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ORIGINAL PAPER

Synthesis, characterization and application of nitrogen–sulfur-doped carbon spheres as an efficient catalyst for the preparation of novel α-aminophosphonates

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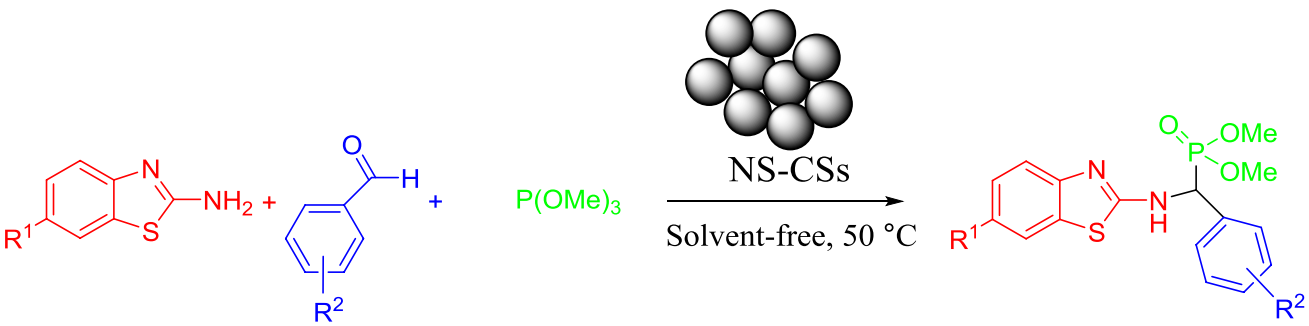
Abstract Nitrogen–sulfur-doped carbon spheres (NS-CSs) were prepared from sucrose and thiourea through a simple hydrothermal process. NS-CSs were characterized by TEM, FTIR, TGA, XRD, Raman spectroscopy and elemental analyses. The results revealed that the synthesized carbon spheres have an amorphous structure with diameters of 300–500 nm. The microspherical carbon catalyst that is recyclable has been used in the synthesis of α-aminophosphonates derived from 2-aminobenzothiazoles. Three-component reaction was performed between 2-aminobenzothiazoles, aromatic aldehydes and trimethyl phosphite in the presence of NS-CSs as microorganocatalyst at 50 °C under solvent-free conditions in high yield.

Keywords Heterogeneous carbon · Hydrothermal synthesis catalyst · α-Aminophosphonates · Kabachnik–Fields reaction · Carbon microspheres

Introduction

During the past years, carbon materials with various shapes such as fibers, onion, sphere, horns and flasks, have been synthesized and implemented in different catalytical applications. Among them, carbon spheres are an important class, due to the high level of thermal stability, unique electronic properties and low density. Carbon spheres are used in lithium-ion batteries, as well as catalytic coatings,

Graphical Abstract



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injectable scaffolds for tissue regeneration, drug delivery, water purification, protecting the enzymes and proteins and magnetic data storage applications [1]. One of the main applications for carbon spheres is known to be as a catalyst in Heck, Suzuki and Sonogashira coupling reactions [2]. α-Aminophosphonates as structural analogs of α-amino acid esters are of interest for potential anticancer drugs [3, 4], enzymes inhibitors [5], haptens of catalytic antibodies [6, 7], pharmacologic agents [8], antifungals [9], insecticides [10], plant growth regulators [11], anti-HIV agents [12] and interesting carriers for the transport of hydrophilic molecules across bilayer lipid membranes [13]. Several multi-step synthetic approaches for the synthesis of α-aminophosphonates have been reported in the literature including alkylation of nucleophilic Schiff bases, Hofmann rearrangement of substituted phosphonoacetic esters and conversion of 1-hydroxyphosphonates to the corresponding α-aminophosphonates [14]. An alternative synthesis of α-aminophosphonates involves nucleophilic addition of phosphite to imine [15–20]. However, since many imines are hygroscopic and are not sufficiently stable for isolation, this method has certain limitations. The most simple and straightforward synthetic method for the synthesis of α-aminophosphonates is the Kabachnik–Fields reaction which involves a one-pot three-component coupling of an aldehyde, amine and phosphite ester [21]. In this regard, numerous protocols for the synthesis of these compounds have been developed using various catalysts such as molecular iodine [22], xanthan sulfuric acid [23], DTP/SiO_2 [24], succinic acid [25], phenylphosphonic acid [26], $SnCl_2$ [27], SiO_2–$AlCl_3$ [28], $Mg(ClO_4)_2$ [29], $CeCl_3{\cdot}7H_2O$ [30], TiO_2 [31], $NaHSO_4$–SiO_2 [32], nano-Fe_3O_4 [33], γ-Fe_2O_3@SiO_2-PA [34], DHAA–Fe_3O_4 [35], IRMOF-3 nano [36], Fe/SWCNTs [37], $ZrOCl_2{\cdot}8H_2O$ [38] and ethyl ammonium nitrate [39]. Herein, nitrogen–sulfur co-doped carbon spheres (NS-CSs) were synthesized by a simple hydrothermal process [40] and the catalytical activity of the new heterogeneous and recyclable micro carbon sphere was investigated for the one-pot synthesis of α-aminophosphonates directly from aldehydes, 2-aminobenzothiazoles and trimethyl phosphites.

Experimental

Chemicals and instruments

All reagents were purchased from Merck and Aldrich and used without further purification. The melting point of the products was determined with an electrothermal type 9100 melting point apparatus. Transmission electron microscope (TEM) images were acquired on a TEM microscope Leo 912 AB120 kV Zeiss, Germany. The FTIR spectra were recorded on an Avatar 370 FTIR Thermal Nicolet spectrometer. X-ray diffraction (XRD) measurements were performed using a Philips X'Pert X-ray diffractometer with Cu Kα radiation (λ = 0.154056 nm). The ^{1}H NMR spectra were recorded on a Bruker DRX 300 spectrometer. Thermogravimetric analysis (TGA) was performed using a Shimadzu thermogravimetric analyzer (TG-50). The Raman spectrum was recorded at the ambient temperature using a Renishaw RM2000 Raman microspectrometer with an argon ion laser at an excitation wavelength of 514.5 nm.

Hydrothermal synthesis of the nitrogen and sulfur-doped carbon

In a typical experiment, sucrose (2.7 g, 7.9 mmol) and thiourea (0.6 g, 7.9 mmol) were dissolved in distilled water (200 ml) and the solution was stirred for 30 min. Afterward, the solution was transferred into a Teflon-lined stainless steel autoclave and heated at 190 °C for 20 h. The synthesized material, then, was filtered and washed several times with excess amount of distilled water to remove impurities. The obtained black powder was dried in oven at 80 °C overnight.

General procedure for preparation of α-aminophosphonates

(CN-CSs) (3 mg) was added to a mixture of aldehydes (1 mmol), 2-aminobenzothiazoles (1 mmol) and trimethyl phosphite (1 mmol, 0.12 gr), and the mixture was stirred at 50 °C. After completion of the reaction as monitored by TLC, the mixture was washed With CH_2Cl_2 (3 × 3 mL). The combined extracts were filtered, and the solvent was removed under reduced pressure. The product was purified by column chromatography by using hexane-ethyl acetate as solvent system in different concentration to obtain the pure compound.

Spectral data phosphonate compounds

Dimethyl ((benzo[d]thiazol-2-ylamino) (phenyl)methyl) phosphonate ***(4a)***

White powder; yield 90%; mp 166–167 °C; IR (KBr, cm^{-1}): ν 3223, 3031, 2952, 2850, 1596, 1567, 1530, 1237, 1217, 1056, 1033; ^{1}H NMR ($CDCl_3$, 300 MHz): δ_H 3.57 (d, 3H, $^3J_{HP}$ = 10.5 Hz, OCH_3), 3.85 (d, 3H, $^3J_{HP}$ = 10.8 Hz, OCH_3), 5.63 (d, 1H, $^2J_{HP}$ =21.9 Hz, CHP), 7.09 (td, 1H, J = 7.5, 1.2 Hz), 7.30 (td, 1H, J = 8.4, 1.2 Hz), 7.34–7.43 (m, 3H), 7.56 (ddd, 2H, J = 8.1, 3.3, 0.6 Hz, CH–Ph), 7.61–7.64 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ_C 165.6

(d, $^{3}J_{CP}$ = 12 Hz, N=C–NH), 151.9, 134.8, 131.2, 128.7 (d, $^{3}J_{CP}$ = 2.25 Hz), 128.4 (d, $^{3}J_{CP}$ = 2.25 Hz), 128.1 (d, $^{2}J_{CP}$ = 6 Hz), 125.8, 121.9, 120.7, 119.4, 55.33 (d, $^{1}J_{CP}$ = 153 Hz, CHP), 54.1 (d, $^{2}J_{CP}$ = 6.7 Hz, OCH_3), 53.9 (d, $^{2}J_{CP}$ = 6.7 Hz, OCH_3); ^{31}P NMR ($CDCl_3$, 121 MHz): δ_p 23.28; MS (m/z): 348 (M+).

Dimethyl ((benzo[d]thiazol-2-ylamino) (4-(diethylamino) phenyl)methyl)phosphonate ***(4b)***

Brownish yellow solide; yield 92%; mp 160–161 °C; IR (KBr, cm^{-1}): ν 3233, 3027, 2974, 1949, 1532, 1443, 1236, 1203, 1056, 1036; ^{1}H NMR ($CDCl_3$, 300 MHz): δ_H 1.16 (t, 6H, J = 7.2 Hz, CH_2CH_3), 3.35 (q, 4H, J = 6.9 Hz, CH_2), 3.58 (d, 3H, $^{3}J_{HP}$ = 10.5 Hz, OCH_3), 3.82 (d, 3H, $^{3}J_{HP}$ = 10.6 Hz, OCH_3), 5.38 (d, 1H, $^{2}J_{HP}$ = 21.3 Hz, CHP), 6.66 (d, 2H, J = 8.7 Hz, CH–Ph), 7.09 (t, 1H, J = 7.5 Hz), 7.29 (t, 1H, J = 8.1 Hz), 7.30 (b, NH), 7.41 (d, 2H, J = 7.5 Hz, CH–Ph), 7.55 (d, 1H, J = 6.9 Hz), 7.57 (d, 1H, J = 7.2 Hz); ^{31}P NMR ($CDCl_3$, 121 MHz): δ_p 23.83; MS (*m/z*): 420 (M+).

Dimethyl ((benzo[d]thiazol-2-ylamino)(4-(dimethylamino) phenyl)methyl)phosphonat ***(4c)***

White powder; yield 90%; mp 168–169 °C; IR (KBr, cm^{-1}): ν 3228, 3032, 2951, 2847, 1569, 1534, 1443, 1242, 1235, 1053, 1029; ^{1}H NMR ($CDCl_3$, 300 MHz): δ_H 2.95 (s, 6H, NCH_3), 3.57 (d, 3H, $^{3}J_{HP}$ = 10.5 Hz, OCH_3), 3.83 (d, 3H, $^{3}J_{HP}$ = 10.8 Hz, OCH_3), 5.49 (d, 1H, $^{2}J_{HP}$ =21.6 Hz, CHP), 6.72 (d, 2H, J = 8.7 Hz, CH–Ph), 7.08 (t, 1H, J = 7.5 Hz), 7.28 (t, 2H, J = 8.4 Hz), 7.30 (b, NH), 7.47 (dd, 2H, J = 8.7, 1.8 Hz, CH–Ph), 7.54 (d, 1H, J = 7.5 Hz), 7.57 (d, 1H, J = 7.8 Hz); MS (*m/z*): 392 (M+).

Dimethyl ((benzo[d]thiazol-2-ylamino) (p-tolyl)methyl) Phosphonate ***(4d)***

White powder; yield 91%; mp 173–174 °C; IR (KBr, cm^{-1}): ν 3228, 3031, 2952, 1597, 1567, 1534, 1240, 1031; ^{1}H NMR ($CDCl_3$, 300 MHz): δ_H 2.35 (s, 3H, CH_3), 3.58 (d, 3H, $^{3}J_{HP}$ = 10.5 Hz, OCH_3), 3.85 (d, 3H, $^{3}J_{HP}$ = 10.8 Hz, OCH_3), 5.63 (d, 1H, $^{2}J_{HP}$ = 21.6 Hz, CHP), 7.08 (td, 1H, J = 7.5, 1.2 Hz), 7.19 (d, 2H, J = 7.8 Hz, CH–Ph), 7.29 (td, 2H, J = 8.4, 1.2 Hz), 7.30 (b, NH), 7.52–7.58 (m, 4H); MS (*m/z*): 363 (M+).

Dimethyl ((benzo[d]thiazol-2-ylamino) (4-methoxyphenyl) methyl) phosphonate ***(4e)*** *[29]*

White powder; yield 85%; mp 170–171 °C; IR (KBr, cm^{-1}): ν 3228, 3032, 2952, 1597, 1534, 1443, 1234, 1251, 1030; ^{1}H NMR ($CDCl_3$, 300 MHz): δ_H 3.58 (d, 3H, $^{3}J_{HP}$ = 10.5 Hz, OCH_3), 3.80 (s, 3H, CH_3), 3.84 (d, 3H, $^{3}J_{HP}$ = 10.8 Hz, OCH_3), 5.54 (d, 1H, $^{2}J_{HP}$ = 21.6 Hz, CHP), 6.92 (d, 2H, J = 8.7 Hz, CH–Ph), 7.03 (b, NH), 7.08 (td, 1H, J = 7.5 Hz), 7.29 (td, 1H, J = 8.4 Hz), 7.53–7.58 (m, 4H); MS (*m/z*): 379 (M+).

Dimethyl ((benzo[d]thiazol-2-ylamino) (2-methoxyphenyl) methyl) phosphonate ***(4f)***

White powder; yield 80%; mp 169–170 °C; IR (KBr, cm^{-1}): ν 3229, 3045, 2952, 1600, 1570, 1535, 1443,1241, 1232, 1055, 1023; ^{1}H NMR ($CDCl_3$, 300 MHz): δ_H 3.55 (d, 3H, $^{3}J_{HP}$ = 10.8 Hz, OCH_3), 3.85 (d, 3H, $^{3}J_{HP}$ = 10.8 Hz, OCH_3), 3.99 (s, 3H, CH_3), 5.95 (d, 1H, $^{2}J_{HP}J_{HP}$ = 21.5 Hz, CHP), 6.98 (t, 2H, J = 8.1 Hz), 7.08 (t, 1H, J = 7.5 Hz), 7.26–7.34 (m, 2H), 7.30 (b, NH), 7.55–7.58 (m, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ_C 165.4 (d, $^{3}J_{CP}$ = 12 Hz, N=C–NH), 151.8, 134.4, 134.3, 133.6, 131.1, 129.5, 128.9, 125.9, 122.1, 120.8, 119.5, 54.5 (d, $^{1}J_{CP}$ = 153.7 Hz, CHP), 54.2, 54.1, 30.9; MS (*m/z*): 379 (M+).

Dimethyl ((benzo[d]thiazol-2-ylamino) (4-isopropylphenyl) methyl) phosphonate ***(4g)***

White powder; yield 89%; mp 168–169 °C; IR (KBr, cm^{-1}): ν 3229, 3032, 2956, 1598, 1567, 1534, 1443, 1240, 1233, 1057, 1031; ^{1}H NMR ($CDCl_3$, 300 MHz): δ_H 1.24 (d, 6H, J = 6.9 Hz, $CHCH_3$), 2.91 (m, 1H, $CHCH_3$), 3.57 (d, 3H, $^{3}J_{HP}$ = 10.8 Hz, OCH_3), 3.84 (d, 3H, $^{3}J_{HP}$ = 10.5 Hz, OCH_3), 5.62 (d, 1H, $^{2}J_{HP}$ = 21.6 Hz, CHP), 7.09 (td, 1H, J = 7.5, 1.0 Hz), 7.23–7.32 (m, 3H), 7.30 (b, NH), 7.52–7.58 (m, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ_C 165.7 (d, $^{3}J_{CP}$ = 12 Hz, N=C–NH), 152.0, 149.6, 132.3, 132.1, 131.2, 128.1, 126.9, 126.8, 125.7, 121.8, 120.7, 119.3, 55.0 (d, $^{1}J_{CP}$ = 155 Hz, CHP), 54.0, 53.9, 33.8, 23.9; ^{31}P NMR ($CDCl_3$, 121 MHz): δ_p 23.47; MS (*m/z*): 391 (M+).

Dimethyl ((benzo[d]thiazol-2-ylamino) (4-chlorophenyl) methyl) phosphonate ***(4h)***

White powder; yield 84%; mp 164–165 °C; IR (KBr, cm^{-1}): ν 3236, 3056, 2645, 1598, 1538, 1444, 1236, 1044, 1017; ^{1}H NMR ($CDCl_3$, 300 MHz): δ_H 3.63 (d, 3H, $^{3}J_{HP}$ = 10.5 Hz, OCH_3), 3.86 (d, 3H, $^{3}J_{HP}$ = 10.8 Hz, OCH_3), 5.65 (d, 1H, $^{2}J_{HP}$ = 21.9 Hz, CHP), 7.11 (t, 1H, J = 7.5 Hz), 7.27–7.37 (m, 3H), 7.55–7.57 (m, 4H); MS (*m/z*): 383 (M+).

Dimethyl ((benzo[d]thiazol-2-ylamino) (2-chlorophenyl) methyl) phosphonate ***(4i)***

White powder; yield 80%; mp 169–170 °C; IR (KBr, cm^{-1}): ν 3218, 3047, 2951, 1596, 1578, 1535, 1442, 1252, 1238, 1075, 1041, 1014; ^{1}H NMR ($CDCl_3$, 300 MHz): δ_H 3.55 (d, 3H, $^3J_{HP}$ = 10.5 Hz, OCH_3), 3.91 (d, 3H, $^3J_{HP}$ = 10.9 Hz, OCH_3), 6.07 (d, 1H, $^2J_{HP}$ = 21 Hz, CHP), 7.1 (td, 1H, J = 7.5, 1.2 Hz), 7.27–7.32 (m, 3H, CH–Ph), 7.45–7.48 (m, 1H), 7.55–7.59 (m, 2H), 7.73–7.76 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ_C 165.5 (d, $^3J_{CP}$ = 12.7 Hz, N=C–NH), 152.0, 134.1, 133.2, 131.2, 129.7, 129.5, 127.3, 125.8, 121.9, 120.8, 119.7, 54.1 (2d, $^2J_{CP}$ = 7.5 Hz, OCH_3), 52.1 (d, $^1J_{CP}$ = 154.5 Hz, CHP); ^{31}P NMR ($CDCl_3$, 121 MHz): δ_p 22.61; MS (*m/z*): 383 (M+).

Dimethyl ((4-(diethylamino) phenyl)((6-methylbenzo[d] thiazol-2-yl)amino)methyl) phosphonate ***(4j)***

Yellow powder; yield 95%; mp 167–168 °C; IR (KBr, cm^{-1}): ν 3231, 3022, 2968, 1571, 1535, 1464, 1237, 1197, 1061, 1030; ^{1}H NMR ($CDCl_3$, 300 MHz): δ_H 1.15 (t, 6H, J = 7.1 Hz, CH_2CH_3), 2.39 (s, 3H, CH_3) 3.34 (q, 4H, J = 6.9 Hz, CH_2CH_3), 3.58 (d, 3H, $^3J_{HP}$ = 10.2 Hz, OCH_3), 3.81 (d, 3H, $^3J_{HP}$ = 10.5 Hz, OCH_3), 5.37 (d, 1H, $^2J_{HP}$ = 21.3 Hz, CHP), 6.66 (d, 2H, J = 8.7 Hz, CH–Ph), 7.10 (dd, 1H, J = 8.3 Hz), 7.36 (s, 1H), 7.40 (dd, 2H, J = 8.7, 1.8 Hz, CH–Ph), 7.46 (d, 1H, J = 8.4 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz): δ_C 165.2 (d, $^3J_{CP}$ = 12 Hz, N=C–NH), 149.9, 147.8, 131.5, 131.2, 129.2, 126.9, 120.8, 120.5, 118.9, 111.6, 55.1 (d, $^1J_{CP}$ = 150 Hz, CHP), 53.9 (d, $^2J_{CP}$ = 7.5 Hz, OMe), 53.8 (d, $^2J_{CP}$ = 6.8 Hz, OMe), 44.3, 21.2, 12.6; ^{31}P NMR ($CDCl_3$, 121 MHz): δ_p 23.89; MS (*m/z*): 434 (M+).

Dimethyl (((6-ethoxybenzo[d]thiazol-2-yl) amino) (phenyl) methyl) Phosphonate ***(4k)***

White powder; yield 90%, mp 170–171 °C; IR (KBr, cm^{-1}): ν 3225, 3032, 2957, 2851, 1594, 1563, 1529, 1237, 1210, 1056, 1030; ^{1}H NMR ($CDCl_3$, 300 MHz): δ_H 1.42 (t, 3H, J = 6.9 Hz, OCH_2CH_3), 3.55 (d, 3H, $^3J_{HP}$ = 10.8 Hz, OCH_3), 3.84 (d, 3H, $^3J_{HP}$ = 10.8 Hz, OCH_3), 4.02 (q, 2H, J = 6.9 Hz, OCH_2CH_3), 5.57 (d, 1H, $^2J_{HP}$ = 22.2 Hz, CHP), 6.81 (b, NH), 6.88 (dd, 1H, J = 9, 2.4 Hz), 7.08 (d, 1H, J = 2.4 Hz), 7.33–7.46 (m, 4H), 7.60 (dd, 2H, J = 7.5, 1.4 Hz, CH–ph); ^{13}C NMR ($CDCl_3$, 75 MHz): δ_C 163.8 (d, $^3J_{CP}$ = 12 Hz, CNH), 154.7, 146.1, 134.9, 132.0, 128.7, 128.3, 128.1, 119.8, 114.11, 106.0, 64.2, 55.3 (d, $^1J_{CP}$ = 153 Hz, CHP), 54.2 (d, $^2J_{CP}$ = 6.5 Hz), 53.9 (d, $^2J_{CP}$ = 6 Hz), 14.9; ^{31}P NMR ($CDCl_3$, 121 MHz): δ_p 23.43; MS (*m/z*): 393 (M+).

Dimethyl ((4-(diethylamino) phenyl) ((6-ethoxybenzo[d] thiazol-2-yl)amino)methyl) phosphonate ***(4l)***

Red powder; yield 90%; mp 161–162 °C; IR (KBr, cm^{-1}): ν 3237, 3031, 2969, 1544, 1522, 1462, 1235, 1206, 1059, 1026; ^{1}H NMR ($CDCl_3$, 300): δ_H 1.15 (t, 6H, J = 7.1 Hz, NCH2CH_3), 1.42 (t, 3H, J = 6.9 Hz, OCH_2CH_3), 3.35 (q, 4H, J = 6.9 Hz, NCH_2), 3.57 (d, 3H, $^3J_{HP}$ = 10.5 Hz, OCH_3), 3.82 (d, 3H, $^3J_{HP}$ = 10.5 Hz, OCH_3), 4.02 (q, 2H, J = 6.9 Hz, OCH_2), 5.37 (d, 1H, $^2J_{HP}$ = 21.3 Hz, CHP), 6.65 (d, 2H, J = 8.7 Hz, CH–Ph), 6.88 (dd, 1H, J = 9, 2.4 Hz), 7.08 (d, 1H, J = 2.4 Hz), 7.40 (dd, 2H, J = 8.7, 1.8 Hz, CH–Ph), 7.45 (d, 1H, J = 9 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz): δ_C 164.2 (d, $^3J_{CP}$ = 12.7 Hz, N=C–NH), 154.5, 147.8, 146.2, 132.0, 129.2, 120.6, 119.6, 114.0, 111.6, 106.0, 64.2, 55.0 (d, $^1J_{CP}$ = 157.0 Hz, CHP), 54.0 (d, $^2J_{CP}$ = 6.7 Hz, OCH_3), 53.8 (d, $^2J_{CP}$ = 7.5 Hz, OCH_3), 44.3, 149, 12.5; ^{31}P NMR ($CDCl_3$, 121 MHz): δ_p 24.01; MS (*m/z*): 394 (M+).

Dimethyl (((6-ethoxybenzo[d]thiazol-2-yl) amino) (p-tolyl) methyl)phosphonate ***(4m)***

White powder; yield 90%; mp 163–164 °C; IR (KBr, cm^{-1}): ν 3244, 3035, 2973, 1576, 1545, 1459, 1241,1210, 1114, 1059, 1025; ^{1}H NMR ($CDCl_3$, 300 MHz): δ_H 1.42 (t, 3H, J = 6.9 Hz, OCH_2CH_3), 2.34 (s, 3H, CH_3), 3.57 (d, 3H, $^3J_{HP}$ = 10.5 Hz, OCH_3), 3.84 (d, 3H, $^3J_{HP}$ = 10.5 Hz, OCH_3), 4.02 (q, 2H, J = 6.9 Hz, OCH_2), 5.55 (d, 1H, $^2J_{HP}$ =21.9 Hz, CHP), 6.87 (dd, 1H, J = 9, 2.4 Hz), 7.07 (d, 1H, J = 2.4 Hz), 7.18 (d, 2H, J = 7.9 Hz, CH–Ph), 7.44 (d, 1H, J = 9 Hz), 7.51 (dd, 2H, J = 8.1, 1.8 Hz, CH–Ph); ^{13}C NMR ($CDCl_3$, 75 MHz): δ_C 164.0 (d, $^3J_{CP}$ = 12.7 Hz, N=C–NH), 154.6, 146.1, 138.1, 132.1, 131.9, 129.4, 128.1, 119.7, 114.0, 106.0, 64.2, 55.1 (d, $^1J_{CP}$ = 151.0 Hz, CHP), 54.0 (d, $^2J_{CP}$ = 4.5 Hz, OCH_3), 53.9 (d, $^2J_{CP}$ = 5.2 Hz, OCH_3), 21.2, 14.9; ^{31}P NMR ($CDCl_3$, 121 MHz): δ_p 23.61; MS (*m/z*): 407 (M+); CHN (%): C:56.23, H:5.66, N:6.88, S:7.84.

Dimethyl (((6-ethoxybenzo[d]thiazol-2-yl) amino) (4-methoxyphenyl)methyl)phosphonate ***(4n)***

White powder; yield 87%; mp 164–165 °C; IR (KBr, cm^{-1}): ν 3235, 3031, 2953, 1542, 1458, 1237, 1213, 1058, 1029; ^{1}H NMR ($CDCl_3$, 300 MHz): δ_H 1.42 (t, 3H, J = 6.9 Hz, OCH_2CH_3), 3.58 (d, 3H, $^3J_{HP}$ = 10.5 Hz, OCH_3), 3.80 (s, 3H, CH_3), 3.84 (d, 3H, $^3J_{HP}$ = 10.8 Hz, OCH_3), 4.02 (q, 2H, J = 6.9 Hz, OCH_2), 5.51 (d, 1H, $^2J_{HP}$ = 21.0 Hz, CHP), 6.90 (b, NH), 6.88 (dd, 1H, J = 8.7, 2.4 Hz), 6.91 (d, 2H, J = 8.4 Hz, CH–Ph), 7.08 (d, 1H, J = 2.4 Hz), 7.44 (d, 1H, J = 8.7 Hz), 7.54 (dd, 2H, J = 8.6, 1.8 Hz, CH–Ph); ^{13}C NMR ($CDCl_3$, 75 MHz): δ_C

163.9 (d, $^{3}J_{CP}$ = 12.7 Hz, N=C–NH), 159.6, 154.5, 146.1, 132.0, 129.4, 126.9, 119.7, 114.1, 114.0, 106.0, 64.2, 55.3, 54.7 (d, $^{1}J_{CP}$ = 154.5 Hz), 54.0, 53.8, 14.9; ^{31}P NMR ($CDCl_3$, 121 MHz): δ_p 23.61; MS (*m/z*): 423 (M+).

Dimethyl (((6-ethoxybenzo[d]thiazol-2-yl) amino) (4-isopropylphenyl)methyl) Phosphonate ***(4o)***

White powder; yield 89%; mp 162–163 °C; IR (KBr, cm^{-1}): *ν* 3230, 3031, 2956, 1574, 1542, 1460, 1241, 1221, 1058, 1029; ^{1}H NMR ($CDCl_3$, 300 MHz): δ_H 1.24 (d, 6H, *J* = 6.9 Hz, $CHCH_3$), 1.42 (t, 3H, *J* = 6.9 Hz, OCH_2CH_3), 2.89 (q, 1H, *J* = 6.9 Hz, CH), 3.56 (d, 3H, $^{3}J_{HP}$ = 10.8 Hz, OCH_3), 3.84 (d, 3H, $^{3}J_{HP}$ = 10.8 Hz, OCH_3), 4.02 (q, 2H, *J* = 6.9 Hz, OCH_2), 5.55 (d, 1H, $^{2}J_{HP}$ = 21.9 Hz, CHP), 6.88 (dd, 1H, *J* = 8.7, 2.4 Hz). 7.09 (d, 1H, *J* = 2.4 Hz), 7.24 (d, 2H, *J* = 8.1 Hz, CH–Ph), 7.45 (d, 1H, *J* = 8.7 Hz), 7.52 (dd, 2H, *J* = 8.1, 1.6 Hz, CH–Ph); ^{13}C NMR ($CDCl_3$, 75 MHz): δ_C 164.0 (d, $^{3}J_{CP}$ = 12 Hz, CNH), 154.5, 149.0, 146.1, 132.2, 132.0, 128.1, 126.8, 119.7, 114.0, 106.0, 64.2, 55.0 (d, $^{1}J_{CP}$ = 153.8 Hz), 54.0, 53.8, 33.9, 23.9, 14.9; ^{31}P NMR ($CDCl_3$, 121 MHz): δ_p 23.62; MS (*m/z*): 435 (M+).

Dimethyl ((4-chlorophenyl) ((6-ethoxybenzo[d] thiazol-2-yl) amino)methyl)Phosphonate ***(4p)***

White powder; yield 83%; mp 160–161 °C; IR (KBr, cm^{-1}): *ν* 3240, 3035, 2973, 1542, 1460, 1230, 1217, 1113, 1058, 1032; ^{1}H NMR ($CDCl_3$, 300 MHz): δ_H 1.42 (t, 3H, *J* = 7.1 Hz, OCH_2CH_3), 3.61 (d, 3H, $^{3}J_{HP}$ = 10.8 Hz, OCH_3), 3.84 (d, 3H, $^{3}J_{HP}$ = 10.8 Hz, OCH_3), 4.05 (q, 2H, *J* = 6.9 Hz, OCH_2), 5.55 (d, 1H, $^{2}J_{HP}$ = 22 Hz, CHP), 6.89 (dd, 1H, *J* = 9, 2.4 Hz), 7.09 (d, 1H, *J* = 2.4 Hz), 7.36 (d, 2H, *J* = 8.2 Hz, CH–Ph), 7.44 (d, 1H, *J* = 9 Hz), 7.54 (dd, 2H, *J* = 8.3, 1.8 Hz, CH–Ph); ^{13}C NMR ($CDCl_3$, 75 MHz): δ_C 158.8 (d, $^{3}J_{CP}$ = 12 Hz, CNH), 150.1, 141.1, 129.6, 128.8, 127.2, 124.7, 124.1, 115.11, 109.5, 101.2, 59.4, 49.7 (d, $^{1}J_{CP}$ = 153.7 Hz, CHP), 49.4 (d, $^{2}J_{CP}$ = 7.5 Hz, OCH_3), 49.1 (d, $^{2}J_{CP}$ = 6.7 Hz, OCH_3), 10.1; MS (*m/z*): 427 (M+).

Dimethyl ((2-chlorophenyl) ((6-ethoxybenzo[d] thiazol-2-yl)amino)methyl)phosphonate ***(4q)***

White powder; yield 78%; mp 165–166 °C; IR (KBr, cm^{-1}): *ν* 3236, 2986, 2953, 1573, 1544, 1463,1268, 1240, 1226, 1060, 1033; ^{1}H NMR ($CDCl_3$, 300 MHz): δ_H 1.42 (t, 3H, *J* = 7.2 Hz, CH_3), 3.53 (d, 3H, $^{3}J_{HP}$ = 10.5 Hz, OCH_3), 3.90 (d, 3H, $^{3}J_{HP}$ = 10.8 Hz, OCH_3), 4.02 (q, 2H, *J* = 6.9 Hz, OCH_2), 5.92 (d, 1H, $^{2}J_{HP}$ = 22.9 Hz, CHP), 6.4 (b, NH), 6.89 (dd, 1H, *J* = 9, 2.4 Hz), 7.10 (d, 1H, *J* = 2.4 Hz), 7.28–7.32 (m, 3H), 7.46 (d, 1H, *J* = 9 Hz), 7.64–7.68 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ_C 163.8 (d, $^{3}J_{CP}$ = 13.5 Hz), 154.7, 146.1134.1, 133.3, 132.1, 129.7, 129.5, 129.1, 127.3, 120.0, 114.3, 105.9, 64.2, 54.1 (d, $^{2}J_{CP}$ = 3.0 Hz, OCH_3), 54.0 (d, $^{2}J_{CP}$ = 3.7 Hz, OCH_3), 52.2 (d, $^{1}J_{CP}$ = 154.5), 14.9; ^{31}P NMR ($CDCl_3$, 121 MHz): δ_p 22.67; MS (*m/z*): 427 (M+).

Result and discussion

Hydrothermal synthesis of carbon spheres

As shown in Scheme 1, an equimolar mixture of sucrose and thiourea was dissolved in water. The solution, then, was transferred to an autoclave and kept at 190 °C for 20 h. The synthesized material was washed, filtered and dried to get a black powder.

The synthesized nitrogen–sulfur-doped carbon spheres (NS-CSs) were characterized by FTIR, X-ray diffraction (XRD), Raman spectroscopy, transmission electron microscopy (TEM), thermogravimetric analysis (TGA) and elemental analysis (CHN).

Catalyst characterization

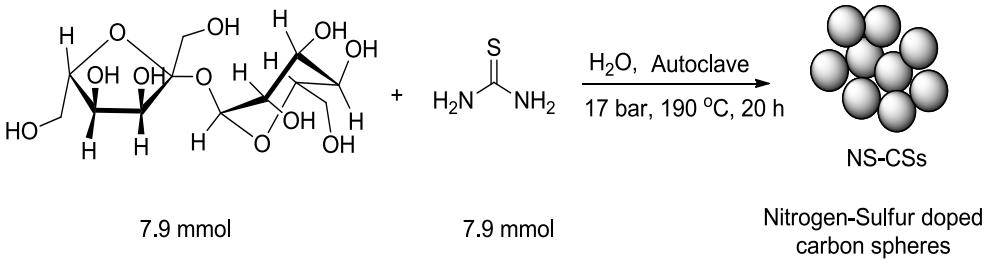
X-ray diffraction (XRD)

Figure 1 illustrates the XRD pattern of the synthesized catalyst with a broad peak positioned at 2*θ* range of 20°–30° indexed to the (002) plane of carbon in a graphitic carbon structure. The observed peak broadening, however, indicates that the structure possesses low crystallinity and is mainly amorphous. The nanocrystalline structure of carbon is a result of Scherrer equation which gives a value of 1.1 nm for the in-plane crystallite size of carbon domains. This is in agreement with other reports indicating to the amorphous nature of carbonaceous phase prepared by the thermal polymerization of glucose and its derivatives [41, 42].

Raman spectroscopy

In accordance with XRD analysis, the Raman spectrum of the synthesized material (bold solid line) shows typical characteristic features of an amorphous carbon structure (Fig. 2) [43]. For an accurate analysis, the spectrum was curve-fitted with 8 distinct gaussian components. The peak at 1584 cm^{-1} (*G* band) is assigned to the E_{2g} mode of graphite and is generated by in-plane bond-stretching motion of pairs of sp^2 carbon atoms [44]. The two peaks located at 1413 cm^{-1} (V_1), 1470 cm^{-1} (V_2) are assigned to aromatic rings with attached alkyl functional groups (sp^2 and sp^3 bonded carbon) typically found in

Scheme 1 Chemical procedure for the synthesis of NS-CSs



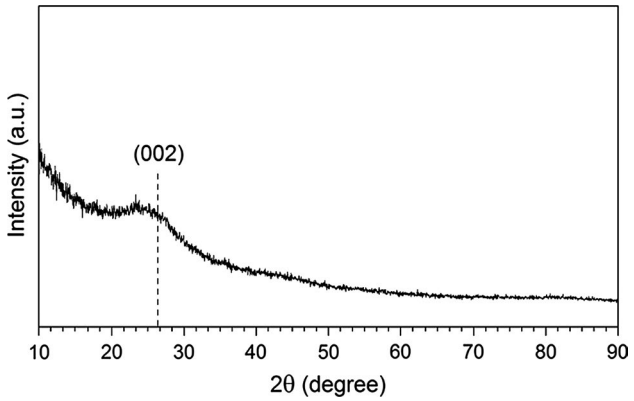


Fig. 1 XRD pattern of the carbonaceous catalyst (the *dashed line* refers to (002) plane of carbon in a graphitic carbon structure)

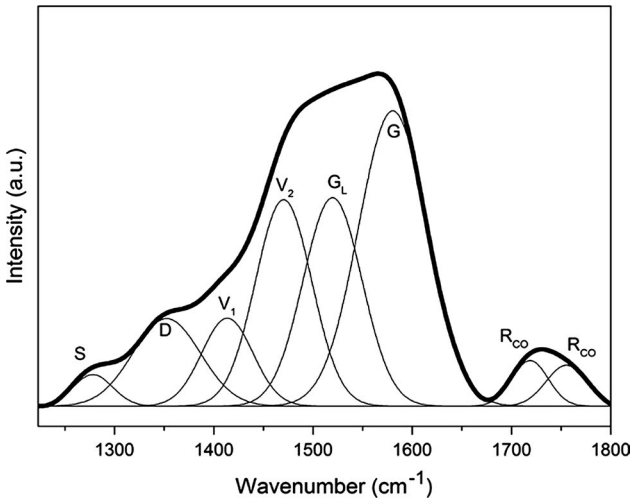


Fig. 2 Raman spectrum of the carbonaceous catalyst

amorphous carbon materials. The band at 1519 cm^{-1} (G_L) represents small sp^2 clusters of 3–5 fused aromatic rings [45–48]. The Raman peak labeled as *D* at 1352 cm^{-1} is attributed to defects in a graphitic structure or any conjugated aromatic systems having more than 6 fused carbon rings. The *D* side band (S) located at 1278 cm^{-1} represents $C_{aromatic}$–C_{alkyl} and sp^2–sp^3 bonded carbon on para-aromatics [47, 48]. Two small peaks at 1718 and 1755 cm^{-1} (labeled R_{CO}) are ascribed to carbonyl (C=O) functional groups [47].

Transmission electron microscopy (TEM)

The size and morphology of synthesized carbonaceous material were investigated by TEM (Fig. 3). As seen, TEM micrographs present that the synthesized product consisted of individual or aggregated carbon microspheres with particles size distribution of 0.2–4 μm.

FTIR spectroscopy

Further chemical bonding structure of the product was conducted by FTIR analysis (Fig. 4). The FTIR spectrum of thiourea exhibits high intense transmission bonds in the range 3100–3400 cm^{-1} assigned to amine groups stretching vibration, while the band located at 1617 cm^{-1} attributed to NH_2 bending vibration. The N–C–N stretching vibration located at 1414 cm^{-1}. The characteristic bonds at 1084 and 730 cm^{-1} assigned to C=S stretching vibration [49] (Fig. 4a). The FTIR spectrum of sucrose shows the characteristic band at 3400 cm^{-1} assigned to OH stretching vibration. The bonds at 2970 cm^{-1} assigned to CH stretching vibration, while the band located at 1461 cm^{-1} attributed to CH bending vibration. The strong bond at 1068 cm^{-1} can be ascribed to C–O stretching [50–52] (Fig. 4b).

In the FTIR spectrum of NS-CSs, a weak band around 300–3400 cm^{-1} may be related to N–H or O–H stretching vibrations. The strong absorption bands at 1696 cm^{-1} attributed to the stretching vibration of the C=O bond. Moreover, the bands at 1608 and 1431 cm^{-1} represent the typical stretching vibration of C=N and C–N, respectively. The characteristic bonds at 1023 and 792 cm^{-1} assigned to C–S stretching vibrations of NS-CSs [52, 53] (Fig. 4c). The above results and it's insolubility in water suggest that the NS-CSs were synthesized successfully.

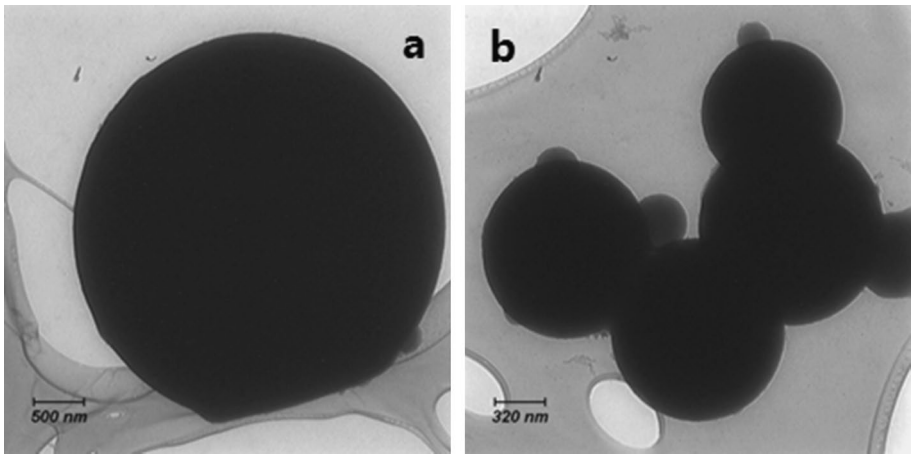


Fig. 3 TEM images of **a** an individual and **b** aggregated carbon spheres

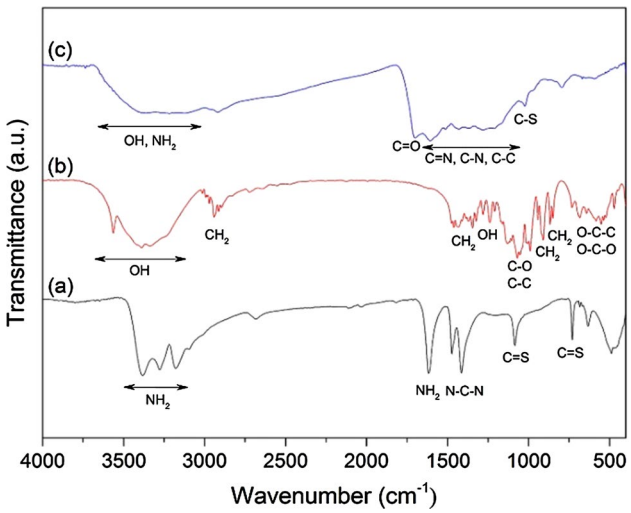


Fig. 4 FTIR spectra of *a* thiourea *b* sucrose *c* NS-CSs

Elemental analysis (CHN)

The amount of doped S and N atoms in the structure of NS-CSs was determined by CHNSO elemental analyzer, and the results are listed in Table 1 for both the reactants (sucrose and thiourea) and NS–. Obviously, a large amount of hydrogen and oxygen in the reactants is removed in the form of H_2O during the hydrothermal processes. By elimination of these elements, the total mass reduces and consequently the weight percent of the remained elements increases in the solid-phase product. A significant increase in the carbon contents (experimental/calculation) is justified by the fact that the sucrose is polymerized to the functionalized spherical carbons during the hydrothermal process. The measured values of 4.28 and 2.86, respectively, for the weight percent of N and S in the product indicate that these elements have successfully incorporated in the structure of carbonaceous spheres and agree well with the

Table 1 Comparison of the amount of elemental analysis substrate and NS-CSs

Element	Reactants		Product (NS-CSs)	
	Thiourea (cal. wt%)	Sucrose (cal. wt%)	(Cal. wt%)	(Experimental wt%)
C	15.78	42.11	37.32	62.68
H	5.30	6.68	6.26	3.41
N	36.80	–	6.70	4.28
S	42.12	–	7.66	2.86
O	–	51.42	42.06	26.77

corresponding FTIR analysis (Fig. 4c). The lower sulfur content in the product in comparison with the reactants is mainly due to the sulfur elimination in the form of sulfur containing species such as H_2S and SO_2 during the hydrothermal process.

Thermo gravimetric analysis (TGA)

In order to know more about the thermal stability of the product, the oxidation of NS-CSs was investigated by heating the powder up to 800 °C in air (Fig. 5). As seen, the TGA and DTG curves demonstrate a slight weight loss at temperatures below 270 °C mainly attributed to the evaporation of free water. The abrupt weight loss at temperatures between 270 and 490 °C is due to the oxidation and degradation of NS-CSs. These results exhibit a good thermal stability for the NS-CSs and indicate that the synthesized catalyst can be feasibly employed in many organic reactions conducted at temperatures below 270 °C.

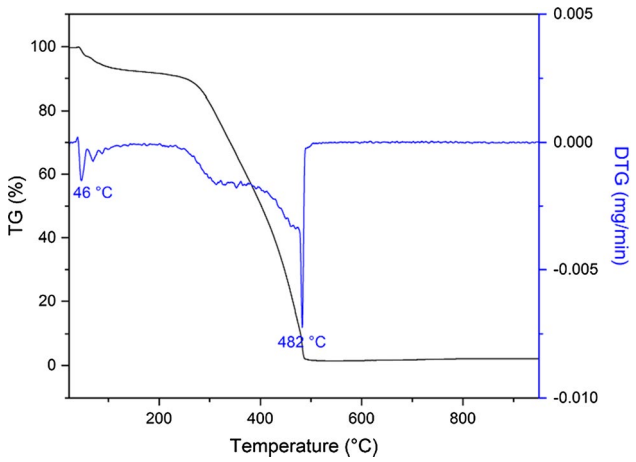


Fig. 5 TGA and DTG curves of NS-CSs

Evaluation of catalytic activity of NS-CSs in the synthesis of α-aminophosphonates

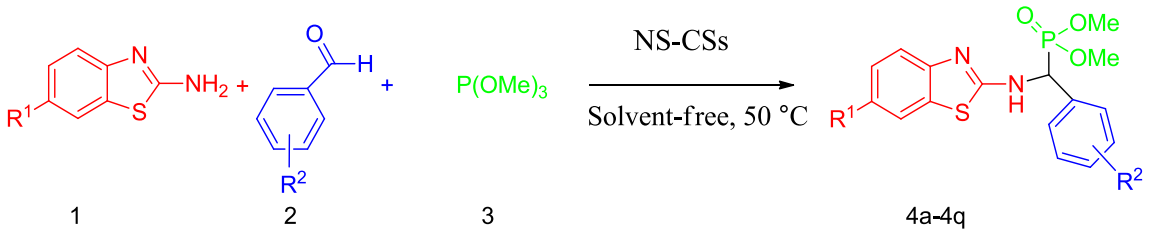
The NS-CSs were employed as a new heterogeneous and recyclable microcatalyst for the one-pot synthesis of α-aminophosphonates directly from aldehydes, 2-aminobenzothiazole and trimethyl phosphite (Scheme 2).

The optimal conditions for the Kabachnik–Fields reaction in the presence of a NS-CSs catalyst

Firstly, the reaction of benzaldehyde, 2-aminobenzoyhiazole and trimethyl phosphite was chosen to optimize the reaction conditions such as, solvents, temperature and molar ratio of the catalyst (Table 2, entries 1–14). The effect of different parameters such as amount of catalyst, solvent, reaction time and temperature were investigated on the final yield.

To evaluate the effect of solvent on the reaction yield, 5 mg of NS-CSs were used to catalyze the reaction in various solvents and solvent-free conditions. As shown in Table 3, the reaction under solvent-free conditions gives significantly higher yields in shorter reaction times than the solution-based experiments. In the next step, the effect of temperature on the reaction progress in the presence of 5 mg NS-CSs and under solvent-free conditions was investigated (Table 2, entries 6–9). As a result, the highest yield was achieved at 50 °C (Table 2, entry 8), while increasing the temperature to 70 °C gives the same yield level of 50 °C.

The catalyst amount is another factor which significantly effects on the reaction yield (Table 2, entries 10–14). In this regard, no product was obtained in the absence of the catalyst (Table 2, entry 1) indicating that the catalyst is necessary for the reaction. The reaction yield rapidly increases when the catalyst amount enhances and reaches the highest level (92%) at 3 mg (Table 2, entry 12). Since further increase in catalyst content beyond this value did not



Scheme 2 Synthesis of α-aminophosphonate derivatives in presence of NS-CSs

Table 2 One-pot reaction of benzaldehyde, 2-aminobenzothiazole and trimethyl phosphite under different conditions

Entry	Catalyst	(mg)	Solvent	Time	Temp (°C)	Isolated yield (%)
1	–		–	10 h	40	Trace
2	(NS-CSs)	5	MeCN	1 h	40	10
3	(NS-CSs)	5	EtOH	1 h	40	15
4	(NS-CSs)	5	H_2O	1 h	40	20
5	(NS-CSs)	5	CH_2Cl_2	1 h	40	30
6	(NS-CSs)	5	Neat	30 min	40	80
7	(NS-CSs)	5	Neat	30 min	r. t	30
8	(NS-CSs)	5	Neat	30 min	50	92
9	(NS-CSs)	5	Neat	30 min	70	92
10	(NS-CSs)	1	Neat	30 min	50	30
11	(NS-CSs)	2	Neat	30 min	50	45
12	(NS-CSs)	3	Neat	30 min	50	92
13	(NS-CSs)	6	Neat	30 min	50	92
14	(NS-CSs)	12	Neat	1 h	50	92

change the reaction yield (Table 2, entries 13 and 14), the optimum amount of catalyst is evaluated to be 3 mg. Moreover, increasing the reaction time more than 30 min did not improve the yield.

After optimization of the reaction conditions, the catalytic activities of NS-CSs were tested by different aldehydes, 2-aminobenzothiazole derivations and trimethylphosphite. The novel compounds (4a–q) were synthesized by the reaction of aldehydes, 2-aminobenzothiazole derivations and trimethylphosphite using 3-mg NS-CSs at 50 °C and under solvent-free conditions. The results are shown in Table 3.

The proposed mechanism of the Kabachnik–Fields reaction in the presence of a NS-CSs catalyst

A plausible reaction mechanism is shown in Scheme 3. The mechanism involves the activation of the carbonyl group of the aldehyde by microorganocatalyst followed by the nucleophilic addition of the amine to afford the imine by the removal of water. The activated imine further reacts with the trimethyl phosphite leading to the formation of corresponding α-aminophosphonates.

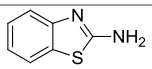
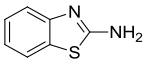
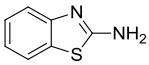
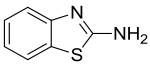
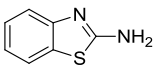
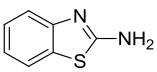
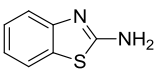
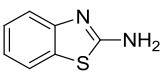
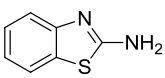
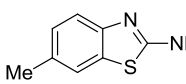
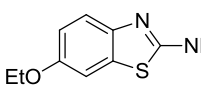
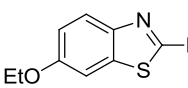
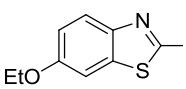
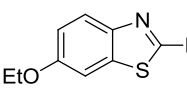
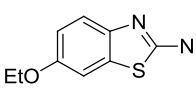
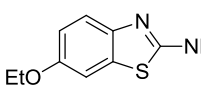
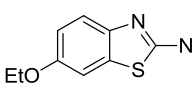
Recyclability of the NS-CSs catalyst was investigated for the synthesis of α-aminophosphonates by the one catalyst in the Kabachnik–Fields reaction

The recyclability and recovery of the catalyst was investigated for the synthesis of α-aminophosphonates by the one-pot three-component condensation of 2-aminobenzothiazole and 4-dimethylaminobenzaldhyde with trimethyl phosphite as model substrates at 50 °C under solvent-free conditions for 30 min. The catalyst can be re-weighted and reused at least for 6 times with only a slight reduction in activity (as shown in Fig. 6).

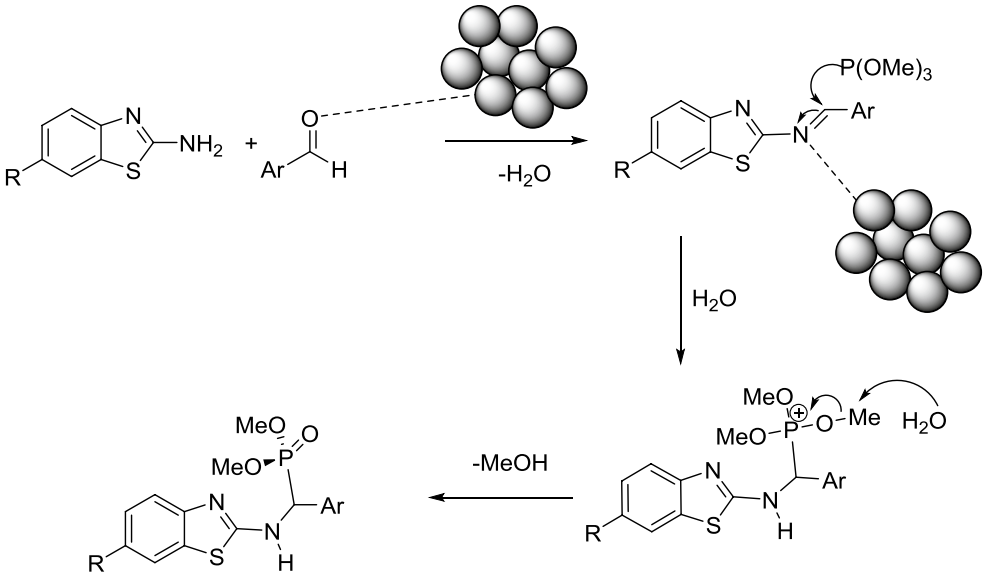
Conclusion

In summary, novel nitrogen–sulfur-doped carbon spheres (NS-CSs) were prepared by a facile hydrothermal process. The results revealed that the size of NS-CSs vary from a few hundred nanometers to a few micrometers and have amorphous structure. The heterogeneous carbon catalyst was successfully employed for the synthesis of α-aminophosphonate derivatives. The highest yield (92%) was achieved when the reaction was carried out at 50 °C for 15 min in the presence of 3 mg of catalyst

Table 3 Synthesis derivatives of α-aminophosphonate in the presence of the catalyst NS-CSs

Entry	2-aminobenzothiazole	Benzaldehyde (R^2)	Products	Time (min)	Mp (°C)	Yield (%)
1		H	**4a**	30	166-167	90
2		4-N(Et)$_2$	**4b**	20	160-161	92
3		4-N(Me)$_2$	**4c**	30	168-169	90
4		4-Me	**4d**	35	173-174	91
5		4-OMe	**4e**	37	170-171	85
6		2-OMe	**4f**	38	169-170	80
7		4-CH(CH$_3$)$_2$	**4g**	34	168-169	89
8		4-Cl	**4h**	53	164-165	84
9		2-Cl	**4i**	45	169-170	80
10		4-N(Et)$_2$	**4j**	20	167-168	95
11		H	**4k**	25	170-171	90
12		4-N(Et)$_2$	**4l**	15	161-162	92
13		4-Me	**4m**	24	163-164	90
14		4-OMe	**4n**	37	164-165	87
15		4-CH(CH$_3$)$_2$	**4o**	32	162-163	89
16		4-Cl	**4p**	40	160-161	78
17		2-Cl	**4q**	44	167-168	83

Isolated yield, conditions: aldehyde (1 mmol), 2-aminobenzothiazole (1 mmol), trimethyl phosphite (1 mmol), catalyst (3 mg), 50 °C, under solvent-free conditions. All the products were characterized by spectroscopic methods



Scheme 3 Proposed mechanism of the Kabachnik–Fields reaction in the presence of a NS-CSs catalyst

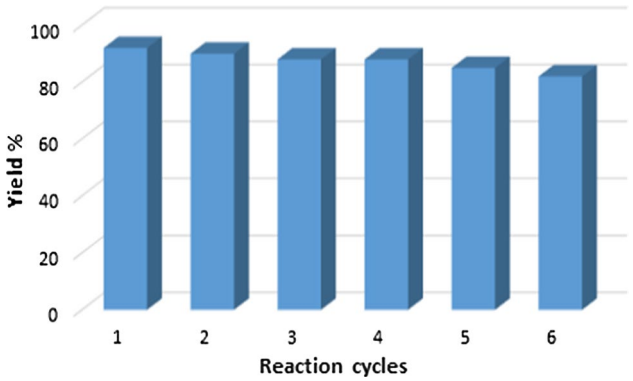


Fig. 6 Recyclability of the NS-CSs catalyst in the Kabachnik–Fields reaction

and under solvent-free conditions. The advantages offered by this protocol include reusability of the catalyst, high conversion, short reaction time and simple experimental procedure.

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