Journal of Industrial and [Engineering](http://dx.doi.org/10.1016/j.jiec.2016.10.040) Chemistry xxx (2016) xxx–xxx

Journal of Industrial and Engineering Chemistry

journal homepage: <www.elsevier.com/locate/jiec> \mathcal{N}

¹ Interconnected ruthenium dioxide nanoparticles anchored on graphite ² oxide: Highly efficient candidate for solvent-free oxidative synthesis of

³ imines

⁴ Guohao Yuan Q1 ^a , Mayakrishnan Gopiramanb, *, Hyung Joon Chac , Hwang Dong Soo^d , ⁵ Ill-Min Chung^b, Ick Soo Kim^{a,*}

A B S T R A C T

⁶ ^aNano Fusion Technology Research Group, Division of Frontier Fibers, Institute for Fiber Engineering (IFES), Interdisciplinary Cluster for Cutting Edge Research (ICCER), Shinshu University, Tokida 3-15-1, Ueda, Nagano Prefecture 386-8567, Japan
8 b Department of Applied Bioscience, College of Life & Environment Science, Konkuk University, 120 Neungdong-ro, Gwangjin-gu, Seoul 05029

^c Department of Chemical Engineering, Pohang University of Science and Technology, Pohang 790-784, South Korea

 $\frac{9}{10}$ Q₂ ^d Integrative Biosciences and Biotechnology, Pohang University of Science and Technology, Pohang 790-784, South Korea

A R T I C L E I N F O

Article history: Received 6 August 2016 Received in revised form 28 October 2016 Accepted 28 October 2016 Available online xxx

Keywords: Graphite oxide Ruthenium dioxide Nanocatalyst Imines Coupling reactions

¹¹ Introduction

12 Imines are very important moieties because of their diverse
13 reactivity which has directed to essential applications in industrial 13 reactivity, which has directed to essential applications in industrial 14 and laboratory synthetic processes 11 . The imines are highly ¹⁴ and laboratory synthetic processes $[1]$. The imines are highly 15 essential as reactive intermediates and pitrogen sources for the 15 essential as reactive intermediates and nitrogen sources for the 16 expression of fine chamicals higherically active compounds and ¹⁶ synthesis of fine chemicals, biologically active compounds and $\frac{17}{12}$ their intermediates [2.2]. As an electron bilis reasonts the reactive their intermediates $[2,3]$. As an electrophilic reagents, the reactive 18 C=N group of imines has played key role in addition, condensation
 19 and eveleptition, reactions $[4]$. Traditionally, imines, were ¹⁹ and cycloaddition reactions [\[4\]](#page--1-0). Traditionally, imines were
 $\frac{20}{2}$ cynthesized by the condensation of aminos with arrhorul 20 synthesized by the condensation of amines with carbonyl
21 separate Herman the dependence of the conductive 21 compounds. However, the drawback of these methods is utiliza-
22 compounds of delay articles are not a second as a particle of the state of $\overline{5}$ $\frac{22}{23}$ tion of dehydrating agents as well as Lewis acid catalysts [\[5\]](#page--1-0). 23 Recently, the imines are being prepared from the oxidative coupling of alcohols with aminos in the presence of motal extaller ²⁴ coupling of alcohols with amines in the presence of metal catalyst
²⁵ under inert (pittegen or argen) or Ω , atmosphere [6], Self ²⁵ under inert (nitrogen or argon) or O_2 atmosphere [\[6\].](#page--1-0) Self-
²⁶ condensation of aminos is also one of the prime routes to obtain 26 condensation of amines is also one of the prime routes to obtain 27 imines [4]. Thus far soveral transition metal based extallers imines $[4]$. Thus far, several transition-metal based catalysts

Corresponding authors. Fax: +81 268 21 5482.

E-mail addresses: gopiramannitt@gmail.com (M. Gopiraman), kimicksoo.gr@gmail.com (I.S. Kim).

Interconnected ruthenium dioxide nanoparticles (RuO2NPs) anchored graphite oxide nanocatalyst $(RuO₂/GO)$ with good BET surface-area (285 m²/g) was prepared. Under feasible reaction conditions, the $RuO₂/GO$ worked well for oxidative synthesis of imines. The RuO₂/GO catalyzed a broad range of amines including less reactive aliphatic amines in good yields (98–58%) with excellent selectivity (100%). This is the most efficient RuO₂-based nanocatalyst for the synthesis of imines among those reported to date. An indirect two-step method was adopted for the coupling of alcohols and amines, and the results found to be excellent. The reusability, stability and heterogeneity of RuO₂/GO were also investigated.

ã 2016 The Korean Society of Industrial and Engineering Chemistry. Published by Elsevier B.V. All rights reserved.

> including nano-Cu(0) [\[7\],](#page--1-0) CuO/Fe₃O₄ [\[8\]](#page--1-0), CuO/CeO₂ [\[9\]](#page--1-0), Fe-MOF ²⁸
[10] Al/MOE [11] V₂O₂ [12] CeO₂/MoO₂ [13] E-doned CeO₂ [14] 29 [\[10\],](#page--1-0) Al/MOF [\[11\]](#page--1-0), V₂O₅ [\[12\],](#page--1-0) CeO₂/MoO₃ [\[13\]](#page--1-0), F-doped CeO₂ [\[14\]](#page--1-0), ²⁹
MpO (HAR [15], meso Cs/MpOx [16], Rd(AlO(OH) [17], Rd(ZrO MnO_x/HAP [\[15\]](#page--1-0), meso-Cs/MnOx [\[16\]](#page--1-0), Pd/AlO(OH) [\[17\]](#page--1-0), Pd/ZrO₂ 30
[18] Au/Al₂O₂ [19] Au/TiO₂ [20] Au/CeO₂ [21] Au/C [22] Pt-Fe₂O₂ 31 $[18]$, Au/Al₂O₃ [\[19\]](#page--1-0), Au/TiO₂ [\[20\]](#page--1-0), Au/CeO₂ [\[21\]](#page--1-0), Au/C [\[22\],](#page--1-0) Pt–Fe₂O₃ ³¹ [\[23\]](#page--1-0), Ag/Al₂O [\[24\]](#page--1-0), Ir/CeO₂ [\[25\]](#page--1-0), and Pt–Sn/y-Al₂O₃ [\[26\]](#page--1-0), have been ³²
reported. Metal free, carbon, based, catalysts, (graphene, oxide. 33 reported. Metal-free carbon based catalysts (graphene oxide, 33
activated carbon and CNTs atc.) are also reported [27]. However, 34 activated carbon and CNTs *etc.*,) are also reported $[27]$. However, 34
these systems leither metal free or (up)supported metal based 35 ³⁵ these systems [either metal-free or (un)supported metal-based catalytic systems] are obviously suffered from at least one of the 36
four main points: (1) Q. atmosphere (2) bigher amount of catalytic 37 four main points; (1) O₂ atmosphere, (2) higher amount of catalyst, 37
 (2) longer reaction time, and (4) reusobility. Notably, under 38 (3) longer reaction time, and (4) reusability. Notably, under $\frac{38}{2}$ solvent-free reaction conditions, most of the catalytic systems 39
showed poor reushility due to unavoidable blocking of catalytic 40 showed poor reusability due to unavoidable blocking of catalytic 40 active sites by the reactants and products. $\frac{41}{1000}$
Wide chamical states ($\frac{11}{100}$ to $\frac{42}{100}$) and tupable preparties $\frac{42}{100}$

> Wide chemical states ($-H$ to +VIII) and tunable properties, 42 ruthenium was found to be a superior catalyst for organic reactions 43 [\[28,29\].](#page--1-0) Notably, the $RuO₂$ is known to be an excellent oxidation 44
catalyst because of its redox proporties [20]. However, Bu based 45 catalyst because of its redox properties [\[30\]](#page--1-0). However, Ru-based 45
catalysts are found to be inefficient for the imines synthesis [41] 46 catalysts are found to be inefficient for the imines synthesis $[4]$. 46
Soveral By complexes were employed as homogeneous satalytic 47 Several Ru-complexes were employed as homogeneous catalysts 47
for iminos synthosis, but the reastions are sarried out under inert for imines synthesis, but the reactions are carried out under inert $\frac{48}{12}$
atmospheres or barsh reaction conditions. Whereas supported By atmospheres or harsh reaction conditions. Whereas, supported Ru 49
catalysts, often promoted, pitrile, formation, from bonzulamines catalysts often promoted nitrile formation from benzylamines

<http://dx.doi.org/10.1016/j.jiec.2016.10.040>

1226-086X/ $\textcircled{\,}$ 2016 The Korean Society of Industrial and Engineering Chemistry. Published by Elsevier B.V. All rights reserved.

Please cite this article in press as: G. Yuan, et al., Interconnected ruthenium dioxide nanoparticles anchored on graphite oxide: Highly efficient candidate for solvent-free oxidative synthesis of imines, J. Ind. Eng. Chem. (2016), <http://dx.doi.org/10.1016/j.jiec.2016.10.040>

2 G. Yuan et al./Journal of Industrial and Engineering Chemistry xxx (2016) xxx–xxx

⁵¹ [\[31\]](#page--1-0). In 2009, Kim et al. [\[32\],](#page--1-0) demonstrated that $Ru(OH)_x/TiO_2$ 52 **Q4** catalytic system is efficient for the cross-coupling of primary ⁵³ benzylic or cinnamyl alcohols with anilines or aliphatic amines.
54 **05** Later Cano at al. [22] reported that $P_{\text{U}}(QU)$, (Fe, Q, can be used for ⁵⁴ **Q5** Later, Cano et al. [\[33\]](#page--1-0), reported that $Ru(OH)_3/Fe_3O_4$ can be used for imines synthesis under inert atmosphere, and they found that 55 imines synthesis under inert atmosphere, and they found that 56 addition of base (KOH or NaOH) would switch the final products 56 addition of base (KOH or NaOH) would switch the final products 57 excity. Upfortunately, most, of the Bu based beteromooyie 57 easily. Unfortunately, most of the Ru-based heterogeneous
 58 extending Bu/HAB and BuCl (TiO, were failed to promote ⁵⁸ catalysts including Ru/HAP, and RuCl_x/TiO₂ were failed to promote
⁵⁹ the coupling of aminos [34]. Hence, developing an efficient Pu ⁵⁹ the coupling of amines [\[34\]](#page--1-0). Hence, developing an efficient Ru-
 $\frac{60}{2}$ based beteroganeous establise system for the imines synthesis is a 60 based heterogeneous catalytic system for the imines synthesis is a challenging task 61 challenging task.

 62 Surface area, nature of support, metal-support interaction, 63 structure of catalyst and particle size are the key factors for the ⁶³ structure of catalyst, and particle size are the key factors for the 64 ⁶⁴ activity of supported metal catalysts [\[35](#page--1-0)–38]. Obviously, graphene
⁶⁵ is a unique 2D material for metal papoparticles (NPs) due to its 65 is a unique 2D material for metal nanoparticles (NPs) due to its 66 important physicochemical properties such as unique structure 66 important physicochemical properties such as unique structure,
 67 high aposifie surface area, and chemical inertness [20, 42] 67 high specific surface area, and chemical inertness [39–[43\].](#page--1-0) ⁶⁸ Efficient nanocatalysts such as CuO/GNS [\[44\]](#page--1-0), Ru/GNS [\[45\]](#page--1-0) and
⁶⁹ PuO NBa/CNS [46] were recently reported by our group (where 69 RuO₂NRs/GNS [\[46\]](#page--1-0) were recently reported by our group (where
 70 GNS is graphene papecheets). The results declared that the 70 GNS is graphene nanosheets). The results declared that the 71 papertalists are efficient for unique examic transformations 71 nanocatalysts are efficient for various organic transformations.
 72 Usesing we propaged interconnected ruthonium disvide pape. 72 Herein, we prepared interconnected ruthenium dioxide nano-
 73 existence (DeO NPs) analyzed examplification association 73 particles (RuO₂NPs) anchored graphite oxide nanocatalyst
74 (D₁O₂/CO) The D₁O₂/CO uses there termined in data like magnetic 74 (RuO₂/GO). The RuO₂/GO was characterized in detail by means of TEM, XPS, XRD, Raman, SEM–EDS, BET and ICP-MS analyses. The $\frac{P_{\text{U}}Q}{P_{\text{U}}Q}$ (CQ was analysed as a betare announce announced by the p 76 RuO₂/GO was employed as a heterogeneous nanocatalyst for the 77 evidative synthesis of iminos oxidative synthesis of imines.

⁷⁸ Experimental

⁷⁹ General

80 Graphite oxide (GO) with >90% purity was purchased from ACS
 81 materials USA $P₁(2525)$ (07%) and mathanol were obtained from ⁸¹ materials, USA. Ru(acac)₃ (97%) and methanol were obtained from $\frac{82}{1}$ sigma Aldrich All other chamicals were purchased from Sigma 82 Sigma Aldrich. All other chemicals were purchased from Sigma $\frac{83}{4}$ Aldrich or Wake Pure Chemicals. Details of materials characteri 83 Aldrich or Wako Pure Chemicals. Details of materials characteri-
84 antion and catalytic product conformation are provided in the 84 zation and catalytic product conformation are provided in the 85 Supporting information Supporting information.

86 Preparation of $RuO₂/GO$

87 0.398 g of Ru(acac)₃ and 1.0 g of GO were dispersed in methanol
 $\frac{88}{2}$ and sopisated for sourced bours. Subsequently, the minture upse ⁸⁸ and sonicated for several hours. Subsequently, the mixture was
 $\frac{89}{25}$ stimed at GE SC for several hours to sympaths the mathemal. The ⁸⁹ stirred at 65 °C for several hours to evaporate the methanol. The $\frac{90}{20}$ required portion in the methanol. $\frac{90}{100}$ resultant powder was grinded well with mortar and pestle until ⁹¹ the homogeneous mixture was obtained and then the resultant $\frac{92}{100}$ mixture was kept under vecuum for 24 b. Finally, the solid mixture ⁹² mixture was kept under *vacuum* for 24 h. Finally, the solid mixture
⁹³ was salsinated in the muffle furnase under N. atmosphere at 93 was calcinated in the muffle furnace under N_2 atmosphere at
94 600 °C (boating rate of 5 °C/min) for 3 b. For comparison pure CO 94 600 °C (heating rate of 5 °C/min) for 3 h. For comparison, pure GO
95 and Pu(2020), were calcinated in the muffle furnace under same ⁹⁵ and Ru(acac)₃ were calcinated in the muffle furnace under same
 96 conditions (N₂ atmosphere at 600 °C for 3 h) and the resultant
 97 pourders (PCO and PuO) were tested powders (RGO and $RuO₂$) were tested.

98 Procedure for the self coupling of primary amines

⁹⁹ 25 mg of RuO₂/GO (0.98 mol% Ru) and 2 mmol of benzylamine
¹⁰⁰ were introduced into 25 mL round bottom flask with a magnetic ¹⁰⁰ were introduced into 25 mL round bottom flask with a magnetic 101 bar. The mixture was stirred under air atmosphere at 100 °C for 3 h ¹⁰¹ bar. The mixture was stirred under air atmosphere at 100 °C for 3 h.
¹⁰² The reaction was monitored by GC analysis. After completion of the 102 The reaction was monitored by GC analysis. After completion of the 103 reaction, the catalyst was separated by centrifugation and the 103 reaction, the catalyst was separated by centrifugation and the 104 crude mixture was checked by CC applyies to calculate the 104 crude mixture was checked by GC analysis to calculate the 105 conversion vield and selectivity. The product was further 105 conversion, yield and selectivity. The product was further 106 confirmed by NMR and MS(CC) analyzes. The catalyzet was also 106 confirmed by NMR and MS(GC) analyses. The catalyst was also 107 converted out from the reaction mixture by simple contributation. ¹⁰⁷ separated out from the reaction mixture by simple centrifugation,
¹⁰⁸ unched well with disthulather dried at 60 °C and then reused (F) ¹⁰⁸ washed well with diethyl ether, dried at 60 °C, and then reused. (E)-
¹⁰⁹ N Bonzylidene 1, phonylmethanamine (22): ¹¹¹ NMP (400 MHz) 109 N-Benzylidene-1-phenylmethanamine (2a): ¹H NMR (400 MHz,

DMSO-d₆): δ (ppm) 4.87 (2H, s, PhCH₂), 7.25–7.35 (5H, m, PhH), ¹¹⁰
7.52 (2U m, PhH), 7.84 (2U m, PhH), 8.65 (1U s, CU N), ¹³C NMP 7.52 (3H, m, PhH), 7.84 (2H, m, PhH), 8.65 (1H, s, CH=N); ¹³C NMR ¹¹¹
(100 MH₂, DMSO, d.); $\frac{8}{3}$ (sam); 64.37 (CH), 13714 (CH), 139.36 (100 MHz, DMSO-d₆): δ (ppm) 64.37 (CH₂), 127.14 (CH), 128.26 ¹¹² (CH), 128.35 (CH), 128.72 (CH), 129.03 (CH), 131.10 (CH), 136.44 (C), 113
129.00 (C), 162.10 (CH); CC, MS (m/z); 105.4 ¹¹⁴ 139.99 (C), 162.10 (CH); GC–MS (m/z): 195.4.

Procedure for cross-coupling of anilines with primary amines 115

A mixture of benzylamine (2 mmol), aniline (6 mmol) and 116
clust (25 mg 0.98 Bu mol%) were stirred under air atmosphere 117 catalyst (25 mg, 0.98 Ru mol%) were stirred under air atmosphere 117
at 100 °C for 3 b (E)-N-Benzylideneaniline (5a): ¹H NMR (400 MHz 118 at 100 °C for 3 h. (E)-N-Benzylideneaniline (5a): 1 H NMR (400 MHz, 118 $DMSO-d_6$: δ (ppm) 7.08 (1H, m, PhH), 7.45–7.55 (7H, m, PhH), 7.84 ¹¹⁹
(2H, m, PhH), 8.60 (1H, s, CH, N); ¹³C, NMP (100 MHz, DMSQ, d,); 120 (2H, m, PhH), 8.69 (1H, s, CH=N); ¹³C NMR (100 MHz, DMSO-d₆): ¹²⁰
 $\frac{\delta(\text{mm})}{\delta(\text{mm})}$ 132.2 (CH) 132.4 (CH) 132.3 (CH) 138.8 (CH) 138.0 (CH) 121 δ (ppm) 122.3 (CH), 122.4 (CH), 127.3 (CH), 128.8 (CH), 128.9 (CH), 121
120.3 (CH), 120.3 (CH), 130.1 (CH), 130.1 (CH), 131.1 (CH), 136.5 (C) 122 129.2 (CH), 129.2 (CH), 130.1 (CH), 130.1 (CH), 131.1 (CH), 136.5 (C), 122
152.1 (C), 160.2 (CH); CC, MS (m/z); 180.5 ¹²³ 152.1 (C), 160.2 (CH); GC–MS (m/z): 180.5.

¹²⁴ Procedure for synthesis of imines from alcohols and amines

25 mg of RuO₂/GO (0.98 mol% Ru) and 2 mmol of benzyl alcohol 125
re magnetiselly stirred under onen air struggehere at 110 °C for 126 were magnetically stirred under open air atmosphere at 110 \degree C for 126
20 b. Subsequently, 2 mmal of benzyl amine, was added to the 127 29 h. Subsequently, 2 mmol of benzyl amine was added to the 127
share assisting with was additional for 10 min (F). M Boundidage 128 above reaction mixture and stirred for 10 min . (E) -N-Benzylidene-
1. above reaction the service (25) , (11) -NMP, $(400 \text{ MHz} - \text{DMCO} - 1)$, (129) 1-phenylmethanamine $(2a)$: ¹H NMR (400 MHz, DMSO-d₆): ¹²⁹ δ (ppm) 4.87 (2H, s, PhCH₂), 7.25–7.35 (5H, m, PhH), 7.52 (3H, 130
m, PhH) 7.84 (2H, m, PhH), 8.65 (1H, c, CH_{-N}), ¹³C MMB (100 MH₇ 131 m, PhH), 7.84 (2H, m, PhH), 8.65 (1H, s, CH=N); ¹³C NMR (100 MHz, ¹³¹
DMSO d. \; ⁸ (ppm) 64.27 (CH), 12714 (CH), 128.26 (CH), 128.25 ¹³² DMSO-d₆): δ (ppm) 64.37 (CH₂), 127.14 (CH), 128.26 (CH), 128.35 ¹³²
(CH), 128.32 (CH), 130.02 (CH), 121.10 (CH), 126.44 (C), 120.00 (C) (CH), 128.72 (CH), 129.03 (CH), 131.10 (CH), 136.44 (C), 139.99 (C), 133
142.10 (CH); CC MS (m/z); 105.4 162.10 (CH); GC-MS (m/z): 195.4.

Results and discussion and the state of the state of

Please cite this article in press as: G. Yuan, et al., Interconnected ruthenium dioxide nanoparticles anchored on graphite oxide: Highly efficient

candidate for solvent-free oxidative synthesis of imines, J. Ind. Eng. Chem. (2016), <http://dx.doi.org/10.1016/j.jiec.2016.10.040>

Physicochemical characterization of $RuO₂/GO$ 136

HRTEM images were taken for GO and $RuO₂/GO$; the results are
provided in [Fig.](#page--1-0) 1. The pure GO is pure, continuous, wrinkled and
transparent sheet with an average thickness of about 0.8, 2 pm transparent sheet with an average thickness of about 0.8–2 nm. 139
The fine dispersion of PuO, papoparticles on the surface of CO was The fine dispersion of $RuO₂$ nanoparticles on the surface of GO was
explained by referring the HRTEM images [\(Fig.](#page--1-0) 1(b–d)). Moreover, 141
the BuO, papoparticles were interconnected to each other and the RuO₂ nanoparticles were interconnected to each other and 142
uniformly covered the surface of CO. This interesting morphology uniformly covered the surface of GO. This interesting morphology 143
might, have saveed from the uniform aggregation of the BuO might have caused from the uniform aggregation of the $RuO₂$ and $H⁴⁴$ have nonparticles during the calcination precess. The size of $RuO₂$ and $H⁴⁵$ nanoparticles during the calcination process. The size of $RuO₂$ and H^{45} nanoparticles was difficult to measure since the BuO, particles are nanoparticles was difficult to measure since the $RuO₂$ particles are
interconnected and irregular in shape. To find out the reason for
the formation of this interconnected antivoral like membelom: the formation of this interconnected network-like morphology, 148
carbon panetubes (CNTs) were also employed as a support carbon nanotubes (CNTs) were also employed as a support. 149
However the membology could be seen only with CO Honce we However, the morphology could be seen only with GO. Hence, we 150
concluded that the morphology is bigbly dependent on the pature concluded that the morphology is highly dependent on the nature 151
of support and in the present sase it is mainly due to the 2D pature of support and, in the present case it is mainly due to the 2D nature 152
of the CO. In addition, the presence of overen functional groups on % of the GO. In addition, the presence of oxygen functional groups on $\frac{153}{154}$ GO might have also contributed for the controlled aggregation of 154
RuOs species. No free RuOs papoparticles were found in the $R\omega_2$ species. No free RuO_2 nanoparticles were found in the 155
hackground of the HRTEM images (Fig. 1(b-d)) which indicate background of the HRTEM images ([Fig.](#page--1-0) 1(b–d)), which indicate 156
strong attachment of RuOs papoparticles on CO. To the best of our strong attachment of $RuO₂$ nanoparticles on GO. To the best of our 158
knowledge, this is the first observation of interconnected 158
ruthenium papenarticles network reported so far ruthenium nanoparticles network reported so far. 159
Fig. 2 precents the SEM, EDS and their corresponding elemental

[Fig.](#page--1-0) 2 presents the SEM–EDS and their corresponding elemental 160
nping images of PuO ICO. The wt^o of Pu O and C in PuO ICO mapping images of RuO₂/GO. The wt% of Ru, O and C in RuO₂/GO ¹⁶¹
was found to be 4.0.18.8 and 77.2 respectively (Fig. 2(d)). Similarly 162 was found to be 4.0, 18.8 and 77.2 respectively [\(Fig.](#page--1-0) 2(d)). Similarly, 162
the atom^o of 84.1, 15.4, and 0.5 was determined for C, Q, and the atom% of 84.1, 15.4, and 0.5 was determined for C, O and 163
Bu respectively The Bu elemental mapping (Fig. 2(d)) revealed Ru respectively. The Ru elemental mapping [\(Fig.](#page--1-0) 2(d)) revealed 164
that the distribution of Ru in RuOs/CO was homogenous Worth that the distribution of Ru in RuO₂/GO was homogenous. Worth 165
the meating that the BuO₂/GO has a span high BFT surface to mention that the RuO₂/GO has a very high BET surface 166
sure of 205 $\frac{2}{\pi^2}$ surface a surface surface 5.05 surface area of 285 m²/g with a pore volume of 0.58 cm³ g⁻¹ and a BJH desorption average pore diameter of 8.1 nm. Generally, most of the ¹⁶⁸

Download English Version:

<https://daneshyari.com/en/article/6668998>

Download Persian Version:

<https://daneshyari.com/article/6668998>

[Daneshyari.com](https://daneshyari.com)