The role of NaOH and papaya latex bio-activator during production of carbon nanoparticle from rice husks

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Abstract
This research explains the role of NaOH and bio-activator from papaya latex in the synthesis of carbon nanoparticles from rice husks in a water medium to produce fullerene-like polytype of SiC. The process begins with the pyrolysis and then the high energy milling (HEM) process followed by dispersion of NaOH and coagulation of bio-activator. The HEM process creates residual stress which produces nanocrack. NaOH dissolved into ions which activate dipole force to create dipole moment on the tip of nanocrack and become the trigger of nanocrack dispersion. The crack dispersion breaks carbon into nanoparticles having polar electrical charge so that they are dispersed homogeneously inside the water. Bio-activator then continues to perform catalytic building molecular chain as a bridge connecting pole sides of carbon nanoparticles with the bonds of van der Walls. Catalytic performance causes the coagulation process of a nanoparticle to occur which resembles the morphological structure of fullerene-like polytype of SiC with the size of 20 up to 100 nm.

Keywords: rice husks, residual stress, dispersion, bio-activation, coagulation, fullerene-like polytype of SiC
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excellent chemical inertness [9, 10]. The unique characteristics of 
SiC make it as an ideal candidate for power electronics, electron-
ics for hostile environment, diodes of blue light transillumi-
nator, sensor, composite and supported heterogeneous catalysts
[11–19]. With low dimension, the presence of quantum effect
and shape effect, nanostructure is expected to be able to show
characteristics which might not be possessed by most of other
semiconductor materials. Intensive research has been focused
on the synthesis or fabrication of the SiC nanocarbon structure
and to connect its morphology with mechanical, optical and
electrical, sensory behaviors etc [20–24].

Various efforts have been made to explore the characteristics
of nanocarbon structure of SiC starting from numerical mod-
eling to experimental research. Several numerical modeling
have been conducted to observe, such as the relation of graphite
and tubular shapes of SiC nanocarbon with optical character-
istics and emission absorption [25]. Ab initio modeling on
structure stability and electrical character of a fullerene-like
cage (SiC)12 and its product derivative has also been published
[26]. Meanwhile, Goudarziasfah et al [27] conducted computa-
tion to figure out the absorptivity of hydrogen in the nano-
structure of silicon carbide fullerene (SiC)16.

Experimentally, various methods have been developed in
the synthesis of SiC nanocarbon depending on the desired
material structure (powder, ceramic, single crystal etc) [28].
A conventional approach widely used for powder synthesis
is known as the Acheson process. In that case, reduction of
SiO2 by C to form SiC nanocarbon is made approximately at
2500 °C. Another method for large scale production of SiC
used the reaction between Si and C with medium enthalpy
change (−73 kJ mol⁻¹) [29]. This reaction is characterized
as combustion synthesis or self-propagating high-temperature
synthesis (SHS) [30].

Besides the conventional approach, material for SiC nano-
carbon can also be synthesized by different non-conventional
methods such as laser-assisted chemical vapor deposition
(CVD) [31], modified CVD method [32], method of change
from sol to gel using tetraethyl orthosilicate (TEOS) [33–35],
and catalyst assisted method [36]. Compared to the conven-
tional approach, the non-conventional one can produce better
products with higher purity level at a relatively lower temper-
ature process. Nevertheless, several weaknesses for the non-
conventional approach are high cost and highly complicated
tool installation. Besides that, a precursor used in the non-con-
ventional approach is usually harmful to the environment.
On the other side, Acheson method also has its negative side since
it requires heating at a very high temperature (the maximum
temperature may reach 2700 °C) because of the less contact
between reactant as a result of the big size of particles.

To complement this issue, researchers have been attempting
to use finer initial material to increase contacts between reac-
tant. One of the possible initial materials is agricultural waste
or plant-based biomass. This plant-based biomass contains
cellulose components that can be easily converted into carbon
(C) and a huge amount of silica (SiO2) on the epidermis
absorbed during the regeneration of cell wall [37]. Several
plant wastes that have been known for containing SiO2 are
rice husks, straw, sugarcane leaves and coconut shell [38].

Some researchers report that a variety of plant extracts can be
used as bio-activator in the synthesis of several types of metals
into nanoparticles [39]. Other research reports that the extract
of papaya callus can be used to synthesize silver nanoparticles
[40]. The research shows that bio-activator in papaya latex
can reduce silver nitrate solution into silver nanoparticles and
reduce carbonyl in carbon charcoal to become porous carbon.
Meanwhile, papaya latex can also increase the yield of carbon
nanoparticles from the material of coconut shell processed
with ball mill [41].

Nowadays, synthesis of carbon nanoparticles of SiC that
comes from biomass waste material such as rice husks, straw
or sugarcane leaves has been done [42–45]. Those various
synthesis processes dominantly use the conventional approach
which requires heating at a high temperature. Meanwhile, it is
complicated to find a synthesis process of carbon nanoparticles
of SiC which combines the use of material from plants with
natural active substance or bio-activator. There is the gap that
requires further studies. Therefore, the research on the synthesis
of carbon nanoparticles of SiC, especially the one from rice huk
waste, using bio-activator from papaya latex is essential to con-
duct in an attempt to develop the new method for the synthesis
of carbon nanomaterial of SiC which is more energy saving and
environmentally friendly. The current research fulfills the gap by
studying the synthesis process of carbon nanoparticles of SiC-
based on carbon charcoal from rice husks. The natural material
used in this research is charcoal from rice husks combined with
natural active substance from papaya latex and precursor of
NaOH. Papaya latex is used because it contains papain enzyme
proved to be able to reduce silver nitrate solution into silver nan-
oparticles [40]. Meanwhile, NaOH is used since it can dissolve
the functional group of alkyl halide on the carbon surface into
primary amino following Gabriel reaction [46].

2. Research methods

2.1. Material preparation

A procedure for preparing material is schematically presented
in figure 1. The process began with the pyrolysis of rice husks
that result in the charcoal of rice husks (C-RHs). The second
process was pounding the C-RHs in a stainless-steel tube
using a steel ball for 2 million cycles. The third process was
depositing the charcoal into water in a tube, then stirred well
and left for 8h. The small C-RHs were obtained by taken off
the sedimentation while the residual left in the water and the
small particles of CP-RHs were then dried out.

2.2. Dissolution and coagulation

The next process was the dissolution of CPs-RHs. One gram
of CPs-RHs was reacted with 3 mol of sodium hydroxide
in water for 2h. After CPs-RHs dissolved in water, then the
cogulation process was made with bio-activator from papaya
latex. Bio-activator from papaya latex sediments carbon that
has been dissolved and produced carbon nanoparticles of rice
husks (CNP-RHs).

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2.3. Determining the physical, chemical and morphological characteristics

The determination of physical, chemical and morphological characteristics of the material from the results of the preparation was done by undertaking a set of tests such as x-ray diffraction (XRD), energy dispersive x-ray spectroscopy (EDX), Fourier transform infrared spectroscopy (FTIR), scanning electron microscope (SEM), and transmission electron microscopy (TEM). TEM, SEM, and EDX are needed to analyze sizes, shapes, and distribution of phase and chemical composition. The machine for TEM test is GEOL JEM-1400, while that for SEM is FEI inspect S-50. XRD test is required to identify the composition of surface phase or surface of CPs-RHs and CNPs-RHs, a XRD test machine is PANalytical X’PertPRO. FTIR is used to determine the name of the group or chemical bonds on the surface of CPs-RHs and CNPs-RHs, a FTIR test machine is Shimadzu.

Table 1. The analysis result of XRD test.

| Sample     | Crystallin | Amorph | Total | Percentage crystallin (%) | Phase crystallin |
|------------|------------|--------|-------|---------------------------|------------------|
| CPs-RHs    | 336        | 1842   | 2178  | 15.4                      | CaC₂O₄ · H₂O     |
| CNPs-RHs   | 144        | 960    | 1104  | 13.0                      | CaCO₃            |

Figure 1. The procedure for material preparation.

Figure 2. The result of FTIR and XRD test: (a) FTIR spectra, (b) peak areas of different bondings, (c) XRD spectra.
3. Results and discussion

3.1. Phase form and surface group

The results of XRD and FTIR test on CPs-RHs and CNPs-RHs are shown in table 1 and figure 2. The XRD test on CPs-RHs results in the crystalline value of CaC2O4. H2O that is of 15.4% (see table 1 and figure 2(C1)) and XRD test on CNPs-RHs results in the crystalline value of CaCO3 that is of 13.0% (see table 1 and figure 2(C2)). Meanwhile, the residual has groups in form of the amorphous phase. Thus, it can be assumed that CNPs-RHs from the results of the process are amorphous-shaped.

Bonds or groups that lie on the carbon surface are a carbonyl, carboxyl, lactone, phenol, ether, carbonyl, anhydride [47]. The result of FTIR test in figure 2(a) shows that the bond form or groups on the surface of CPs-RHs are amine (C-N), aromatic ring (C-Car), carboxyl/ether/alcohol (C-O), alkene (C-H), alkane (C-H) and phenol (O-H) (curve a1 in figure 2(a)). Meanwhile, groups on the surface of CNPs-RHs are amine (C-N), carboxyl/ether/alcohol (C-O), carboxyl (O-H), alkene (C-H), an alkane (C-H) and phenol (O-H) as shown in curve a2 of figure 2(a).

NaOH in water has a highly significant role in the dispersion of molecular groups on the surface of carbon particles. It can be seen from figure 2(b) that there was a change of peak area on several functional groups. Aromatic ring (C-Car) groups on CPs-RHs after the process are invisible on CNPs-RHs. Carboxylate groups (O-H) that were initially invisible on CPs-RHs became visible on CNPs-RHs. Peak area of the amine group (C-N), alkene (C-H), an alkane (C-H) and phenol (O-H) decreased significantly, but on carboxyl/ether/alkyl alcohol groups (C-O) there was an increase. The amount of value change of peak area on amine group is −2.701, alkene group is −5.580, alkane group is −48.197 and phenol group (O-H) is −134.043.

The change of group is caused by ion of Na+ and OH− inside the solution during dispersion process of CPs-RHs into CNPs-RHs as in figure 2(b), showing that there was a phenomenon of peak area difference on the carbon surface groups on CPs-RHs and CNPs-RHs. The phenomenon of peak area change is illustrated in figure 3. The peak area of the aromatic ring (C-Car) on CPs-RHs was invisible when turning into CNPs-RHs, while the peak area of phenol groups on CPs-RHs decreased drastically. The process of peak area change suggested in figure 3(a) occurred with the opening of double bonds on carbon by hydroxyl ions of OH−. The opening of double bonds causes the carbon to bind hydroxyl ions to form phenol group. The final step is sodium ions of Na+ got closer to the phenol group stimulating hydrogen to be released to form hydrogen ions of H+ and finally O−Na+ bond. This bond gives polar characteristic to the carbon surface.

Synthesis shows the occurrence of amine reaction with sodium hydroxide [46]. The mechanism of the change in amine group on the carbon surface by sodium hydroxide in water is shown in figure 3(b). Hydroxyl ions of OH− stimulated N bond so that the bond got released and resulted in 2H+ to form bond with the N. The alkane change on carbon surface by sodium hydroxide is shown in figure 3(c). Hydroxyl ions of OH− stimulated hydrogen in CH3 to form Phenol and H+, then natrium ions of Na+ stimulated hydrogen in Phenol so that the surface became polar and created H+. The mechanism of sodium hydroxide changing alkene group on carbon
surface is shown in figure 3(d). Hydroxyl ions of OH$^-$ opened the double bonds to form phenol, then, ion Na$^+$ stimulated hydrogen until released to create H$^+$ which caused the group to become polar. The change of ether group is shown in figure 3(e). Hydroxyl ions of OH$^-$ followed by ion Na$^+$ stimulated R$^-$ to form HO-R$'$ so that the carbon surface became polar.

3.2. Morphology and dissolution

3.2.1. Morphology of CNPs-RHs from the results of dissolution. Figure 4 explains the result of SEM and EDX test on CPs-RHs and CNPs-RHs. Carbon particles of rice husks which are produced from milling process with steel ball are shown in SEM photograph in figure 4(a) and the result of EDX test in figure 4(b). From figure 4(a), it can be seen that the particle size of CPs-RHs is still in micron scale. Cracks in nanometer scale which are created on carbon surface are illustrated as nanocrack. The chemical elements that are contained in the carbon can be seen in figure 4(b). Figures 4(c) and (e) are results of SEM and EDX test on CNPs-RHs which are results from the corrosion of CPs-RHs with sodium hydroxide which are then sedimented using bio-activator.

From figure 4(c), it can be seen that the size of CNPs-RHs is varied between 20-100 nm. The role of sodium hydroxide as carbon disperser affects the percentage number of chemical elements in carbon as shown in figure 4(e). In CNPs-RHs, there was an increase of C, O, and Si, while Ca element decreased. The contents of Al, K, and Fe that were initially in CPs-RHs did not appear again in CNPs-RHs. Elements of Al and Fe reacted with sodium hydroxide in water turning into Al(OH)$_4$ and Na$_2$[Fe(OH)$_4$]. The elements of Ca and K turned into CaOH and KOH. After being washed with water, the elements of Al, K, Fe and some part of Ca were detached from (CPs-RHs) so that they became invisible in CNPs-RHs which caused the percentage increase on the elements of C, O, and Si due to the loss of Al, Fe, and K element. The increase of Mg element came from the Mg element that was in bio-activator. The result of TEM test on CNPs-RHs from the results of dispersion of sodium hydroxide is processed using ImageJ as
shown in figure 5(a). CNPs in an image with a scale of 200 nm in figure 5(a1) are shaped in granules with a variation of sizes between 20–100 nm. CNPs morphology in an image with the scale of 20 nm in figure 5(a2) is seen as little granules which resemble balls connected to other balls. The balls are made obvious in figure 5(a3) as the size less than 2 nm.

In figure 5(a3), transparent granules are visible in a very small size. The image is made obvious using ImageJ. The result is shown in figure 5(b1). From the image processing, ball morphology is obtained in which it consists of very small particles resembling molecules where the image is made obvious in figure 5(b1.1). According to the result of EDX test, the dominant chemical composition is silica Si and carbon C as shown in figure 4(e). Therefore, the morphology of CNPs-RHs in figure 5(b1) can be illustrated as a SiC composite consisting of polytypes [48, 49]. The morphology of Si and C is shown in figure 5(b1.1) which can be explained from the color. The white color is Si, and the red color is C according to the composition of SiC consisting of polytypes. The shape resembles the ball as if the shape of fullerene. Based on this elaboration, the result of the study on the morphology of CNPs-RHs is that composite SiC resembles fullerene [50–52] in which the morphology is illustrated in figure 5(b2).

### 3.2.2. Carbon dissolution.

The result of the SEM test in figure 4(a) and illustration of the morphology of CNPs-RHs in TEM test in figure 5(b2) shows the existence of cracks. Cracks usually occur because the dispersion process of CPs-RHs uses alkali and they are initiated by the formation of Na⁺ and OH⁻ ions with sodium hydroxide in water that releases heat energy. These ions enter the cracks that size in nanocrack in which in the location of nanocrack, excitation of electron might happen as a result of residual stress formed because of the collision of steel balls. The illustration of the dissolution process is shown in figure 6.

Figure 6(a) explains the initial process of ion Na⁺ and OH⁻ entering the location of electron excitation. Ion OH⁻ stimulated electron so that the bond was open to forming phenol bond in carbon and ion Na⁺ was alongside the phenol. Furthermore, Na⁺ ion stimulated hydrogen in phenol group to produce H⁺, and on the carbon surface, C-O-Na⁺ which is polar was formed. The carbon surface that is polar gave dipole force (FD) and dipole moment (MD) [53]. Force and moment dipole create new stress in bonds between carbons. As a result, a decrease of energy of electron bonds causes crack dispersion so that current electron excitation is created as shown in figure 6(b). This reaction continued until the ball connection was broken as shown in figure 6(c). The result was the former connection created a polar surface. The surface of the broken connection had a powerful polar characteristic so that dipole force occurred between pieces of nanoparticles which resulted in a constant motion of CNPs-RHs in the water, a phenomenon that makes it difficult for sedimentation to take place in water. Therefore, NaOH in solution does have a role to open nanocrack and help the dispersion process so that the polar carbon nanoparticles can be produced. Since it is polar, the particle does not sediment due to the interaction force with the water molecule.

### 3.3. Morphology of CNPs and coagulation

#### 3.3.1. Morphology of CNPs-RHs in the coagulation result.

The result of the TEM test on CNPs-RHs from coagulation result is processed using ImageJ as shown in figure 7(a). The size of CNPs according to the image with the scale of 200 nm in figure 7(a1) is varied in its granule forms which is between 20-100 nm. The morphology of CNPs in an image with the scale of 20 nm in figure 7(a2) shows the small granules resembling balls connected to other balls. These balls are made obvious in figure 7(a3) which sizes less than 2 nm. In figure 7(a3), transparent granules are seen in...
a very small size. The figure is made obvious using ImageJ
and the result is shown in figure 7(b1). In the figure, it is
shown that the morphology of CNPs-RHs balls consists of
very small particles resembling molecule and the figure is
made obvious in figure 7(b1.1). Based on this elaboration,
then the morphology of CNPs-RHs is illustrated as resem-
bling fullerene [50, 52–54] so that the morphology is as
illustrated in figure 7 (b2).

3.3.2. Coagulation of CNPs-RHs by bio-activator. The pres-
ence of bio-activator in the dispersion solution of carbon
nanoparticles played a role in performing the catalytic perfor-
mance which connects the polar sides of carbon nanoparticles
with van der Walls bonds. As a result, a bridge connecting
each particle was formed. It can be seen from figure 7(a2) that
two surface shapes are coarse, for the one looking dark, and
fine, for the one looking bright. The dark part is the dispersed
carbon nanoparticles while the bright part is the group of
bio-activator that has bonded particles of aromatic group and
groups from the results of decomposition by NaOH, as can be
seen in figure 3. The series of groups then create bridges that
connect fullerene-like particles.

The phenomenon is illustrated as the result of the coag-
ulation process as shown in figure 8(a), the notation (a1) as
CNPs-RHs which is coarse and index (a2) as CNPs-RHs
which is fine. In figure 8, index (a2) is an illustration of
connecting area of CNPs-RHs which is coarse. This image
is then processed again to be figure 8(b). In figure 8(b), index
(a2.1) is illustrated as residual bio-activator and index (a2.2)
is illustrated as fine CNPs-RHs which relates to one another
by bio-activator. This connection phenomenon is a change of
CNPs-RHs that is polar into non-polar so that the CNPs-RHs
can sediment. The process stages of the phenomenon of coag-
ulation reaction by bio-activator are illustrated in figure 9.

In figure 9(a), bio-activator from papaya latex [55] in water
creates bio$^{-}\text{-ion}$ and bio$^{+}\text{-ion}$ [56, 57]. Bio negative ion
stimulated Na$^{+}$ and released oxygen O as shown in figure 9(b)
which then produced carbonyl group and Na$_{2}$O then formed
bio-activator again by stimulating hydrogen in bio$^{\text{-}}$-ion until
it got released to produce 2H$^{+}$ as shown in figure 9(c). The
next step is that bio-activator in water created bio ion again
as shown in figure 9(d). In figure 9(e), bio$^{\text{-}}$-ion releases
oxygen to create bonds with carbonyl so that bonds as in
figure 9(f) are created and figure 9(g) is the result of coagula-
tion of CNPs-RHs after being dried out. The illustration of this
phenomenon caused CNPs-RHs to become non-polar so that it
could sediment. Based on the elaboration, it can be stated that
bio-activator plays a highly important role in doing a catalytic
performance to build molecular chain as a bridge connecting
polar sides of carbon nanoparticles with van der Walls bonds
in the coagulation process of dispersed nanoparticles so that
sedimentation is easily formed. This process is the excellence
of the synthesis of carbon nanoparticles under the condition of room temperature so that it efficiently saves energy. The result of this process is the structure of nanoparticles of fullerene-like polytypes of SiC with a size between 20 and 100 nm. This kind of structure is the high potential to be developed as a semiconductor application, a coating on a component of radiation, sensor, and optic material [20–22, 24].

4. Conclusions

NaOH in this research had a very significant role in breaking the carbon group by forming dipole moment that could accelerate the dissolution of nanocrack so that polar nanoparticles dispersed in water are formed. Meanwhile, bio-activator of papaya latex played a role in the coagulation process of the nanoparticles so that it could easily sediment. Therefore, the synthesis process of nanoparticle from rice husks could occur at room temperature so that it can be very potential to be developed as a method that is cheap, effective and efficient. The whole process worked simultaneously and created nanoparticles of fullerene-like polytypes of SiC in the size that is between 20 and 100 nm. The material with such structure is very potential to be developed as a semiconductor application, a coating on the component of radiation, sensor and optic material.

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