IOP Conf. Series: Materials Science and Engineering **349** (2018) 012026 doi:10.1088/1757-899X/349/1/012026

Photocatalyst of Perovskite $CaTiO_3$ Nanopowder Synthesized from CaO derived from Snail Shell in Comparison with The Use of CaO and $CaCO_3$

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Abstract. Calcium titanate belongs to the important group of compounds with a perovskite structure having high dielectric loss for various applications including photocatalysis mechanism. Refer to the principles of green chemistry, in this work preparation of $CaTiO_3$ was conducted by using CaO derived from snail shell. Aim of this research are to study the physicochemical character of perovskite derived from snail shell and its comparison with CaO and $CaCO_3$ as Ca sources. Material preparation was performed by solid reaction of Ca sources with TiO_2 under comparison with CaO and $CaCO_3$ precursors. Mixture of Ca sources with TiO_2 in certain proportion were ground and calcined at the temperature of 200 °C for 2 hs. Materials were characterized by using X-ray diffractometer (XRD), Fourier Transform-Infra Red (FTIR) and the photocatalytic activity was tested by using methylene blue photooxidation. Perovskite synthesized using CaO derived from snail shell exhibits the similar XRD pattern with that were prepared by using CaO and $CaCO_3$. From the photooxidation activity test, it is proven that $CaTiO_3$ shows similar photocatalytic activity correspond to that were prepared by CaO and $CaCO_3$. Utilazation of shell as agricultural waste of the synthesis of $CaTiO_3$ perovskite is the novelty of this work. Furthermore, the study on material structure and photoactivity is the main focuses for the application in industry and environment.

1. Introduction

During last two decades, photocatalysis becomes developing technology in wastewater treatment and intensively studied. Some advantageous of photocatalysis utilization are laid on the reusability of the material in further process and the more economist and efficient process. [1-3]. Conventional methods for the dye removal from waste water and textile industries viz. physical methods, chemical methods, adsorption, absorption, incineration and biological. Each method has some merits and drawbacks. For example due to large number of dyes molecules and the stability of modern dyes, conventional biological methods are ineffective for decolorization and degradation.

Some previous works explore the utilization of semiconductor materials instead of TiO_2 and ZnO that has been an interest for photocatalysis application. One of these materials is perovskite. Perovskites are the class of compounds presenting the general formula ABO_3[1]. The perovskite crystal structure has corner connected BO_6 octahedra and 12 oxygen coordinated A cations, located in between the eight BO6 octahedra (Figure 1). Some of perovskite material are $CaTiO_3$. $PbZrO_3$, $BaTiO_3$, $PbTiO_3$ commonly used piezoelectric compounds[2,3].

Perovskite of $CaTiO_3$ is the economist material for photocatalysis application and can be synthesized from the reaction of CaO and TiO_2. The high content of $CaCO_3$ in snail shell is a high potential commodity for precursors in the synthesis of $CaTiO_3$ material[4–6]. Aim of study is to evaluate chemical properties of $CaTiO_3$ derived from sail shell in comparison with $CaTiO_3$ synthesized from CaO and $CaCO_3$.

2. Materials and Method

2.1. Materials:

Snail shell (*Philla ampulacea*) was obtained from Paddy field in Bantul District, Special Region of Yogyakarta Indonesia. The determination of snail was performed by Faculty of Biology, Gadjah Mada University, Indonesia. TiO_2, methylene blue (MB), H_2O_2, CaO and $CaCO_3$ were purchased from Merck.

2.2. Synthesis of $CaTiO_3$

$CaTiO_3$ nanocrystalline powder was prepared by using stoichiometric mixture of Ca and TiO_2 at mole ratio of 1:1. The mixture was grinded until 20 minutes by using mortar and pastle and followed by calcination at 200°C for 2 hours. The syntheses were at varied source of Ca consist of snail shell, CaO and $CaCO_3$, prepared $CaTiO_3$ were encoded as $CaTiO_3$-ss, $CaTiO_3$-CaO and $CaTiO_3$-$CaCO_3$ respectively

2.3. Characterization of $CaTiO_3$

Materials were characterized by using x-ray diffractometer (XRD). XRD Shimadzu X6000 was utilized for the analyses. The corresponding X-ray diffraction patterns recorded agreement with the reported values of Joint Commitee on Powder Difraction Standards (JCPDS). FT-IR spectra of a powder sample was recorded using Perkin Elmer Spectrum 10^{TM}. Spectrophotometer and SEM profile of materials were recorded by JEOL JSM-7001F instrument.

2.4. Photodegradation experiments

Photodegradation experiment of MB using prepared $CaTiO_3$ was conducted in a photocatalytic reactor equipped with Philips UV Lamp 360nm at 40 watt of power (Figure 1). A solution containing the proper concentration of the dye, e.g., 1, 2, 3 and 5 ppm was transferred into the reactor batch photocatalyst, and then 0.5 g of $CaTiO_3$ nanocrystalline powder and 1 mL H_2O_2 was added. This mixture was irradiated under ultraviolet light with variations time 5; 10; 15; 30; 45; 60 and 120 minutes, which induced the photochemical reaction to proceed. The samples of the test were monitored on UV-visible spectrophotometer (Shimadzu 1800) at wavelength 664 nm. Co and C are the initial and sample concentration obtained by photometric method using calibration standard method.

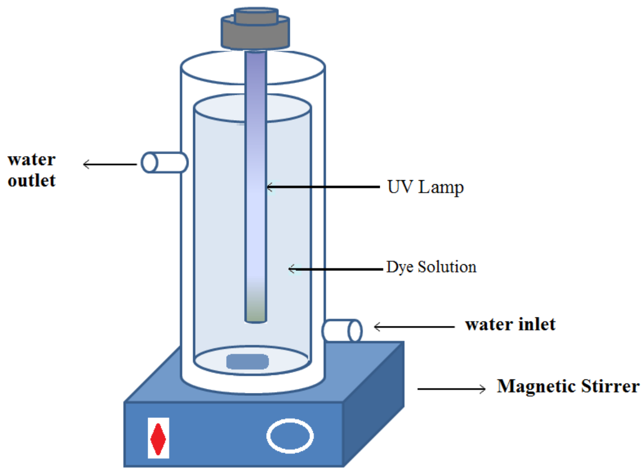

Figure 1. Schematic photoreactor

3. Results and Discussion

The crystallinity of prepared materials was identified by using XRD and the patterns are presented in Fig.2. The patterns indicate that all samples exhibit the formation of $CaTiO_3$ in mixture with TiO_2, CaO and $CaCO_3$ phases. The spectra of $CaTiO_3$ shows the reflections as indication of (012), (006), (202), (116), (018) and (214) refered to the JCPDS (Card No.22-0153)[7].

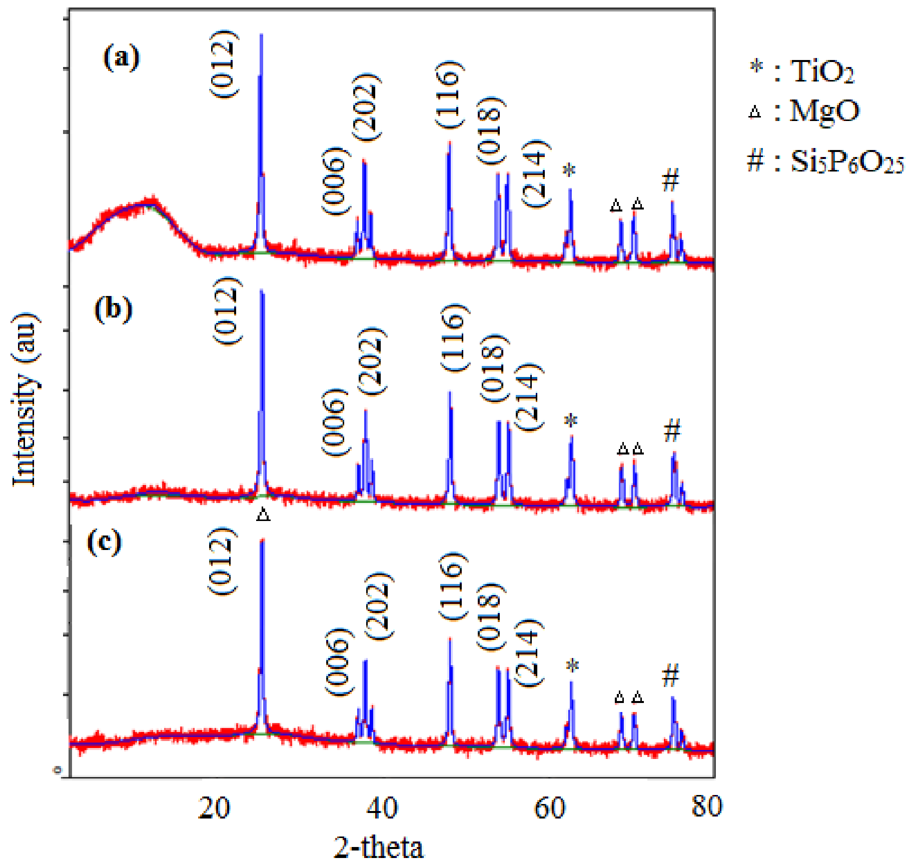

Figure 2. XRD pattern of (a) $CaTiO_3$-CaO, (b) $CaTiO_3$-$CaCO_3$,(c) $CaTiO_3$-ss,

However, some reflections are appeared as an indication of the other minerals than the perovskite phases in the solids . The indentified minerals are silica (SiO_2), MgO and $Si_5P_6O_{25}$. The presence of impurities related to the incomplete reaction during calcination at 200ºC.
Comparison on surface profile of materials is described by SEM-EDX profile in Figure 3. It can be seen that there is a surface evolution of snail shell powder to $CaTiO_3$ in which the smaller grain obtained after modification to $CaTiO_3$. There is no significant difference between $CaTiO_3$ from different CaO source indicating that the chemical interaction in the synthesis is not affected much by the impurities in snail shell content (Table 1).

Table 1. Composition of snail shell

Component	Percentange (% wt.)
Na_2O	0.12
C	14.2
CaO	83.9
Si	0.32
Mg	0.21

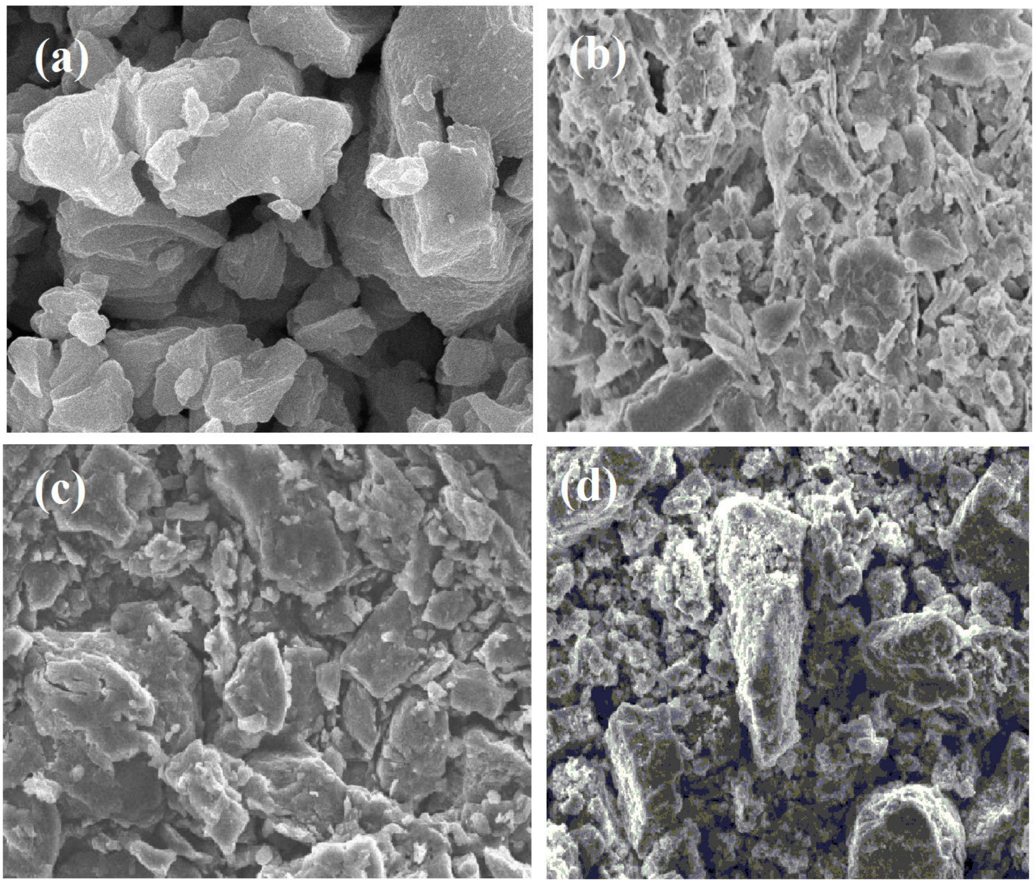

Fig.3. SEM profile of (a) snail shell powder (b) $CaTiO_3$-CaO, (c) $CaTiO_3$-$CaCO_3$,(d) $CaTiO_3$-ss

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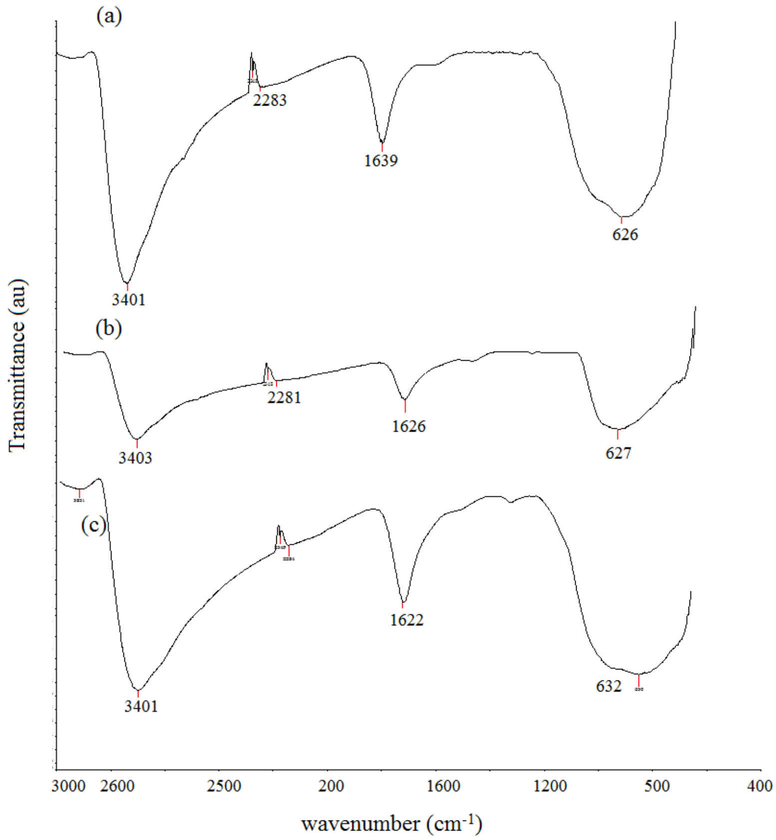
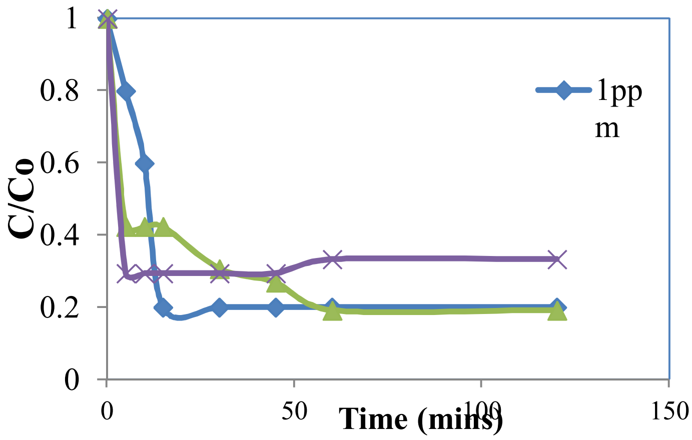


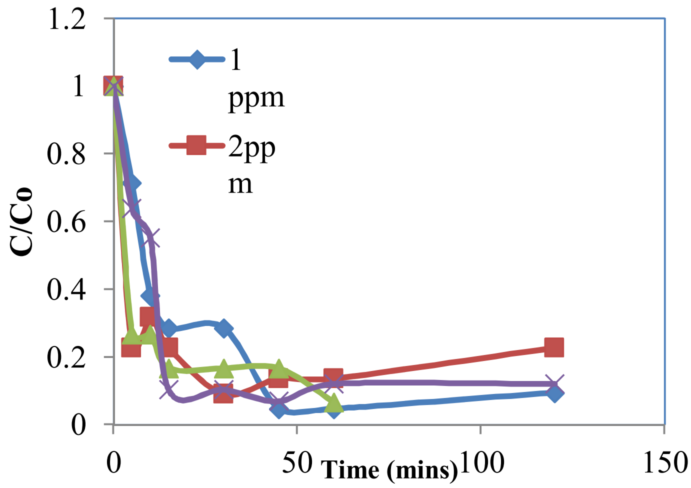
Fig. 4. FTIR spectra of (a) $CaTiO_3$-CaO, (b) $CaTiO_3$-$CaCO_3$,(c) $CaTiO_3$-ss

The FTIR spectra of materials presented in Fig.4 demonstrate some important peaks at around 632cm-cm^{-1}, 1626 cm-1 and 3403 cm^{-1}. The peaks at 1626 cm^{-1} can be ascribed to the bending vibration of O-H and the peak in the range of 500–900 cm^{-1} was assigned to the Ti-O stretching and Ti–O–Ti bridging stretching modes. The bands at 3400 cm^{-1} are clearly shows the presence of moisture and water molecular.

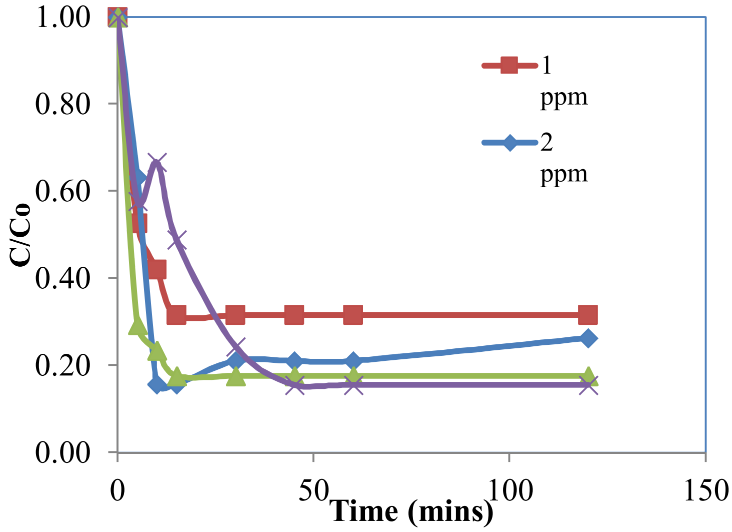
Photocatalytic activity of materials was evaluated in MB photodegradation and the kinetics are presented in Fig.5. The photodegradation was conducted in varied MB concentration. It is seen that all $CaTiO_3$ demonstrate the photoactive properties as decreasing MB concentration along increasing time of treatment is found.



(a)



(b)



(c)

Fig 5. Kinetics of MB over (a) $CaTiO_3$-CaO, (b) $CaTiO_3$-$CaCO_3$,(c) $CaTiO_3$-ss,

From photooxidation test, kinetics of MB degradation shows that $CaTiO_3$ derived snail shell is in similarly values with the kinetics degradation over $CaTiO_3$ synthesized from CaO and $CaCO_3$. The initial rate data of MB degradation over varied $CaTiO_3$ are presented in Table 2. From the data it is found that photocatalytic activity of $CaTiO_3$-ss is lower compared to other $CaTiO_3$ samples.
The kinetics of MB photooxidation occurs in random trend but the in general lowest rate over $CaTiO_3$-ss. The possible reason for the photoactivity is from the presence of impurities in the sample.

Table 2. Initial rate of MB photooxidation over prepared materials

[MB]/ppm	Initial rate (ppm/mins)		
	$CaTiO_3$-CaO	$CaTiO_3$-$CaCO_3$	$CaTiO_3$-ss
1	0.0533	0.047	0.045
2	0.022	0.103	0.112
3	0.115	0.167	0.164
5	0.235	0.299	0.170

From the kinetic simulation, it is found that the MB photodegradation obeys second order reaction.

4. Conclusion

The $CaTiO_3$ synthesis was carried out under ecofriendly, easily and cheap solid state mechanochemical method. Synthesis of $CaTiO_3$ exhibits photocatalytic activity in MB photodegradation.

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