Synthesis and characterization of silver nanoparticles supported on highly ordered Biphenylene-Bridged Periodic Mesoporous Organosilica

A M Khikmah¹, Y K Krisnandi¹ and I Abdullah¹,*

¹Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Indonesia

*E-mail: iman.abdullah@sci.ui.ac.id

Abstract. Biphenylene-Bridged Periodic Mesoporous Organosilica (Bph-PMO) has been successfully synthesized using sol-gel method in the presence of Octadecyltrimethylammonium bromide (ODTMABr) surfactant as a template. Furthermore, Bph-PMO has been functionalized using amine (NH₂-Bph-PMO) in a two-step reaction, comprising nitration using HNO₃ 65% / H₂SO₄ 96% and reduction with SnCl₂ / HCl 37%. The white powder of Bph-PMO and the pale yellow powder of NH₂-Bph-PMO were characterized using FTIR, XRD, and TEM. Bph-PMO and NH₂-Bph-PMO showed long order periodicity between 2θ from 7.5-38.0 (7.5°, 14.9°, 22.5°, 30.1°, and 38.0°). The SEM images confirmed that all materials have uniform spherical morphology. Impregnation and reduction of silver nanoparticles in NH₂-Bph-PMO have been carried out using AgNO₃ as a precursor and NaBH₄ as a reducing agent. The TEM characterization showed that the structure of NH₂-Bph-PMO material is confirmed to have a hexagonal mesoporous structure with molecular periodicity. While in Ag/NH₂-Bph-PMO has homogeneous particle size distribution of 240-280 nm. The crystalline size of silver nanoparticles on the surface of NH₂-Bph-PMO calculated using the Debye-Scherrer equation is 8.05 nm. Nitrogen adsorption-desorption showed NH₂-Bph-PMO and Ag/NH₂-Bph-PMO were classified into mesoporous materials with pore diameters of 3.3 nm and 3.2 nm, respectively.

1. Introduction

Periodic Mesoporous Organosilica (PMO) as advanced porous hybrid material have been calling much attention due to the wide application in catalysis, adsorption, molecular recognition, sensor, applications in the electronic and optical fields [1]. The organic bridge of the PMO can be changed to obtain various properties and different interfacial interactions. Therefore, it can produce material for a variety of desired applications. In previous reports, the various organic bridges were incorporated into the framework of the PMO such as: ethane [2], benzene (C₆H₆) [3], and biphenylene (C₁₂H₁₀) [4]. PMO is easily prepared and exhibits crystal-like walls, high specific surface areas, high pore volume, and high thermal stability. The presence of mesopores with high surface area and uniform diameter at PMO allows the effectiveness and ease to access to the active sites of catalyst [5].

In addition, the insertion of functional groups after synthesis has been widely reported. Ohashi et al. [3] reported 28% amination of the phenyl group PMO in a two-step chemical transformation procedure, the first functionalization process was carried out with the addition of a strong acid to incorporate a nitro group into the phenyl ring and followed by a reduction to the amine. The insertion of the amine functional groups into the organic bridge framework of PMO is expected to produce useful materials.
This is because the amine groups can be converted into various functional groups via amides (-NCO-R), imides (-NHC-R), and the formation of diazo urea (-NN-R).

The functionalized mesoporous silica surface can be grafted with various metal nanoparticles such as Pd [6], Pt [7], Ag [8], Ir [9], Ru [10]. Mesopore silica not only helps uniform dispersion of metal nanoparticles but also offers a high surface area for efficient catalysts [11]. Silver is a relatively inexpensive metal that is increasingly being used in various fields of the chemical industry because it has unique electrical, thermal, optical, and electrochemical properties. Silver nanoparticle grafting in catalytic support is a promising approach in designing heterogeneous catalysts for various variations of organic transformation [12]. Karimin et al. [13] added gold nanoparticles to the surface of phenylene PMO with the bottom impregnation and reduction methods for the Ulman aryl iodide coupling reaction. Zhang et al. [6] reported Pd impregnation at PMO for the same application.

In this report, we synthesized a highly ordered biphenylene-bridged PMO (Bph-PMO) and further functionalized the biphenylene bridge with the addition of amine functional group. Furthermore, we describe for the first time, modification of amine-functionalized Bph-PMO with silver nanoparticles through chemical impregnation followed by reduction. The material formed was evaluated for several characteristics such as surface morphology, crystallinity, surface area, pore size, and particle size. The results of these characterizations can then be used to see the potential utilization of Ag/NH$_2$-Bph-PMO in its application as a heterogeneous catalyst for organic reactions.

2. Materials and method

2.1. Materials

4,4′-Bis(triethoxysilyl)-1,1′-biphenyl, octadecyltrimethylammonium bromide (Aldrich), SnCl$_2$, and NaBH$_4$ were obtained by Sigma Aldrich. NaOH pellet, HNO$_3$ 65%, isopropylamine, AgNO$_3$, and acetonitrile were provided by Merck. Ethanol and HCl 37% were purchased from Smart Lab, H$_2$SO$_4$ 96% was obtained from Mallinckrodt.

2.2. Synthesis of Biphenylene Periodic Mesoporous Organosilica (Bph-PMO)

The Bph-PMO preparation was carried out by following method in the previous report[14] with modification. First, 4,4′-bis(triethoxysilyl)-1,1′-biphenyl (2.5 mmol) was added to a mixture of octadecyltrimethylammonium bromide (3.2 mmol), 6 M NaOH (30.4 mmol) and deionized water (3.3 mmol) under stirring at room temperature for 24 hours. The suspensions were moved to an autoclave and heated (100°C) for 24 hours. The materials were then filtered and washed with deionized water. The surfactant removal was done by extracting 1.5 g of as-prepared material in 150 mL ethanol with 6.2 g of 2 M HCl at ambient temperature for 8 hours.

2.3. Functionalization of Bph-PMO with amino functional group

Functionalization of Bph-PMO with amine group was conducted using a previously reported method for mesoporous phenylene-silica [3] through a two-step treatment. Nitration of Bph-PMO (1.05 g) was conducted in a mixed solution of 96% v/v H$_2$SO$_4$ (34.4 ml) and 65% v/v HNO$_3$ (13.3 ml). The suspension was stirred for 48 hours at ambient temperature. After the reaction, the suspension was poured into cold water (600 ml). The solid product was filtered and washed with deionized water. The reduction of nitro group was done by suspending the NO$_2$-Bph-PMO in a mixture of 37% v/v HCl (15 ml) and SnCl$_2$ (1.59 g). The mixture was stirred continuously at ambient temperature for 48 hours, then was poured into deionized water (600 ml), filtered and washed with deionized water, followed by isopropylamine (20 ml). The obtained NH$_2$-Bph-PMO is a pale yellow powder.

2.4. Impregnation and reduction of silver nanoparticles on NH$_2$-Bph-PMO

Impregnation and reduction of silver nanoparticles were performed by following the method in the previous report for impregnated silver nanoparticles on NH$_2$-SBA-15 [8] with solvent modification. 500 mg NH$_2$-Bph-PMO was dispersed in 11.6 ml acetonitrile and sonicated for 16 minutes. The suspension
was then moved to another beaker containing silver nitrate solution (50 mg of AgNO₃ in 0.3 ml acetonitrile was added in dark condition, under magnetic stirring). The mixture was stirred for 24 hours at room temperature. The mixture had a pale brown color.

In a separate beaker, NaBH₄ solution was prepared by dissolving 23.75 mg NaBH₄ in 2.6 ml acetonitrile. To this solution, the suspension (silver ion adsorbed on NH₂-Bph-PMO in acetonitrile) was added, and stirred for 1 hour. Finally, the suspension was filtered and washed with an amount of acetonitrile. This product was named Ag/NH₂-Bph-PMO.

3. Results and discussion
Powder X-ray Diffraction (XRD) analysis of the parent Bph-PMO, NO₂-Bph-PMO, NH₂-Bph-PMO, and Ag/NH₂-Bph-PMO can be observed in figure 1a. The molecular-scale periodicity for Bph-PMO was observed through five sharp diffractions apparent at intermediate diffraction angle (7.5°, 14.9°, 22.5°, 30.1° and 38.0°). Similar diffraction pattern was observed for NO₂-Bph-PMO and NH₂-Bph-PMO. Both meso periodicity and molecular scale are maintained after nitration and nitro reduction into amine groups. The first strong low angle peak (2θ<5°) assigned to the (100) reflection attributable to an ordered arrangement of meso channel [4] could not be observed due to the limitations of the instrument used.

After the impregnation with silver nanoparticles, the structure of NH₂-Bph-PMO was preserved. The sharps diffraction peaks at 38.1°, 44.2°, 64.5°, and 77.4° could be assigned to the Ag(111), (200), (220) and (311), which indicated the presence of silver nanoparticles with face center cubic nanostructure (JCPDS card no. 04-0783) at NH₂-Bph-PMO. Based on calculation using the Debye Scherer equation, the average crystal size of silver nanoparticles is 8.05 nm, respectively.

The nitration and amination reaction on Bph-PMO was characterized using FTIR (figure 1b). The nitro groups in the biphenylene ring was confirmed by the presence of a C-N stretching band at 1262 cm⁻¹ and by two strong bands at 1353 and 1534 cm⁻¹ which corresponded to the N-O stretching band of the nitro group. The band at 1301 cm⁻¹ originating from the C-N stretching vibration, indicates the covalent linkage of nitro groups (NO₂) to biphenylene moieties in Bph-PMO. The transformation of nitro to amine group was observed by the disappearance of the N-O stretching band and the presence of a N-H bending band at 1619 cm⁻¹. The stretching vibration of N-H from primary amine normally found at 3300-3400 cm⁻¹, could not be observed, since the vibration peak in this wave number area overlap with the strong and broad peak of the OH stretching of physisorbed water molecules [15]. The FTIR spectrum of Ag/NH₂-Bph-PMO is similar to that of NH₂-Bph-PMO, but appeared at a lower intensity due to the presence of silver nanoparticles in NH₂-Bph-PMO.

The nitrogen adsorption-desorption isotherm (figure 1c) confirm the type IV isotherms for NH₂-Bph-PMO and Ag/NH₂-Bph-PMO with small loop hysteresis each, indicating the occurrence of capillary condensation, which is typical of mesoporous material. The BET surface area and total pore volume of NH₂-Bph-PMO are 601 m²/g and 0.36 cm³/g, respectively. After the introduction of silver nanoparticles on NH₂-Bph-PMO, the surface area and pore volume decreased to 267 m²/g and 0.17 cm³/g, respectively. These results confirmed that the presence of silver nanoparticles on the surface fills the pore of NH₂-Bph-PMO. The Barrett, Joyner and Halenda (BJH) pore size distribution of NH₂-Bph-PMO and Ag/NH₂-Bph-PMO (figure 1d) are 3.3 nm and 3.2 nm, respectively. Therefore, both of them could be classified into mesoporous materials.

The Transmission Electrons Microscopy images (figure 2a and 2b) show the hexagonal mesoporous order of NH₂-Bph-PMO with pore diameter of 3.15 nm. Dark light lines show hexagonal pore channels with the periodicity of molecular scales. The morphology of NH₂-Bph-PMO and Ag/NH₂-Bph-PMO were observed by SEM-EDS analysis as shown in Figure 2c and 2d. Both materials have a uniform morphology with spherical in shape. Ag/NH₂-Bph-PMO shows a smoother surface compared to NH₂-Bph-PMO. Table 1 shows the presence of silver metal with loadings of 2.1%. It shows that NH₂-Bph-PMO have been successfully impregnated with silver nanoparticles. Compared with other supports of amine functionalized mesoporous silica materials such as NH₂-SBA-15, the impregnated silver nanoparticles had a larger crystallite size of 9-20 nm [16]. The presence of organic moieties with molecular periodicity of Bph-PMO results in uniform functionalization of the amines. The presence of
amine group on the organic biphenylene bridge results in the formation of smaller and monodispersed silver nanoparticles [17].

4. Conclusion
Amine functionalized Bph-PMO was successfully synthesized by a two-step reaction. The presence of the amine functional groups in biphenylene bridge of the Bph-PMO was confirmed by FTIR analysis. Silver nanoparticles were also successfully embedded over the surface and pore of NH₂-Bph-PMO with loadings of 2.1%. Bph-PMO, NH₂-Bph-PMO, and Ag/NH₂-Bph-PMO exhibited a highly ordered mesostructured hexagonal. The TEM characterization confirms that amine-functionalized Bph-PMO had hexagonal mesostructures. All of the materials have spherical morphology from SEM images. In addition, calculation of the crystallite size using the Debye Scherrer equation provides the size of silver nanoparticles in the NH₂-Bph-PMO of 8.05 nm.

![Figure 1](image-url)

Figure 1. (a) XRD pattern, (b) FTIR spectrum of Bph-PMO, NO₂-Bph-PMO, NH₂-Bph-PMO and Ag/NH₂-Bph-PMO, (c) nitrogen adsorption-desorption isotherm and (d) pore size distribution of NH₂-Bph-PMO and Ag/NH₂-Bph-PMO.
Figure 2. TEM images of NH₂-Bph-PMO (a) scale bar 50 nm (b) scale bar 20 nm, (c) SEM images of Ag/NH₂-Bph-PMO (5000x) and (d) mapping analysis of atoms in Ag/NH₂-Bph-PMO.

Table 1. Elemental analysis of Ag/NH₂-Bph-PMO.

| Element | Wt. % |
|---------|-------|
| C       | 54.7  |
| O       | 19.5  |
| N       | 18.9  |
| Si      | 4.8   |
| Ag      | 2.1   |

Acknowledgements

The authors acknowledge Universitas Indonesia for funding this research through PUTI Prosiding research grant with contract No. NKB-1021/UN2.RST/HKP.05.00/2020.

References

[1] Inagaki S, Guan S, Fukushima Y, Tetsu O and Terasaki O 1999 *J. Am. Chem. Soc.* **121** 9611
[2] Asefa T, Ishii C Y, MacLachlan M J and Ozin G A 2000 *J. Mater. Chem.* **10** 1751
[3] Ohashi M, Kapoor M P and Inagaki S 2008 *Chem. Commun.* **7** 841
[4] Lourenço M A O, Mayoral A, Díaz I, Silva R A and Ferreira P 2015 *J. Micropor. Mesopor. Mat.* **217** 167
[5] Van Der Voort P, Esquivel D, De Canck E, Goethals F, Van Driessche I and Francisco J R S 2013 *Chem. Soc. Rev.* **42** 3913
[6] Zhang F, Yin J, Chai W and Li H 2010 Chem. Sus. Chem. 3 724
[7] Zhang X, Wang L J and Jiang W 2013 Mater. Sci. Forum. 745-756 539
[8] Khan A Y and Bandyopadhyaya R 2014 J. Elect. Chem. 727 184
[9] Gruning W R, Siddiqi G, Safonova O V and Coperet C 2014 Adv. Synth. Catal. 356 673
[10] Haghshenas Kashani S, Moghadam M, Tangestaninejad S, Mirkhani V and Moh. Baltork I 2018 Catal. Lett. 148 1110
[11] Wooh S, Huesmann H, Tahir M N, paven M, Wichmann K, Vollmer D, Tremel W, papadopoulos P and Butt H J 2015 Adv. Matter. 27 7338
[12] Yan Z, Xu Z, Yu J and Jaroniec M 2017 J. Colloid. Interf. Sci. 501 164
[13] Karimi B and Esfahani F K Chem. Commun., 47 10452
[14] K M P, Yang Q and Inagaki S 1999 J. Am. Chem. Soc. 124 15176
[15] Suriyanon N, Punyapalakul P and Ngamcharussrivichai C 2015 J. Matter. Chem. Phys. 149 701
[16] Kayal U, Mohanty B, Bhanja P, Chatterjee S, Chandra D, Hara M and Bhaumik A 2019 Dalton Trans 48 2220
[17] Zhang W, Mei Y, Huang X, Wu P, Wu H and He M 2019 J. Matter. Interfaces 11 44241