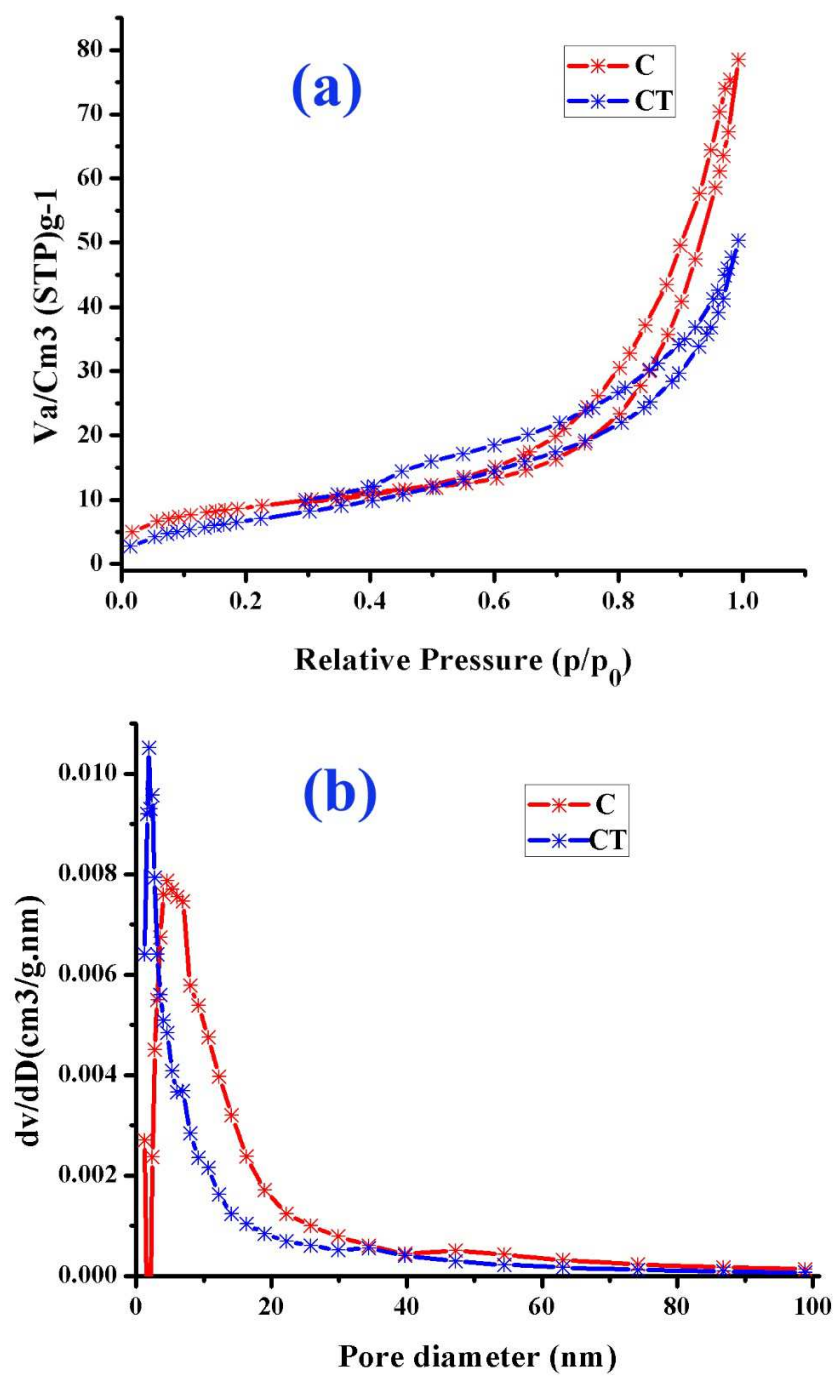


Fig. 6

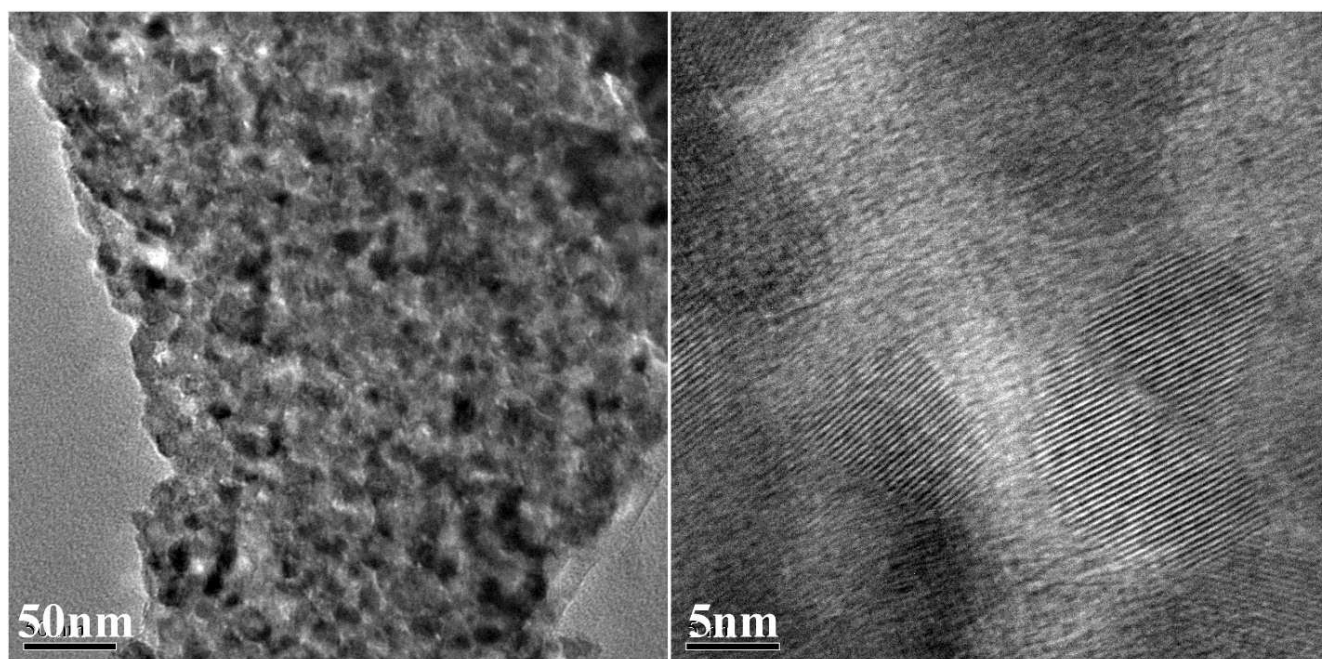
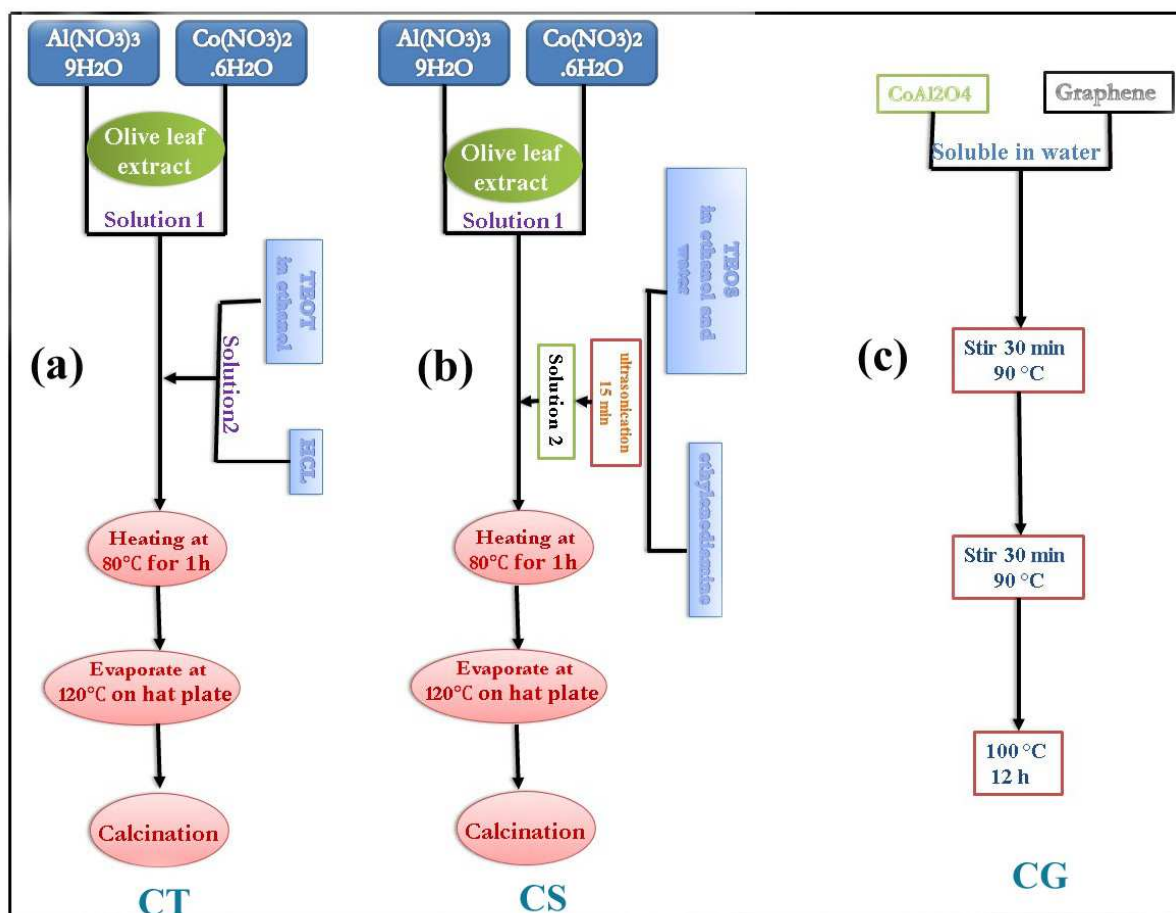


Fig. 7



Schmeme1.

- The CoAl_2O_4 spinel was synthesized via olive leaf extract.
- Hydrogen storage capacities of CoAl_2O_4 with its composites were compared.
- The Coulombic efficiency of samples was calculated, for the first time.
- The discharge capacity increased with the increase of cycle number.
- Hydrogen adsorption sites increased by repeating cycles of charge and discharge.

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Effect of adding TiO₂, SiO₂ and graphene on of electrochemical hydrogen storage performance and Coulombic efficiency of CoAl₂O₄ Spinel

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