

Green Synthesis of MgO Nanoparticles using Caesalpinia Sappan Seeds and their Application for Direct Conversion of Alcohol to Azide

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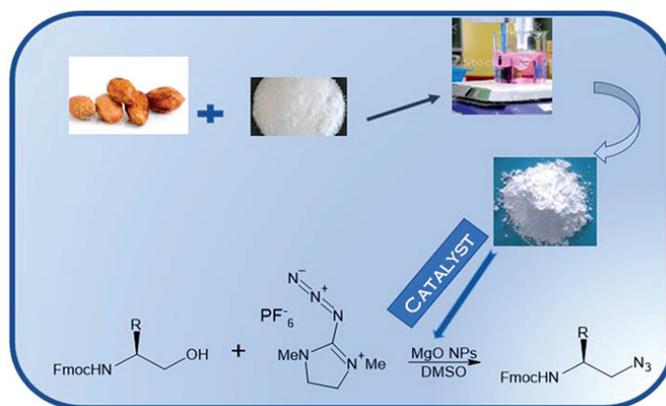
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Abstract:

Azides have been considered as one of the energy rich functional groups as they are prominent precursors for reactive species like nitrenes and nitrenium ions. Also, they were utilized in synthesis of triazoles, triazolines and triazenes. The present work reports an eco- friendly synthesis of MgO NPs by utilizing Caesalpinia Sappan seeds as a novel fuel by solution combustion method. Multiple characterization techniques encompassing FTIR, UV- visible, XRD and SEM were used to study physico-chemical properties of synthesized MgO NPs. A convenient synthesis of amino alcohol via mixed anhydride method was carried out in the first step. Further, amino alkyl azide has been synthesized under mild condition by using the green synthesized MgO nanoparticles as a catalyst along with the addition of 2-azido-1,3- dimethylimidazolium hexafluorophosphate, a safe, stable and efficient diazo transfer reagent. Structures of newly synthesized compounds were well characterized by HRMS, Proton and C-13 analysis techniques.



Keywords: Caesalpinia Sappan, green synthesis, MgO NPs, ADMP and amino alkyl azide

1.0 Introduction

Organic azides have flourished as crucial intermediates when Peter Grieb first synthesized phenyl azide in the late 1800s. These energy rich molecules are of high synthetic utility because they provide several reaction pathways for the synthesis of

triazoles, tetrazoles, anilines, glycopeptides and peptides. Azide group contains three nitrogen atoms arranged in a linear manner which are slightly bent. The structural features of azide group allow it to act as nucleophile, electrophile as well as a radical acceptor. The availability of innumerable synthetic methods for synthesis of azides is an additional benefit.

Simple nucleophilic substitutions, Mitsunobu reaction, ring opening of epoxides, simple synthesis by amines, polar 1,2 and 1,4 additions and diazo transfer reactions have been proven to be successful methods for synthesis of azides [1-6].

Azides are desirable functional groups where they are involved in multistep synthesis of various natural products such as marine bisindole alkaloids, costistatins A and J, streptolydigin kealiinines, naamine G and naamidine H, huperzine A, coralydine, stenimona alkaloid meloscine, amphorogynine C and many more [7-9]. Organic azides afford [3+n] cycloaddition product by behaving as 1,3 dipolar moiety. They are fashionable, as their reaction with terminal alkynes to give a five membered ring has built a strong foundation of click chemistry approach which is simple, highly stereospecific and indomitable in affording extremely high yields. They can be diverted for the synthesis of amines, iminophosphoranes, indazoles, quinolines, benzimidazoles. Aza-Wittig reaction which is analogous to Wittig reaction is other striking reaction where carbonyls and phosphoranimines yield imines. These phosphoranimines could be feasibly prepared by organic azides reduction. Phosphoranimines provides diverse outcome for the synthesis of primary amines, imines, imidates, imidamides, heterocumulenes and many such valuable functionalized groups. Besides this, the Aza-Wittig reaction is used for pyrrolysin, clavolonine and cicindelone natural products total synthesis [10-14]. Therefore, these azides are considered to be magnificent weaponry for construction of large variety of organic molecules.

Mitsunobu displacement is the well-acquainted method for furnishing good quantity of azides, where in hydrazoic acid is used as an azide source along with diethyl azodicarboxylate (DEAD). Triflyl azide, a similar reagent in diazo transfer used for the accomplishment of azides is not safe and unstable. Therefore, these reagents are often circumvented. Hence there was increase in demand for stable and safer alternative. To sort out the problems of toxicity and instability, 2-azido-1,3-dimethylimidazolium chloride (ADMC) and its related hexafluorophosphate were explored [15-16].

In recent times, green synthesis of nanomaterials is considered as a cornerstone as conventional methods are expensive, health hazardous, require higher operating conditions and utilize high energy. The use of water-soluble metabolites has acquired an upper hand. Metal oxide has incalculable applications

in diversified domains. Among them, magnesium oxide nanoparticles (MgO-NPs) are endowed with distinguished refractive index, finest corrosion resistance, high mechanical strength, low thermal and high electrical conductivities. They are efficacious as photonic sensors, adsorbents, antimicrobial agents, photocatalysts, antioxidants and catalyst support [17].

MgO nanoparticles succeed to multifarious advantages in catalysis and many organic transformations. MgO nanocrystals are used as bases in Claisen-Schmidt reaction. They are also found to provide greater yield by acting as a catalyst in Knoevenagel condensation. In addition to these organic transformations, MgO nanoparticles are used in synthesis of coumarins, pyridines, imidazoles, thiazoles, pyrazoles, isoxazole and amides. Hence attention is laid to this specific nanoparticle [18].

In the current report, we validate for the first time, the appropriate use of Caesalpinia Sappan seeds for the practical synthesis of MgO NPs. Direct conversion of alcohols to azide was achieved by addition of ADMP, a safe and stable diazo transfer reaction and MgO as an energetic green catalyst.

2. Experimental details

2.1 Chemicals and reagents

All the required chemicals and solvents were procured from Spectrochem, SD fine chemicals, and Merck. They were used without any purification. The seeds of Caesalpinia Sappan were congregated from the Bannerghatta forest, near Bangalore.

2.2 Materials and methods

Examination of the crystalline size and phase identity of synthesized materials were recorded by Shimadzu X-ray diffractometer (PXRD-7000) using Cu-K α radiation of wavelength λ -1.541Å. Hitachi-7000 scanning electron microscopy was used to examine the morphology of the obtained material. UV - Vis spectrophotometer was used to record the absorbance. For recognizing the functional groups of the obtained products, Bruker Alpha-T FT-IR spectrometer was used. TMS was used as an internal standard and DMSO was employed as a solvent for recording the proton and C-13 NMR spectra on a Bruker AMX (400 MHz) spectrometer. TLC plate used was silica gel 60 F254 for monitoring the reactions. Mass spectra were tracked using mass spectrometer.

2.3 Synthesis of Fmoc-amino alcohols through mixed anhydride method

A measured quantity of N-protected amino acid was dissolved in THF in round bottomed flask and stirred for 5 minutes using magnetic stirrer by maintaining temperature at 0°C. A calculated amount of NMM and ECF were added. After 20 min, a known quantity of NaBH₄ was added followed by the addition of few drops of water. This mixture was filtered off to obtain the desired product. Acidic and basic work up was carried out to remove the impurities. Finally, the formed amino alcohol was cleansed with water and brine solution several times. The formation of compounds was validated by eluting with 40% ethyl acetate-hexane mixture.

2.4 Preparation of Caesalpinia Sappan seed extract and green synthesis of MgO NPs

The seeds were air dried in sunlight for several days and was stored in airtight container. To prepare seed extract, 100 ml distilled water was heated up to 80°C and then 10g of dried Caesalpinia Sappan seeds powder was added and boiled for 30 min. Then above mixture was filtered. MgO NPs were prepared by nontoxic green combustion route using Caesalpinia Sappan seeds extract as a fuel. Mg(NO₃)₂·6H₂O was added to Caesalpinia sappan seeds extract in 10 ml of deionized water. This mixture was placed in a muffle furnace which was pre-heated to 450°C and subjected for combustion for 5h. White coloured product obtained was stored in airtight container.

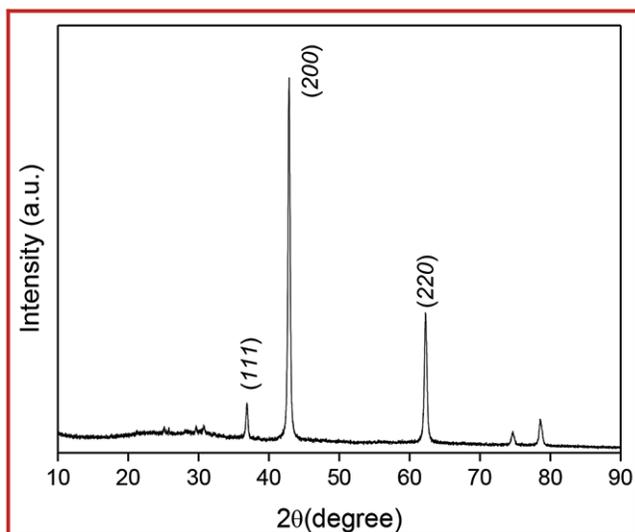


Figure 1: XRD pattern of MgO nanoparticles synthesized from Caesalpinia sappan seed extract

2.5 Formation of N-Fmoc-amino alkyl azides

The formed amino alcohol was further used for the synthesis of amino alkyl azides. The protected amino alcohol was dissolved in DMSO, then ADMP and synthesized MgO NPs were added. The reaction was kept for stirring for 5-6h. The resulting solution was extracted with EtOAc and the organic part was cleansed with water and dried over anhydrous sodium sulfate. The solvent was removed in vacuo and the remainder was purified using flash chromatography by availing 10% EtOAc in hexane as eluant to obtain the corresponding amino alkyl azides as solids.

3.0 Results and Discussion

3.1 Characterization of MgO NPs

3.1.1 X-ray Diffraction analysis

The crystalline nature of MgO nanocrystal was scrutinized by XRD analysis. Each one of the sharp diffraction lines of the sample are sharp signifying esteemed crystallinity. The sharp diffraction peaks aroused at 37.0°, 42.8°, 62.4° corresponding to (111), (200) and (220) planes respectively evidence the formation of MgO. The diffraction peaks of MgO were fitted with standard Joint Committee on Powder Diffraction Standards.-JCPDS data [JCPDS file: 45-0946].

To compute the average crystallite size, the Debye-Scherrer's equation was adopted with formula

$$D = \frac{K\lambda}{\beta \cos \theta}$$

where, D is crystalline size, K is Scherrer constant, λ is X-ray wavelength, β is full-width at half-maximum and θ is Bragg's angle. The Debye Scherrer's calculations reveal the average crystallite size of the MgO NPs was obtained to be 25.66 nm.

3.1.2 Fourier - Transform Infrared Spectroscopy

IR spectroscopy was performed by preparing KBr disc and scrupulously analysed for metal oxide bond stretching frequencies. A prominent peak at $\nu=457.47$ cm⁻¹ in the FTIR spectrum (Figure 2) imputes the bond stretching vibrations of Mg-O. The peak observed at 1636.56 cm⁻¹ is for carbonyl functionality and 3442.86 cm⁻¹ is regarded to be due to stretching and deformation of -OH stretching due to H₂O adsorption on the surface of metal.

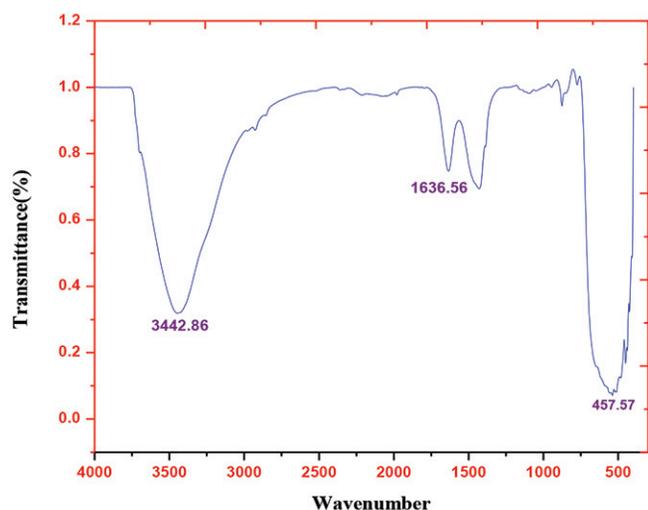


Figure 2: FTIR Spectra of MgO nanoparticles synthesized from Caesalpinia sappan seed extract

3.1.3 Scanning Electron Microscopy analysis and Energy dispersive analysis of X-ray

To contemplate the morphology as well as the particle size of nano MgO, the SEM images were tracked in the scanning electron microscope. Figure 3a shows SEM images of MgO NPs prepared from Caesalpinia sappan seeds. It is evidenced from the image that the particles are distributed irregularly to form clusters. They are illustrated to have rough surface and the voids shows the evolution of gases. The energy dispersive X-ray spectrum (Figure 3b) of MgO sample persuaded the existence of Mg and O at appropriate concentrations. The atomic % of Mg and O

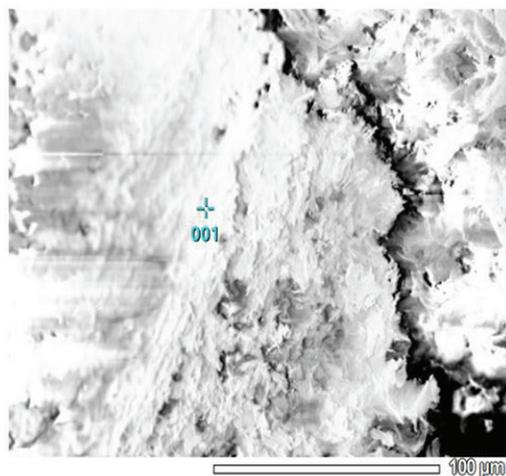


Figure 3a
SEM and EDAX of MgO nanoparticles synthesized from Caesalpinia sappan seed extract

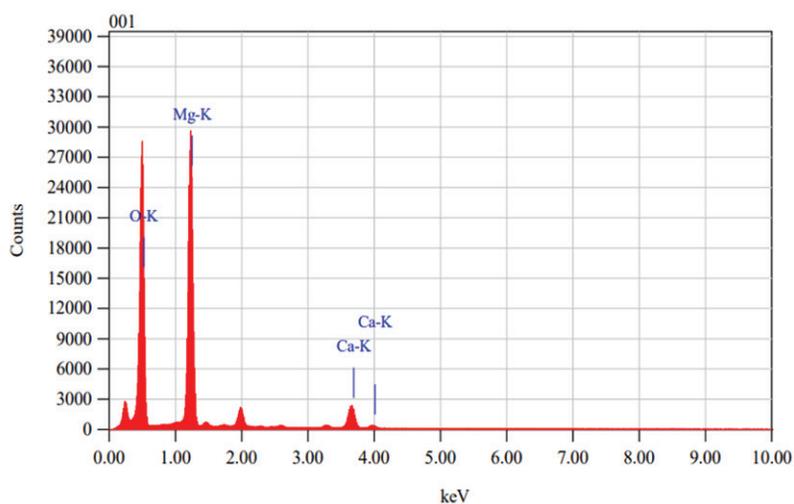


Figure 3b

element in MgO is found to be 42.85 and 56.26 respectively and shows the stoichiometric relationship (1:1) between magnesium and oxygen.

3.1.4 UV-Visible spectroscopy

UV-visible spectroscopy is extensively used to inspect optical properties of nanomaterials. We recorded the electronic spectra of MgO NPs prepared by combustion route which was dispersed in ethanol. These NPs showed the maximum absorption at 296 nm as shown in the Figure 4. The absence of other peaks except at 296 nm confirms that the NPs obtained have high level of purity.

3.1.5 Direct conversion of alcohol to azide using nano MgO as a green catalyst

In the current study, an effective approach for the synthesis of Fmoc-amino alkyl azides employing 2-azido-1,3-dimethyl imidazolium hexafluorophosphate and nano MgO has been achieved. Fmoc-amino alcohols were treated with ADMP, to yield the desired compounds in excellent yields. Sturdy reaction conditions, exorbitant utility of chemicals, unstable intermediates were the problems posed in the production of azides. Therefore, efforts were made to overcome these hindrances. Direct conversion of alcohols to azides is a reliable and efficient strategy for the production of alkyl azides. A two-step approach is adopted, where Fmoc-amino acids were initially reduced to the corresponding β -amino alcohols via the treatment of mixed anhydride of the acid with NaBH_4 in the first step shown in Scheme 1 and direct conversion of alcohol into azides in the second step

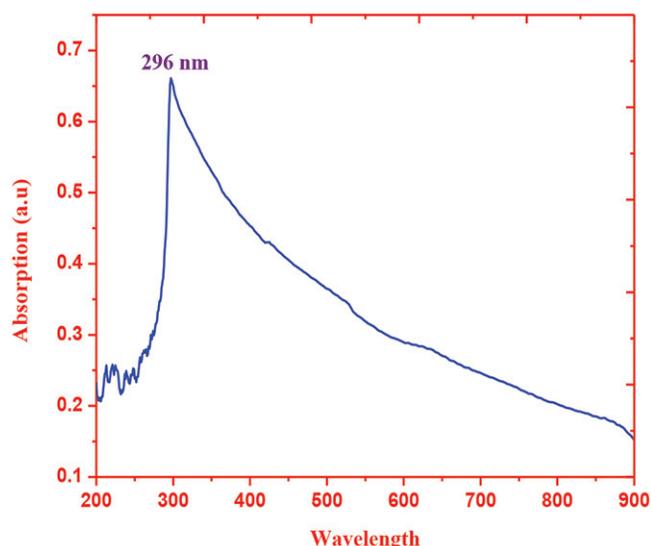
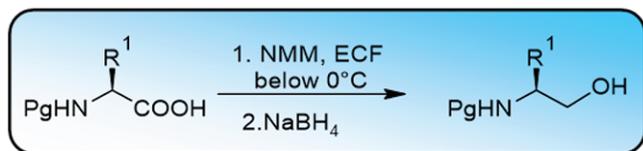
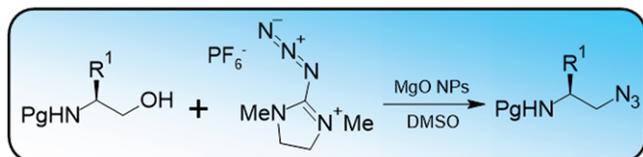


Figure 4: UV-vis spectrum of MgO nanoparticles synthesized from *Caesalpinia sappan* seed extract

using green synthesized MgO NPs as shown in Scheme 2. The reaction scheme involves amino alcohol derivative of N^α -protected amino acid and ADMP employing MgO as a catalyst to enrich the yield of the reaction to furnish azides (1a-lj, Table 1). The reaction was monitored by TLC. The solvent was evaporated in vacuo after completion of the reaction. The residue was diluted with ethyl acetate and the extracted organic phase was recurrently washed with H_2O and saturated solution of NaCl to get crude product. This was dehydrated using sodium sulphate. Solvent was removed by employing rotatory evaporator and purification of the crude product was accomplished through flash chromatography technique (CombiFlash Nextgen column chromatography). The produced N^α -protected amino azides were characterized by a sequence of proton NMR, HRMS and ^{13}C NMR spectroscopic techniques.



Scheme 1: Synthesis of N^α -protected amino alcohol derivatives



Scheme 2: Direct conversion of N^α -protected amino alcohol to azide

Table 1: List of synthesized N -Fmoc-amino alkyl azides

Entry	N -protected azides	Yield (%)
1a		87
1b		94
1c		80
1d		84
1e		87
1f		91
1g		86
1h		88
1i		84
1j		80

3.1.6 Spectral data of synthesized organic compounds

Fmoc-Gly- ψ [CH_2N_3] (1a): Proton NMR ($CDCl_3$) δ 3.21 (br, 2H), 3.45 (m, 2H), 4.30 (t, $J = 6.4$ Hz, 1H), 4.52 (d, $J = 5.8$ Hz, 2H), 5.12 (br, 1H), 7.34-7.74 (m, 8H); C-13 NMR ($CDCl_3$) δ 41.3, 44.6, 47.9, 67.5, 120.4, 125.6, 127.5, 128.1, 141.8, 144.0, 156.6; ESI-MS calculated for $C_{17}H_{16}N_4O_2$ m/z 331.1414 [$M + Na$] $^+$, found 331.1450.

Fmoc-Ala- ψ [CH_2N_3] (1b): Proton NMR ($CDCl_3$) δ 1.28 (d, $J = 6.4$ Hz, 3H), 3.95 (br, 1H), 4.21 (d, $J = 6.4$ Hz, 2H), 4.38 (m, 1H), 4.56 (m, 2H), 4.83 (d, $J = 6.4$ Hz, 1H), 7.30-7.76 (m, 8H); C-13 NMR ($CDCl_3$) δ 18.6, 47.3, 47.7, 50.5, 67.3, 120.6, 125.5, 127.5, 128.1, 141.8, 144.0, 156.0; ESI-MS calculated mass for $C_{18}H_{18}N_4O_2$ m/z 345.1210

[M+Na]⁺, Observed mass 345.1209.

Fmoc-Val-ψ[CH₂N₃] (1c): Proton NMR (CDCl₃) δ 0.97 (d, J = 6.8 Hz, 6H), 1.86 (m, 1H), 3.45 (d, J = 4.2 Hz, 2H), 3.54 (m, 1H), 4.23 (t, J = 6.8 Hz, 1H), 4.45 (m, 2H), 4.78 (d, J = 8.2 Hz, 1H), 7.24-7.78 (m, 8H); C-13 NMR (CDCl₃) δ 18.8, 19.2, 29.3, 42.4, 47.8, 55.1, 67.3, 120.5, 125.6, 127.6, 128.2, 142.0, 144.1, 156.4; ESI-MS calculated mass for C₂₀H₂₂N₄O₂ m/z 373.1780 [M + Na]⁺, Observed mass 373.1790.

Fmoc-Leu-ψ[CH₂N₃] (1d): Proton NMR (CDCl₃) δ 0.92 (d, J = 5.6 Hz, 6H), 1.45 (m, 2H), 1.62 (m, 1H), 3.68 (dd, J = 4.2 Hz, 1H), 3.82 (d, J = 4.1 Hz, 2H), 4.21 (t, J = 6.4 Hz, 1H), 4.42-4.56 (m, 2H), 4.80 (d, J = 7.6 Hz, 1H), 7.28-7.82 (m, 8H); C-13 NMR (CDCl₃) δ 22.3, 23.4, 41.1, 47.8, 50.1, 55.6, 67.2, 120.5, 125.5, 127.6, 128.2, 141.9, 144.0, 156.3; ESI-MS calculated mass for C₂₁H₂₄N₄O₂ m/z 387.1220 [M + Na]⁺, Observed mass 387.1230.

Fmoc-Ile-ψ[CH₂N₃] (1e): Proton NMR (CDCl₃) δ 0.92-0.97 (m, 6H), 1.14 (m, 1H), 1.54 (m, 2H), 3.46 (d, J = 6.8 Hz, 2H), 3.58 (m, 1H), 4.24 (t, J = 6.4 Hz, 1H), 4.46 (d, J = 7.0 Hz, 2H), 4.83 (d, J = 7.2 Hz, 1H), 7.31-7.43 (m, 4H), 7.61 (d, J = 7.2 Hz, 2H), 7.78 (d, J = 7.6 Hz, 2H); C-13 NMR (CDCl₃) δ 11.7, 16.0, 25.7, 36.7, 47.8, 53.4, 55.4, 67.1, 120.5, 125.5, 127.6, 128.2, 141.9, 144.4, 156.5; ESI-MS calculated mass for C₂₁H₂₄N₄O₂ m/z 387.1011 [M+Na]⁺, Observed mass 387.0821.

Fmoc-Phe-ψ[CH₂N₃] (1f): Proton NMR (CDCl₃) δ 2.87 (br, 2H), 3.46 (m, 1H), 3.96 (m, 2H), 4.20 (t, J = 6.8 Hz, 1H), 4.40 (d, J = 4.0 Hz, 2H), 4.94 (br, 1H), 7.15-7.72 (m, 13H); C-13 NMR (CDCl₃) δ 38.5, 47.7, 49.0, 52.4, 67.4, 120.6, 125.7, 127.5, 128.1, 129.0, 129.3, 129.7, 136.8, 142.0, 144.2, 156.0; ESI-MS calculated mass for C₂₄H₂₂N₄O₂ m/z 421.2706 [M+Na]⁺, Observed mass 421.2701.

Fmoc-Glu(OtBu)-ψ[CH₂N₃] (1g): Proton NMR (CDCl₃) δ 1.47 (s, 9H), 1.82-1.86 (m, 2H), 2.29-2.36 (m, 2H), 3.42-3.48 (m, 2H), 3.75-3.87 (m, 1H), 4.23 (t, J = 6.9 Hz, 1H), 4.38-4.50 (m, 2H), 5.03 (d, J = 7.7 Hz, 1H), 7.31-7.45 (m, 8H); C-13 NMR (CDCl₃) δ 25.9, 27.4, 30.2, 46.6, 48.4, 50.3, 66.5, 80.4, 119.3, 124.6, 126.3, 127.0, 140.6, 143.0, 155.1, 171.5; ESI-MS calculated mass for C₂₄H₂₈N₄O₄ m/z 459.2021 [M+H]⁺, Observed mass 459.2032.

Fmoc-Asp(Bzl)-ψ[CH₂N₃] (1h): Proton NMR (CDCl₃) δ 2.53 (d, J = 4.2 Hz, 2H), 3.29-3.43 (m, 2H), 4.08 (m, 2H), 4.26 (m, 2H), 5.02 (s, 2H), 5.34 (d, J = 8.8 Hz, 1H), 7.17-7.30 (m, 9H), 7.46 (d, J = 7.2 Hz, 2H), 7.64 (d, J = 7.6 Hz, 2H); C-13 NMR (CDCl₃) δ 36.6, 47.7, 48.21, 54.0, 67.3, 67.4, 120.6, 125.6, 127.6, 128.3, 128.9, 129.0, 129.2, 135.9, 141.8, 144.3, 156.1, 171.3; ESI-MS calculated mass for C₂₆H₂₄N₄O₄ m/z 479.2029 [M+Na]⁺, Observed mass 479.2021.

Fmoc-Glu(Bzl)-ψ[CH₂N₃] (1i): Proton NMR (CDCl₃) δ 2.06 (m, 2H), 2.42 (m, 2H), 3.41 (m, 2H), 4.19 (m, 1H),

4.32-4.40 (m, 3H), 5.10 (s, 2H), 5.52 (br, 1H), 7.25-7.39 (m, 9H), 7.57 (d, J = 7.2 Hz, 2H), 7.76 (d, J = 7.6 Hz, 2H); C-13 NMR (CDCl₃) δ 27.0, 30.5, 47.1, 50.6, 62.5, 66.9, 69.4, 120.2, 125.3, 126.8, 127.2, 127.9, 128.4, 128.6, 135.9, 141.4, 143.9, 156.0, 172.6; ESI-MS calculated mass for C₂₇H₂₆N₄O₄ m/z 493.2230 [M+Na]⁺, Observed mass 493.2236.

Fmoc-Ser(Bzl)-ψ[CH₂N₃] (1j): Proton NMR (CDCl₃) δ 1.28 (s, 2H), 3.40-3.62 (m, 2H), 3.98 (br, 1H), 4.21 (d, J = 5.3 Hz, 1H), 4.43 (m, 2H), 4.54 (s, 2H), 5.12 (d, J = 7.2 Hz, 1H), 7.28-7.77 (m, 13H); C-13 NMR (CDCl₃) δ 47.0, 50.5, 52.3, 67.1, 68.4, 73.3, 120.1, 125.2, 127.0, 127.6, 128.1, 128.5, 129.2, 137.1, 141.3, 143.9, 155.8; HRMS calculated mass for C₂₅H₂₄N₄O₃ m/z 451.2824 [M+Na]⁺, Observed mass 451.2822.

4.0 Conclusions

In summary, MgO nano particles were prepared via a simple combustion method by employing Caesalpinia sappan seeds best known as Brazil or sappan wood. These MgO NPs were established by XRD, FTIR, SEM and EDAX techniques. The synthesized MgO NPs act as energetic green catalyst for the efficient conversion of alcohols to azides by making use of ADMP, a diazotransfer agent. All the products were separated after easy work up and were thoroughly characterized by Proton and C-13 NMR and mass spectrometry. With persistent research on azides, they can be exploited in innovative research spheres.

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Conflicts of interest

No conflict of interest

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