Chapter

Preparation of Hollow Nanostructures via Various Methods and Their Applications

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Abstract

The hollow nanomaterial is a unique material to be developed because of its characteristics, especially the surface area where it has more surfaces than other materials. In general, hollow nanomaterials could be synthesized using hard-templated, soft-templated, self-templated, template-free and simple methods. In this chance, the catalyst preparation focused on using a simple method to study its activity on the dyes photodegradation reaction, deNOx reaction, carbon dioxides utilization, and photoconversion of chemical compounds. The characterization is emphasized on Scanning electron and Transmission electron Microscopes were used to identify its structure and characteristics. Furthermore, the analysis of UV-Vis spectrophotometer and HPLC is done to point out its activity on the photo-degradation of dyes, deNOx reaction, and photoconversion of cellulose and carbon dioxides utilization.

Keywords: simple method, hollow, nano material, spinel, perovskite

1. Introduction

Material that has space or cavity inside or not solid within is called a hollow material. The surface of hollow material has more area than regular materials. For example, a cube-shaped material (**Figure 1a**) has six surface areas, but if its shape changes to a hollow cubic structure (**Figure 1b**), so that it has eight surface areas. For instance, the surface area of the hollow cubic unit cell is 1.333 times the surface area of a regular cube per unit cell. The difference in the surface area depends on the geometric shape of the material if it is cylindrical or tubular, the difference in a surface area becomes much large.

In nature, some inorganic compounds have hollow structures such as zeolites even though the size of the hollow has not in the range of the nano category. However, the utilization of the hollow zeolite structures turned out to be quite a lot, for example, as function as molecular sieves [1], absorbents [1], and selective catalysts [2]. Although the application categories that can be covered come in microns.

In line with the development of nano and hollow materials, the manufacture of nano hollow single-crystal zeolites was carried out and shown in **Figure 2** below.

One of the applications that can be covered is the nano-sized material, such as zeolite, one of which is the molecular sieve where the application of purification

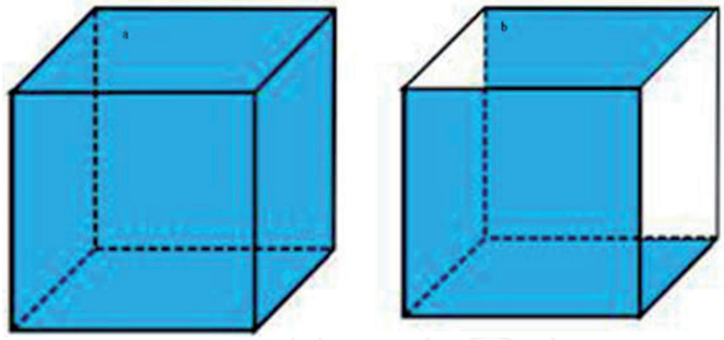

Figure 1.
The structure area of regular and hollow cubic shapes.

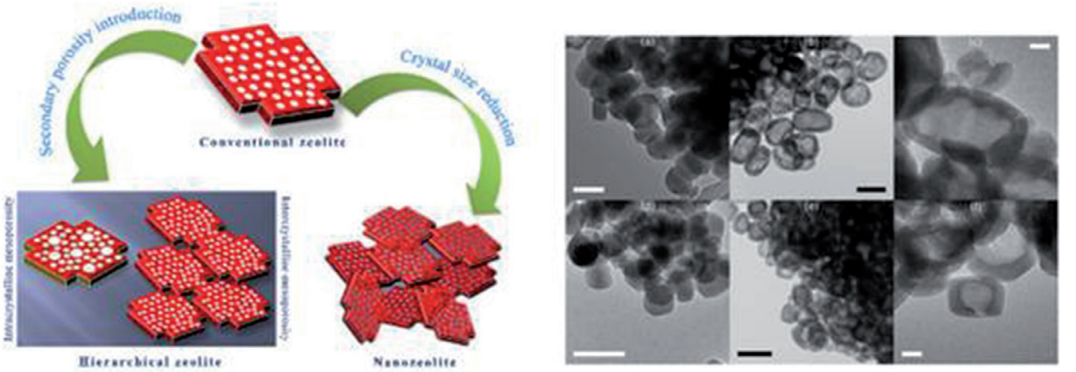

Figure 2.
A flowchart and the example of Zeolite nano hollow formation [3, 4].

or separation of pollutant particles from plastic contaminated water with nano-microns or microbes was able to be done [5].

Based on the study of specific surface area, load capacity, material transfer as well as storage, the size of the cavity makes hollow materials have extraordinary advantages in their characteristics. Having driven by these unique characteristics, the research groups eager to explore the more possible applications such as catalysis, photocatalysis, drug delivery, solar cells, supercapacitors, lithium-ion batteries, electromagnetic wave absorption, and sensors. The challenge faced in producing hollow materials at this time is to synthesize nano hollow materials which have a series of controlled structures in terms of composition and geometric configuration so that their applicative development is still constrained. However, the progress regarding the ability to manipulate both structure and morphology of nano hollow scale solid materials will have greater control over the local chemical environment [6–9].

Furthermore, the simple method used in the manufacture of nano hollow materials emphasizes the preparation process, economic review, and environmental friendliness for each of the chemicals used. This simple method is possible to produce nano hallow materials of various shapes such as nano hollow spheres (NHS), nano hollow cubes (NHC), nano hollow squared tubes (NHST), and related fibers. The applications described are the catalytic utilization of carbon dioxide into alcohol compounds, degradation of dyes, and the conversion of nano-cellulose to alcoholic sugars by photocatalysis.

2. Preparation methods

Hollow materials, in general, can be prepared using the Kirkendall effect and Ostwald ripening based on events, as well as the templating method (hard, soft, or one-pot/self-templating and free) based on the use of templates. In more detail, it described below:

2.1 Kirkendall effect

Kirkendall effect, a vacuum ordering occurs due to a change in the rate of diffusion between two or more components diffusing simultaneously. The process of different diffusion movements was proven experimentally by Smigelkas and Kirkendall [10] in 1947 that atomic diffusion occurs through the exchange of vacancies rather than by the direct replace of atoms. One example of this method is the preparation of metal oxides that can change the morphology of nanowires to nanotubes [11]. The example of nanowire formation based on Kirkendall effect is shown in **Figure 3**.

The mechanism explaining the formation of a cavity or hollow material in the inner direction could be described as follows: cations will flow rapidly outward through the oxide layer and flow inward from the void as a counterweight to the metal oxide interfacial void. Then, the direction of flow of the material is equalized by the direction of flow of the void through condensation into the pore or eliminating the crystalline defects. The direction of material flow can also result from the phenomena of diffusion and reaction pairs at the gas/solid or liquid/solid interfaces, the formation of deformations and vacancies, or both during the growth of metal oxide or sulfide layers [13, 14]. It should be remembered that the hollows produced in the metal-metal diffusion pair or near the metal oxide interfaces of an oxide growth do not produce mono-spheres in regular directions but form a very heterogeneous molecular collection.

2.2 Ostwald ripening

Ostwald Ripening is a phenomenon that is observed in solid solutions or liquid soles and explains changes in the structure of inhomogeneity with time, for example, small crystals or sol particles dissolving and being deposited back into crystals or larger sol particles. This phenomenon was first described by Wilhelm Ostwald in 1896 [15, 16] and is commonly found in oil-in-water [17] emulsions

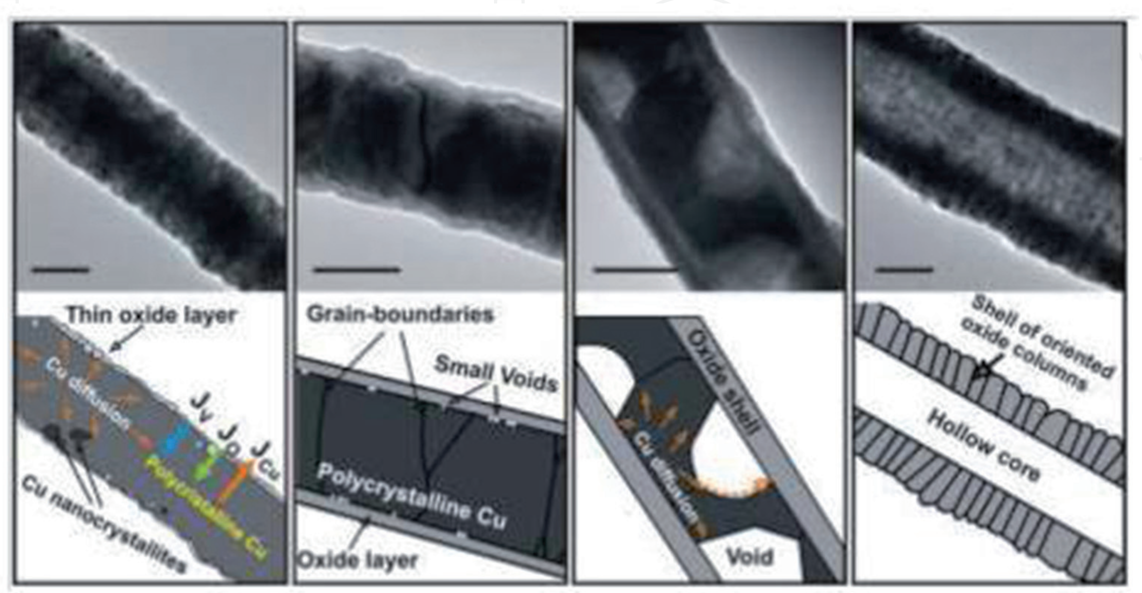

Figure 3.
The schematic formation of Hollow Cu nanowires based on Kirkendall effect during the thermal oxidation process in air at 300°C [12].

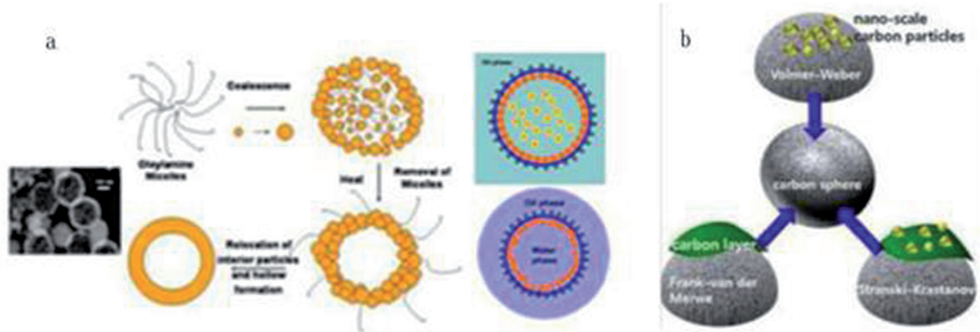

Figure 4.
Schematic of both w/o and o/w emulsion and hollow particles formation (a) using oleyamine micelles [19], and the growth of solid carbon sphere (b) based on Ostwald repining mechanism [23].

when flocculation is found in water-in-oil [18] emulsions. Schematically the w/o and o/w emulsions are presented below in **Figure 4a**.

Ostwald ripening mechanism is well-known through several growth methods, such as island formation [20], layer by layer formation [21], and the mixed layers and islands formation [22] as illustrated in a solidified growth of carbon sphere in **Figure 4b**.

The emulsion produced in the w/o or o/w system is affected by various factors such as pressure (Laplace and osmotic), the concentration of the dispersed phase, the concentration of surfactants, and the additives used. Furthermore, the emulsifiers or surfactants used are generally biopolymers such as various proteins (whey protein isolate (WPI), β-lactoglobulin, casein, soy protein isolate (SPI), and pea protein [24], polysaccharides such as xanthan, Arabic gum, modified starch, carrageenan, pectin, and modified celluloses frequently utilized to stabilize emulsions, especially O / W and W/O/W double emulsions [25].

2.3 The Smoluchowski process

The Smoluchowski process is a process to produce nano hollow complex materials in an “integrative” nature from colloidal particles. An example of this preparation was the manufacture of titanium oxide, TiO_2, and the yield observed by a high-resolution TEM [26]. The HRTEM TiO_2 micrograph showed that the tiny nanocrystallites stuck to each other in the aggregated end product while keeping the overall orientation unchanged. An example of the formation of particles based on the Smoluchowski mechanism is presented in **Figure 5** below.

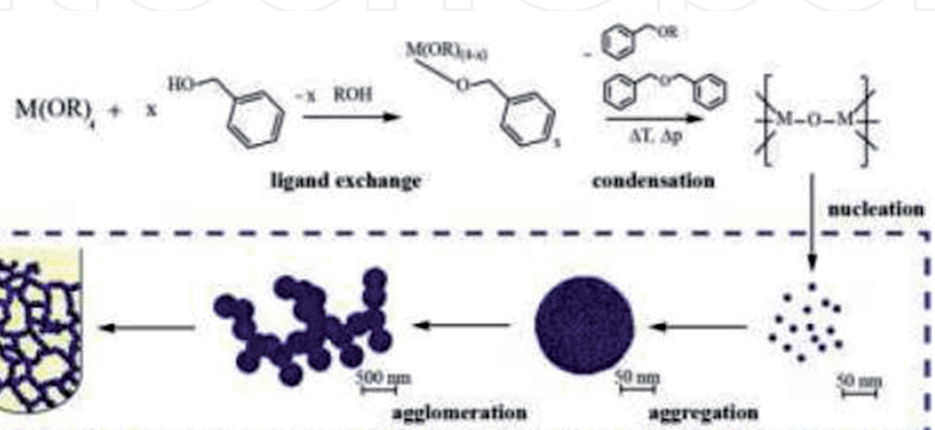

Figure 5.
An example of a particle formation mechanism based on the Smoluchowski process with an emphasis on agglomeration and aggregation [27].

2.4 Template methods

These methods can effectively control the morphology, particle size, and structure during the nanomaterial manufacturing process. In general, these methods consist of two types/categories, namely: hard methods and soft (or one-pot or self) templates according to different structures. The methods of templates in their preparation are insensitive, easy to operate, and practice.

2.4.1 Hard-template method

In principle, this method is for the preparation of one-dimensional hollow materials. Materials used as hard-templates are polymer microspheres, porous membranes, plastic foam, ion exchange resins, carbon fiber, and anodic aluminum oxide (AAO) [28, 29]. Because the templates and the resulting target products have a unique structure and influence the particle size range, they play an important role in many areas of application. Furthermore, after the desired target is obtained so that a template used is moved/separated or modified.

One example of using the hard template method is making the ordered mesoporous CeO_2 prepared via a hard-template method using SBA-15 as a structure-directing agent. Leaching with NaOH and thermal treatment at 500°C enabled the removal of the inorganic template, thus resulting in the formation of long-range ordered CeO_2. Nevertheless, small amounts of silica were present in the final oxides. The resulting CeO_2 samples were used as supports for Au nanoparticles as shown in **Figure 6** below.

2.4.2 The soft templating or the endotemplate method

The soft templating or the endotemplate method refers to supramolecular entities like self-assembled arrangements of structure-directing molecules such as surfactants, leading to mesopores up to 30 nm [31, 32].

In the soft template method as shown schematically in **Figure 7**, compounds that function as templates are organic compounds whose molecules form aggregates through inter-molecular or intra-molecular interactions such as hydrogen bonds, chemical bonds, and electrostatic forces. The metal cations as the target as the hollow material are deposited on the surface or in the inside of the aggregate. The process of placing metal cations in the aggregate carried out using electrochemical methods, precipitation, and other synthesis/preparation methods to form metal oxide or composite materials of various shapes and sizes. Organic compounds that commonly function as templates are surfactants, polymers, biopolymers, supramolecules,

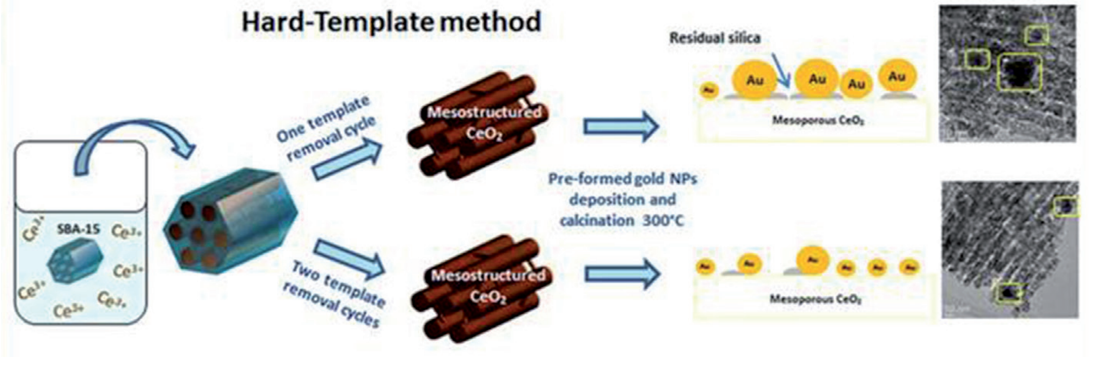

Figure 6.
Schematic pathways of Au doped CeO using hard template method [30].

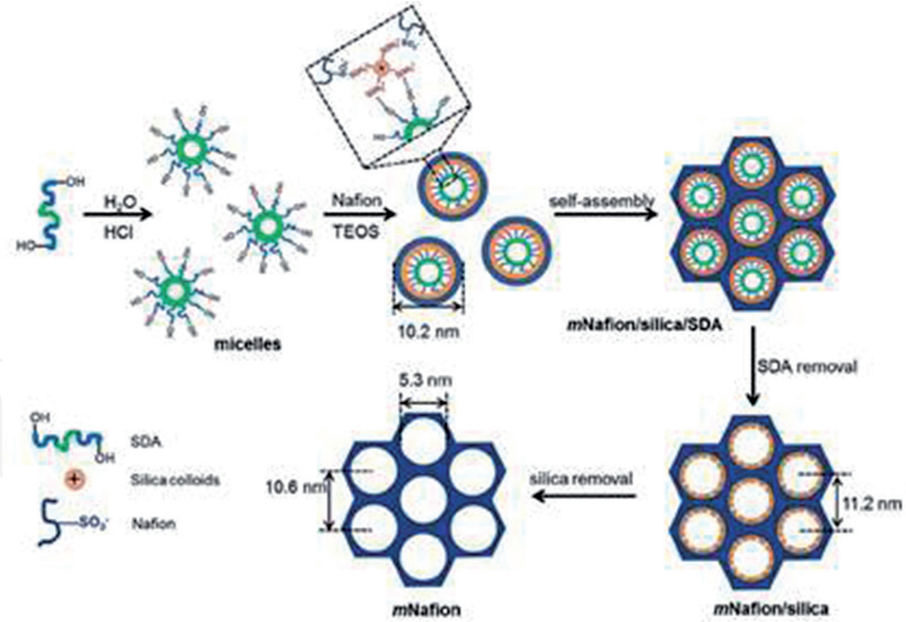

Figure 7.
Soft template pathways to produce hollow material [33].

and inorganic compounds. Based on the type of compound that can act as a soft template, it is possible to develop nanomaterial synthesis because this method has advantages such as simplicity of the process, repetition of the process with good results, and does not require removal of targets from the aggregates [34–38].

One example of a soft template method to generate ABO_3/AB_2O_4 nano hollow is spinel compounds of both Fe_3O_4 and $CoFe_2O_4$, respectively [39, 40]. Magnetite hollow spheres, Fe_3O_4 were prepared using a soft/free template with the solvothermal method described by Chen et al. [39] as follows: 13 g $FeCl_3.6H_2O$ was dissolved in 350 mL of ethylene glycol and diethylene glycol. Subsequently, 2 g NaAc, 2 g polyvinyl pyrrolidone (PVP), and sodium citrate (Na_3Cit) were added to the solution's ultrasonic processing. After an hour, the solution was sealed in a 400 mL Teflon-lined stainless-steel autoclave. The autoclave was heated to 210°C for 12 h and then cooled to room temperature naturally. The black products were collected by magnetic decantation and centrifugation, followed by repeated washing with deionized water and ethanol. The final products were dried in a vacuum oven at 50 C for 12 h. Another procedure with the same steps and only differs in the number of materials used and the washing process of the solution which turned black was washed with alcohol several times and dried at 60°C overnight. The diameter size of the product magnetite hollow spheres can be adjusted by changing the concentration of the added PVP [41]. Preparation of Fe_3O_4 using urea and PVP as a binder for Fe^{n+} cations gives nano hollow spheres as shown in the following figure.

Mandal et al. [41] have synthesized of hollow Fe_3O_4 particles via a one-step solvothermal approach for microwave absorption materials: effect of reactant concentration, reaction temperature, and reaction time as shown in **Figure 8j** below.

Then, another method of a template-free preparation of Fe_3O_4 nano hollow spheres has prepared by researcher Shi et al. [42] using the following procedure, hydrated ferrous chlorine salt ($FeCl_3.6H_2O$, 1.084 g) was dissolved in 80 mL of deionized water under rigorous and constant stirring for 10 minutes. Then added Na-citrate salt (2.352 g), PAM (0.8 g), and urea (0.72 g) while stirring vigorously for 30 minutes. The mixture was then transferred to Teflon and tightly closed before being placed into the autoclave and heated at 200°C and held at the temperature for 24 hours. Then cooled naturally with air. The result of a black precipitate Fe_3O_4 was washed with water and ethanol, separated by magnetic attraction, and finally dried

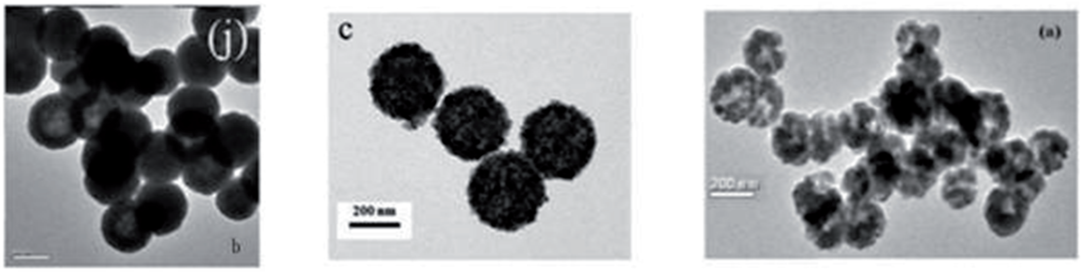

Figure 8.
The TEM results of NHS Fe_3O_4 (j), NHS Fe_3O_4 (c), and NHS $NiFe_2O_4$ spinel (a) using the solvothermal method.

at 50°C for 12 hours in an oven. An example of the results obtained by the research group of Shi et al. [42] is shown in **Figure 8c** below. Furthermore, $NiFe_2O_4$ nano hollow spinel preparation used a template-free method, namely the solvothermal process was carried out using oleyl amine capping agent. Hydrated chlorine salts of nickel ($NiCl_2.6H_2O$) and iron ($FeCl_3.6H_2O$) respectively mixed with urea with a 1:2 molar ratio. The solvent uses a mixture of ethylene glycol and ethanol with a ratio of 2:1. After all these substances put into a glass chemical 100 mL, added as much as 1 mL while stirring. After 30 minutes stir, the solution becomes transparent and homogeneous, then put the Teflon which is tightly closed and put into the autoclave steel and heated at 200°C for 24 hours. The product was then passed with ethanol and collected by separation and heated at 60°C for 30 minutes. Product samples were analyzed by TEM with a result in the following **Figure 8a** below [43].

2.5 Simple method

The simple method for producing hollow nanomaterials in question is in terms of the use of chemicals to produce nano hollow materials and environmentally friendly products. In the nano hollow material preparation, water and pectin or egg white solution is used as media. The procedure to obtain the nano hollow material is explained in brief here. The procedure to obtain the nano hollow material is explained in brief here. A stoichiometric amount of Ni (II) nitrate hydrates, ammonium vanadates, and Fe (III) nitrate hydrates were dissolved in distilled water, having compositions of $Ni_{1-x}V_xFe_2O_4$ under magnetic stirring for 1 h, respectively, followed by mixing each solution to make the final solution weight ratio between nitrates to pectin is 3:2. Adjust the pH = 11 in the above solution by an addition of ammonia, and heat it at 80 °C with continuous stirring to form a viscous gel. Then, dried the gel using the freeze dryer for 7 h to form the precursors' networks and calcined at 600 °C for 3 h. The results are shown in **Figure 9** below.

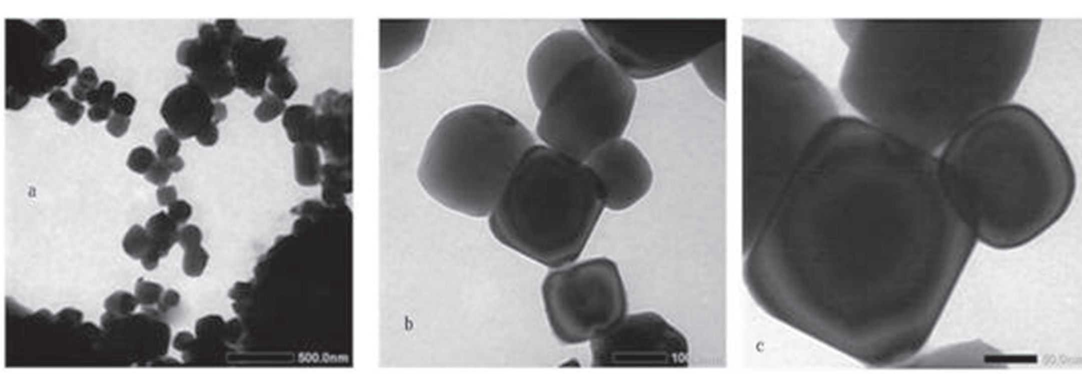

Figure 9.
TEM results of hollow material $Ni_{1-x}Fe_2O_4$ (where x = 0.1 – 0.5) were prepared using sol-gel method [44].

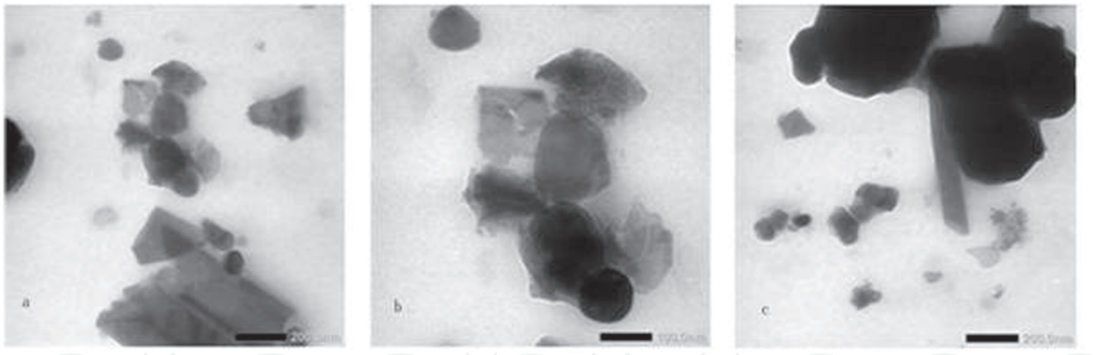

Figure 10.
TEM results of hollow nanomaterial $LaCr_{1-x}Mo_xO_3$ (x = 0.01-0.05) were prepared using sol-gel method [45].

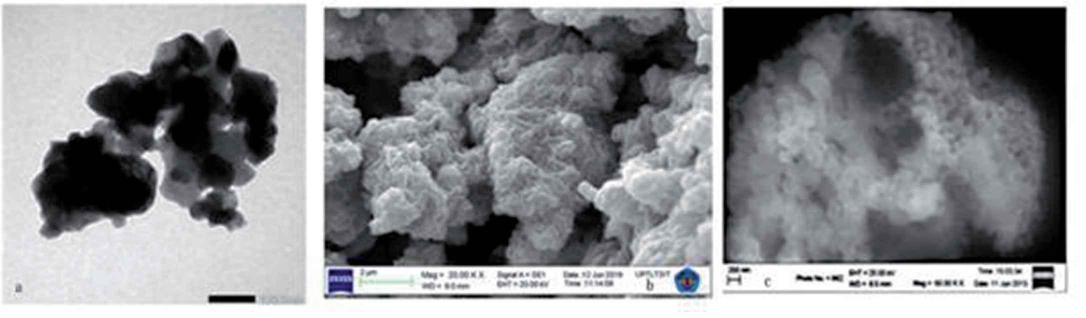

Figure 11.
TEM and SEM results of $LaCrO_3$ and $LaCr_{1-x}V_xO_3$ materials prepared using pectin and egg-white solution [46, 47].

Figure 9b and **c** clearly show the formation of nano hollow cube (NHC) from $Ni_{1-x}V_xFe_2O_4$ (x= 0.1 – 0.5) spinel. Furthermore, in **Figure 9a**, if you notice there are the cubic hollow aggregate and also a squared nano hollow tube (SNHT).

Then, in **Figure 10a** the micrograph shows that squared hollow pipes, hollow cube, and hollow tubes formed. In **Figure 10b**, you can see the nano hollow cubes (NHC) and micron sizes and nano spherical tubes (NST). Whereas in **Figure 10c**, you can see the interconnected pillars of micron and nano hollow cube sizes.

In the preparation of both pure $LaCrO_3$ and modified $LaCrO_3$ by the sol-gel method [46] gave SEM micrograph results shown in **Figure 11a** and **b**. It seemed that the shapes of material are varied that are nano hollow cubes (NHC), nano hollow tubes (NHT), and the blended shapes presented in **Figure 11a**. In **Figure 11b**, the interconnected microfiber structure and the hollow micro material formed. Meanwhile, **Figure 11c** shows the homogeneous nanoscale grains of hollow $NiFe_{2-x}Co_xO_4$ spinels prepared using the egg white solution.

3. Applications

After the preparation of all the catalysts is done, it is used respectively for both thermic catalytic reactions and photocatalysis. The compounds that are the research targets are CO_2, NOx, dyestuffs, and cellulose. The selection of the four targets intensely focused on the impact factor and the benefits that can gain.

Carbon dioxide (CO_2) and NOx gas emitted from the use of fossil energy sources containing the main elements H, C, and O as well as other minor elements N, and S. The overall reaction can be described below:

$$\text{Substrate}(C, H, O, N, S) + O_2 \rightarrow CO_2 + NO_x + SO_x + H_2O + \text{Energy}$$

The greater use of energy sources for activities, causing the emission of CO_2, NOx, and SOx gases to increase [48]. Continuous emissions without treatment will cause acid rain and the greenhouse effect. This emission will stimulate global warming and even higher. One way to participate in the handling of COx and NOx wastes is through its utilization. One of the handling methods is using the nanocatalysts to handle thermally and photonically by converting the organic wastes (solid, liquid, and gaseous) such as cellulose, dyes, and COx and NOx pollutant into products that are economically valuable and environmentally friendly as described below.

3.1 Catalytic reaction: thermis

Catalytic reaction - thermic is a catalytic reaction that takes place with the help of thermal energy. These catalytic reactions control more than 90% of processes in the chemical industry [49]. In thermic catalytic research, the study is the hydrogenation reaction of CO_2 and the decomposition of NOx exhaust gases. The research results of this reaction are briefly presented below.

3.1.1 CO_2 hydrogenation reaction

The CO_2 hydrogenation reaction was carried out using the perovskite $LaCrO_3$, and spinel $Ni_{1-x}Fe_2M_xO_4$ catalysts (M = Cu, Co, and Zn) with the reactor scheme shown in **Figure 12a** below.

The catalytic reaction takes place at a temperature of 100 to 400°C with a composition of CO_2/H_2 = 1/3 in the gas flow. Examples of reaction results using rapid tests and several quantitative analyzes are shown in **Figure 12b** and **c**, respectively.

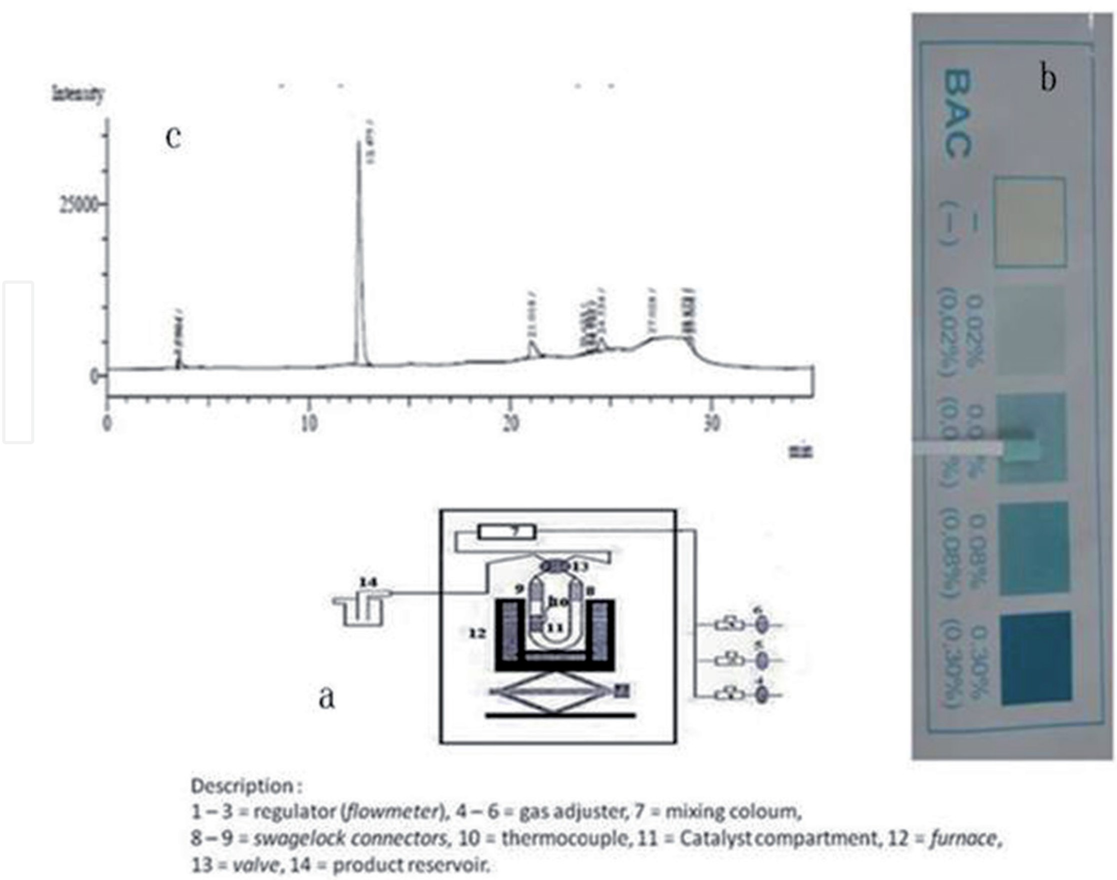

Figure 12.
Lab scale reactor (a) of CO_2 hydrogenation reaction [50], results of rapid test (b) for alcohol product [51], and chromatogram results (c) of the CO_2 hydrogenation reaction [52].

3.1.2 deNO$_x$ reaction

The decomposition reaction of NO_2 and NO or NOx is a type of reaction that uses a selective catalyst reduction (Selective Catalyst Reduction). In general, the catalyst (SCR) is used to reduce NOx, COx, and SOx emissions with the ability to reduce more than 90% of emission gases from boilers [53], power stations [54], and motorized vehicles [55] to be applicable. The results of the deNOx reaction research conducted by our team are presented in **Figure 13** below.

The NO_2 conversion results obtained using NiO/$LaCrO_3$ nanocatalyst (**Figure 13a**) is relatively better than those obtained using Fe/Zeolite Catalyst (**Figure 13b**) at the same reactant conditions and reaction temperature ranges.

3.2 Photocatalysis

Photocatalytic reactions are catalytic reactions that take place with the help of photon energy, so they are often called catalytic reactions - photonics. This reaction has been going on for a long time while the development is taking quite a while. It was a German chemist, Dr. Alexander Eibner who is firstly doing research in photocatalysis by irradiated ZnO in a concentrated Prussian blue solution and the solution became clear [58, 59]. Then, it has grown rapidly from 1964 until now, for various chemical reactions such as the production of hydrogen gas [60], and to photosynthetic-mimic reactions [61, 62]. Furthermore, our research related to photocatalysis is described below.

3.2.1 Dyes decomposition reaction

The textile and other industries usually use dyes in their products to make them look attractive. However, the remaining dyes have gone through a waste treatment process, especially in large factories but not necessarily in medium and small factories. As usual, the dye waste is thrown away into water bodies such as rivers and seas. Since the dye waste is very toxic and difficult to degrade naturally, so it can disturb the aquatic biota. One of the dyes that difficult to degrade and widely used in the small batik textile industry (home industry) is methylene golden yellow. Our research team also studied the decomposition of these dye compounds using $NiFe_2O_4$ nanocatalysts stimulated by sunlight and UV rays. An example of the result of the decomposition reaction is shown in **Figure 14** below [44].

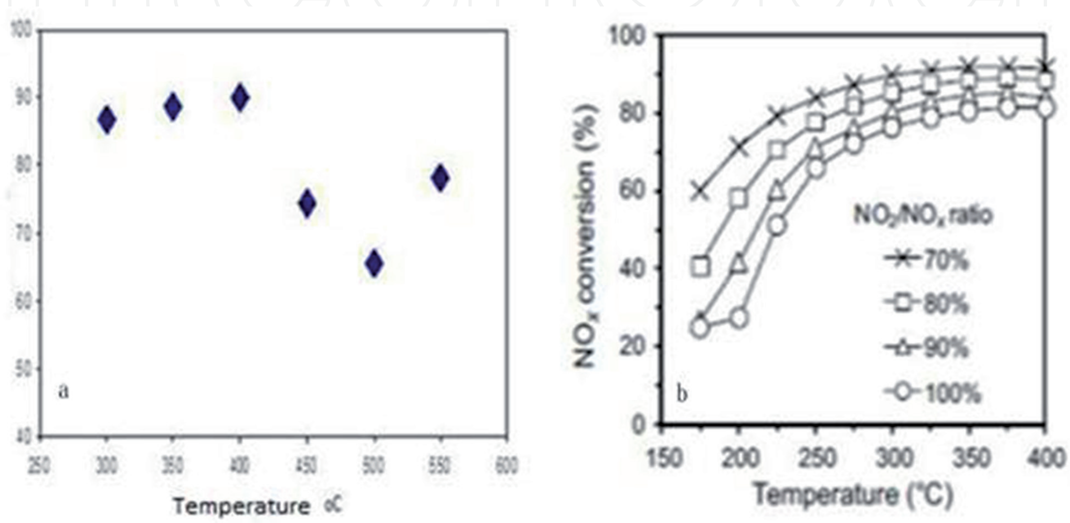

Figure 13.
Decomposition of NO$_x$ using catalysts (a) NiO/LaCrO$_3$ [56], and (b) Fe/Zeolite [57].

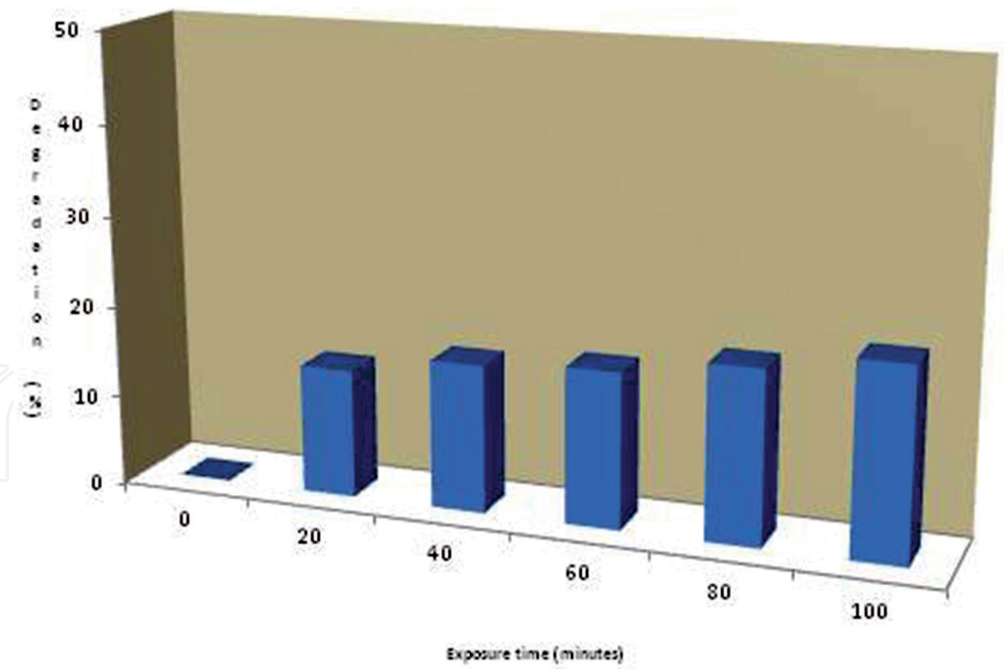

Figure 14.
RGY decomposition using $NiFe_2O_4$ nano hollow catalyst under the irradiated light of: (a) Sun, and (b) UV.

In the decomposition reaction of the remazol golden yellow dye under solar and UV irradiation, as shown in **Figure 14**, the difference in activity occurs because of sunlight contains UV rays and the nanocatalysts are active for both rays [63].

3.2.2 Cellulose conversion reaction

This type of reaction was studied considering the abundant availability of residual raw materials for agri-industrial products in Lampung Province and various conversion results such as glucose, xylitol, mannitol, sorbitol to fuel alcohol. The research team's target in the conversion of cellulose is a sugar alcohol, and the reaction takes place at room temperature and is environmentally friendly. The results achieved are shown in **Figure 15** below.

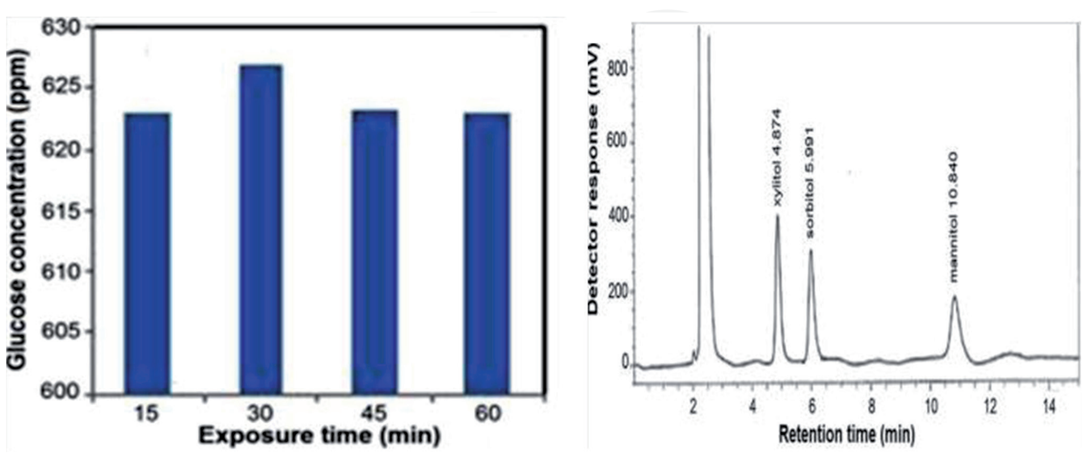

Figure 15.
Results of nano cellulose conversion (a) and the chromatogram of alcohol sugar (b) using HPLC [64].

4. Conclusion

The brief description of nano hollow materials presented in this paper is basically to provide an overview of the potential for nano hollow materials in managing reactions with results that are environmentally friendly and have economic value. Furthermore, nano hollow materials can be resulted using simple methods in terms of the chemicals used, economics point of view, and environmental considerations such as pectin, egg white, and monosaccharides in water media.

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