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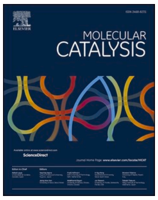

Synthesis, characterization and catalytic application of Bi_2S_3 microspheres for Suzuki-Miyaura cross-coupling reaction and chemoselective ring opening of epoxides

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ABSTRACT

Bismuth sulfide (Bi_2S_3) prepared using L-cysteine, which served as both the sulfur source and the directing molecule for the formation of Bi_2S_3 as heterogeneous catalyst through solvothermal method. The prepared catalyst was examined by various techniques such as XRD, BET, FE-SEM, TEM, and TGA analysis. The results and analysis revealed that bismuth microspheres have better catalytic behavior for the preparation of biphenyl in water as a greenest solvent and for the ring opening of epoxides by nucleophiles including amines, alcohol, and thiol compared to pure $Bi(NO_3)_3$. $3H_2O$ under solvent-free condition. Moreover, the novel catalyst could be recovered and reusedat least four times without loss of its catalytic activity.

Introduction

Suzuki-Miyaura cross coupling of aryl halides with phenyl boronic acids is one of the most powerful approaches for the formation of C—C bonds. In particular, for the synthesis of bi-aryl compounds, the resulting products are widely used [1–6]. Suzuki-Miyaura coupling reaction promoted by different palladium based catalysts [7]. Much recent attentions in Suzuki-Miyaura cross- coupling has been focused on palladium-free conditions and catalyst system including nickel [8], copper [9], iron [10], and cobalt [11] because it is much cheaper and more earth-abundant than the palladium containing compounds. In order to accomplish these valuable reactions under environmentally benign conditions, many studies focused on designing of new catalytic systems and methodologies to cover the twelve green chemistry principles.

Optically pure epoxides are key synthons for the generation of chiral compounds and enantio specific ring opening of readily available enantio enriched epoxides provides an efficient and straightforward protocol for the wide range of highly functionalized [12,13]. Many research have been reported for the asymmetric ring opening of epoxides using stoichiometric or catalytic amounts of chiral, nonracemic reagents or catalysts under homogeneous conditions [14]. The reported metal complex catalysts for epoxide ring opening reactions is of great challenging. In this sense, it is necessary to find a new approach to conquer the difficulties. Nanoparticles (NPs) are strongly investigated because they offer an advantages of both heterogeneous and homogeneous catalysts, because they are sometimes called “semi--heterogeneous” catalysts [15]. Nanoparticles easily agglomerate and oxidize due to high surface energy in aqueous solutions; hence, it is crucial to find a method to solve the problem [16]. In many cases, metal nanoparticles are immobilized various solid supports. A Series of different classes of porous organic polymer frameworks, including conjugated microporous polymers (CMPs) [17], covalent organic frameworks (COFs) [18], polymers of intrinsic microporosity (PIMs) [19], and hypercrosslinked polymers (HCPs) [20], have been prepared. Among these microparticles or microspheres have intrinsic properties including large specific surface area [21], narrow pore size distribution [22], high chemical stabilities [23], and low skeleton density [24] exhibition of potential applications in coatings [25], adhesives [26], leather finishing [27], constructions [28], biomedicines [29], catalysis [30], paints [31], effective strategies to improve the hydrogen storage and CO_2 adsorption capacity [32], and in electronics [33]. Microspheres are small spherical particles, with diameters of 1 μm–1000 μm, and depending upon the encapsulation of active drug moieties there are two types of microspheres: microcapsules (are loosely defined as (spherical) particles in the size range between 50 nm to 2 mm) and micro matrices

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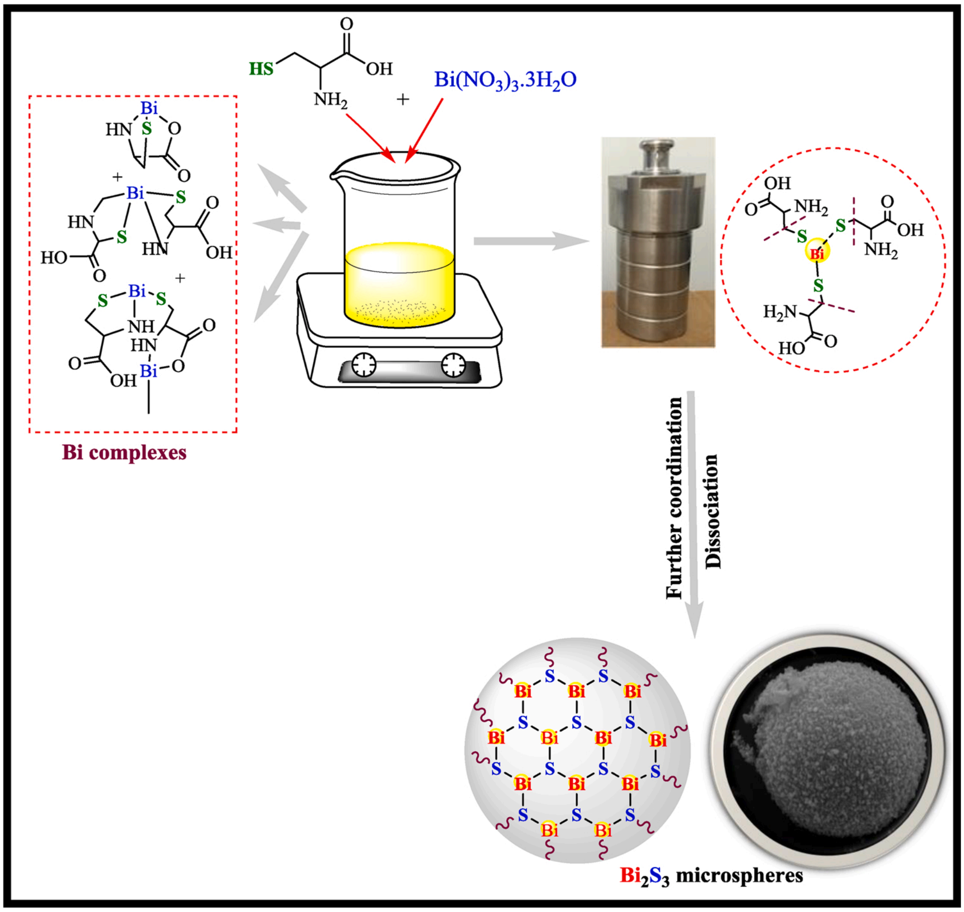


Scheme 1. Schematic synthesis of Bi_2S_3 microspheres.

[34].

Techniques such as dispersion polymerization [35], emulsion polymerization [36], and precipitation polymerization [37] have been used to prepare polymer microspheres. Polymer-based chiral microspheres [38,39] have aroused much attention recently due to their significant application in asymmetric catalysis [40], chemoselective crystallizations [41], chiral recognitions/resolution [42] as media for high- performance liquid chromatography (HPLC) and carriers for catalysis [43]. Bismuth is known as an environmentally benign element due to low toxicity, low cost, and good stability. In the past decades, considerable efforts have been made on the designing of effective methods to synthesis various morphologies of Bi_2S_3 nanomaterials by using different sulfur sources [44–48]. The different nanostructured materials of Bi_2S_3 such as nanorods [44,45], nanowires [46] nanotubes [48,49] and nanobelts, [50] have been prepared. The biomolecule-assisted synthesis method has been proven to be a novel, environmentally friendly, and promising approach in the preparation for various nanomaterials due to the convenient control of the morphology [51].

As part of our ongoing research program [52] to design a green-catalysts using (L-cysteine as an inexpensive, simple, and environment-friendly, thiol-containing amino acid) and $Bi(NO_3)_3$. $3H_2O$ for formation of Bi_2S_3 through solvothermal method (Scheme 1).

Results and discussion

The structure properties of the as-obtained bismuth microspheres characterized by using a field emission scanning electron microscopy (FESEM), Transmission Electron Microscopes (TEM), the powder X-ray diffraction patterns (PXRD), thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), EDS (Energy-dispersive X-ray spectroscopy), elemental mapping and nitrogen adsorption-desorption isotherm.

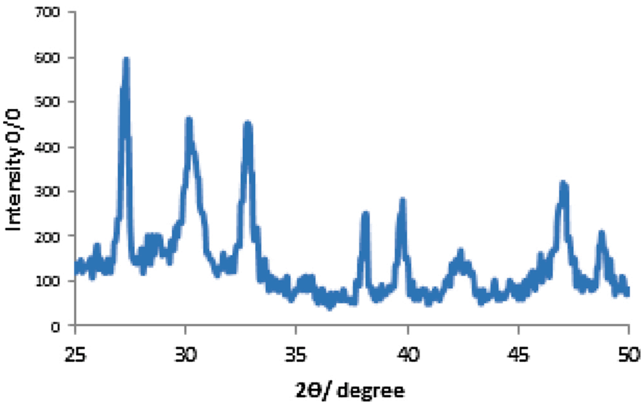


Fig. 1. XRD pattern of Bi_2S_3 microsphere.

Fig. 1 shows the XRD pattern of Bi_2S_3 microsphere, which major reflections located at 27.82°, 32.31°, 33°, 38°, 39°, 42°, and 47° that correspond to Bi_2S_3 crystal with a cubic phase. These results are in agreement with the standard XRD pattern of Bi_2S_3 [53].

In order to study the thermal stability of prepared bismuth containing material, a thermogravimetric analysis performed on Bi_2S_3 microspheres that heated from 25 to 800 °C in air at a heating rate of 10 °C/min (Fig. 2). Mass loss (7%) occurs at a temperature from 480−800 °C, it is attributed to decomposition of Bi_2S_3 microspheres.

To determine the spatial distribution of elements in the Bi_2S_3

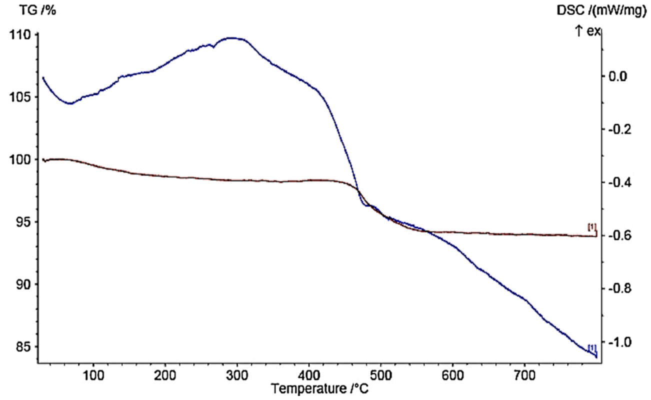


Fig. 2. TGA thermograms of Bi_2S_3 microsphere.

microspheres, elemental mapping performed. The EDS mapping of the Bi_2S_3 material is presented in Fig. 3. The EDS mapping revealedthe presence of the Bi and S, in the powder.

The morphology and size of the products were observed by SEM and TEM; the results were shown in Figs. 4 and 5. As shown in SEM and TEM images in Figs. 4 and 5 the morphology of the as-obtained Bi_2S_3 microspheres are spherical with average diameter of around 200 nm-0.0795 μm. It should be noted that microspheres/microcapsules in nanometer size are usually called as nanospheres/nanocapsules to emphasize their small size. [34]

The porous properties of the sample were investigated by measuring the nitrogen adsorption isotherm, as shown in Fig. 6. The BET surface area and pore volume were estimated to be 28.9 m^2/g and 6.6 cm^3/g respectively, based on the N_2 adsorption-desorption measurement. The BJH pore size calculations using the adsorption branch of the nitrogen isotherm indicate the diameter of pores are about 1.6 nm (Fig. 6).

Catalytic performance of the bismuth microspheres for C—C cross coupling reaction and chemoselective ring opening of epoxides.

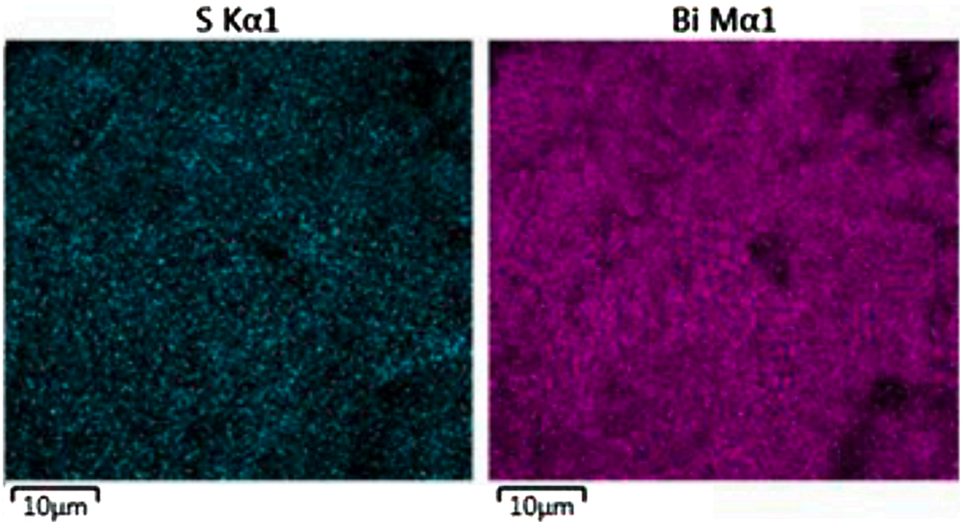


Fig. 3. EDS mapping images of Bi_2S_3 microsphere.

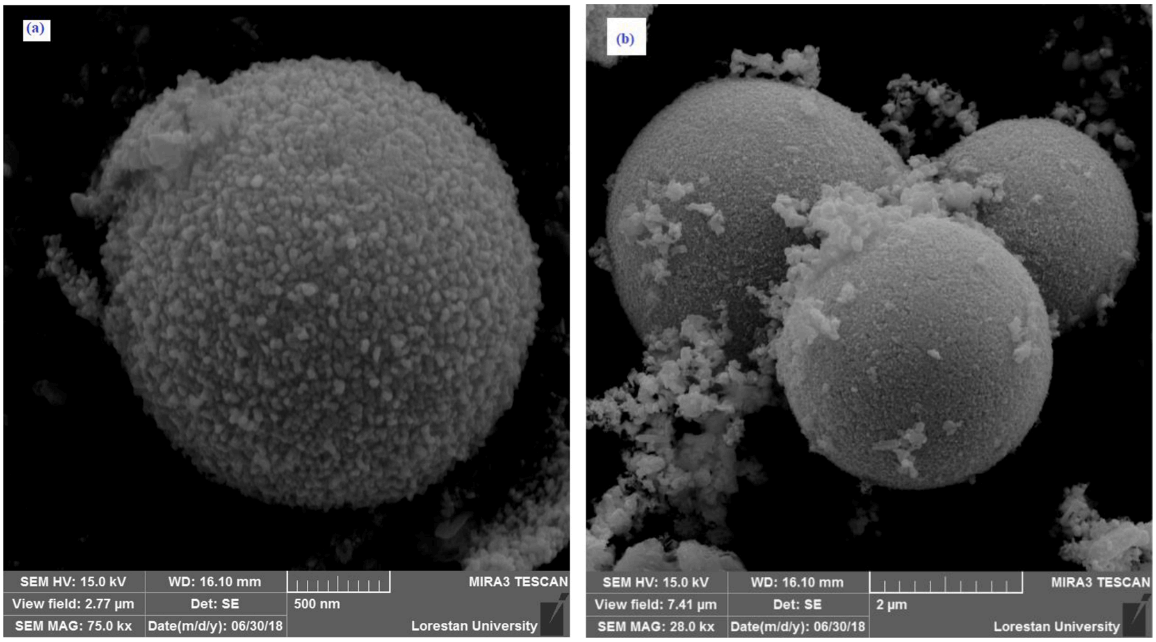


Fig. 4. SEM images of Bi_2S_3 microspheres.

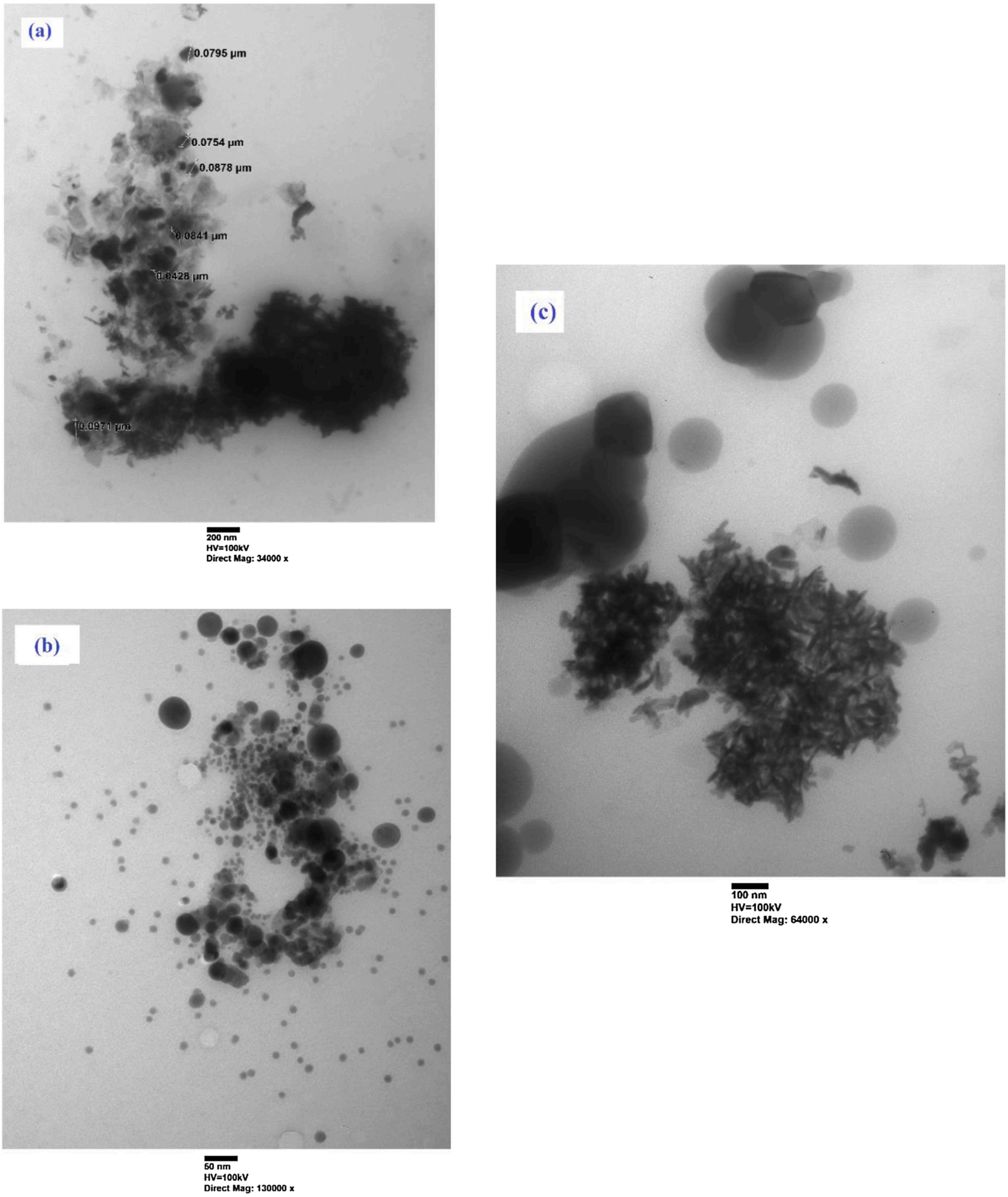


Fig. 5. TEM images of Bi_2S_3 microspheres.

It must be noted we have reported homocoupling of aryl halides in the presence of L-cysteine, recently. [54] In this research project, any effort to perform C—C cross coupling of aryl halides with phenyl bronic acid in the presence of L-cysteine was failed (Table 1, entry 19).

After synthesis and characterization of the Bi_2S_3 microsphere as catalyst, we tested the catalytic treatment of bismuth microspheres for the cross-coupling reaction between iodobenzene and phenylboronic acid as model reaction to screen the solvent, bases, temperature, and catalyst amount and the results are outlined in Table 1. In our first set of experiments, we evaluate the performance of bismuth microspheres (65 mg) *via* reaction iodobenzene (1 mmol) with phenylboronic acid (1.2 mmol) and 3 equivalents of potassium tert-butoxide in DMSO as solvent.

Increasing the temperature reaction to higher temperature, afforded the cross-coupling product with higher yield after 3 h (Table 1). As can be found in Table 1, the optimum temperature for C—C cross-coupling reaction was 100 °C (Table 1, entry 1). To obtain the best optimal reaction conditions, the effect of different solvents were investigated (Table 1). The results obtained for all tested solvent (H_2O, DMSO: H_2O, PEG) are shown in Table 1; it can be seen clearly that H_2O is the most effective solvent for this reaction.

After, the different bases were evaluated for the C—C cross-coupling reaction potassium tert-butoxide gave the best yield. It was found that the use of 65 mg of catalyst leads to 90 % of isolate yield.

With optimal condition in hand, activity of bismuth microspheres was investigated on a series of aryl halides with different functional groups for C—C cross coupling reaction. Under the optimal reaction conditions (Table 1), a variety of aryl halides reacted with phenylboronic acid to achieve a variety of biphenyls (Table 2, Scheme 2). The

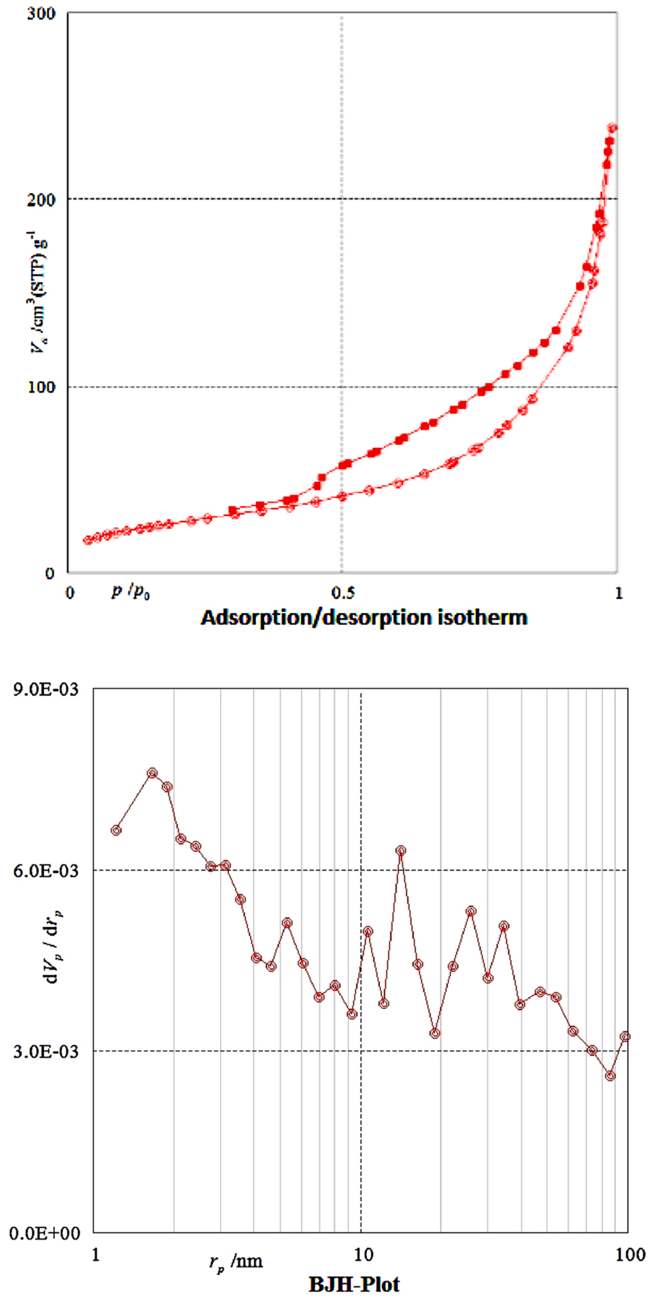


Fig. 6. The N_2 gas adsorption isotherms and BJH pore size distribution of Bi_2S_3 microsphere.

coupling reactions of aryl iodides and aryl bromides provides the biaryl compounds with good to high yields. In this study, the electronic and steric effects on the yields and reaction rates was also evaluated. This catalytic system showed a high activity for electron deficient and electron rich aryl halides (including 4-$NO_2C_6H_4$, 4-$OMeC_6H_4$, 2-$OMeC_6H_4$, 3-$OMeC_6H_4$, 4-MeC_6H_4, 2-MeC_6H_4, 3-$CF_3C_6H_4$). Electron-donating groups show excellent catalytic activity in C—C coupling reaction, when compared toelectron-withdrawing substituents. The ortho substituted aryl halides generated the corresponding product with acceptable yield in longer reaction time (Table 2, compare entries 2 and 3).

In the second part of this research project, another aspect of catalytic properties of Bi_2S_3 microspheres was investigated in epoxide ring-opening reaction. Initially, reaction of 2-phenyloxirane and aniline (Scheme 3) was selected as a model reaction to obtain the best reaction

Table 1

Optimization of reaction conditions for the synthesis of biphenyl.[a].

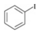
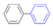
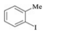
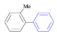
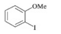
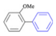
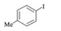
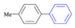
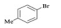
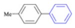
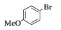
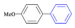
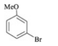
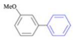
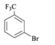
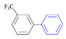
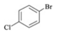
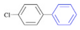
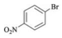
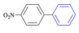
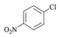
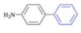
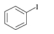
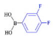
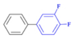
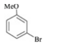
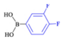
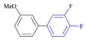
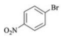
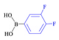
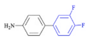
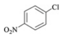
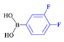
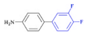
Entry	Solvent	Temp. (°C)	Cat(mg)	Base (mmol)	Base	Yield (b) (%)[b]
1	H_2O	100	65	3	Potassium *t*-butoxide	90
2	DMSO: H_2O	100	65	3	Potassium *t*-butoxide	65
3	H_2O	100	50	3	Potassium *t*-butoxide	75
4	H_2O	100	30	3	Potassium *t*-butoxide	55
5	H_2O	80	65	3	Potassium *t*-butoxide	53
6	tert-Butanol	80	65	3	Potassium *t*-butoxide	20
7	tert-Butanol: H_2O	100	65	–	–	N.R
8	DMSO	100	65	3	Potassium *t*-butoxide	45
9	PEG	100	65	3	Potassium *t*-butoxide	21
10	H_2O	100	65	3	KOH	35
11	H_2O	100	65	3	KF	15
12	H_2O	100	65	3	Imidazole	25
13	DMSO	100	65	3	K_2CO_3	trace
14	DMSO	100	65	3	Na_2CO_3	trace
15	DMSO	100	65	3	Na_2CO_3	N.R
16	DMSO	100	65	3	Et_3N	N.R
17	H_2O	100	–	3	Potassium *t*-butoxide	N.R
18	DMSO	100	L-Cysteine	0.4g	KOH	N.R
19	tert-Butanol: H_2O	80	L-Cysteine	3	Potassium *t*-butoxide	N.R

[a] Reaction conditions:benzene iodide (1 mmol), phenylboronic acid (1.2 mmol), Base (mmol), Time (3 h), and solvent (2 mL).

[b] Isolated yield.

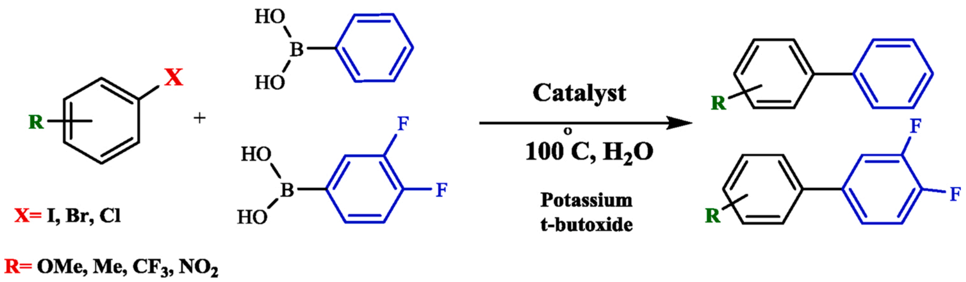
Table 2

C—C cross coupling reaction of aryl halides and phenylboronic acid.[a]

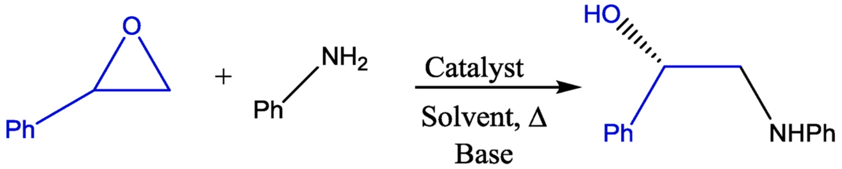
Entry	Ar-X	Phenylating reagent	Product	Time(h)	Yield [b] (%)
1				3	90
2				3	80
3				2	88
4				2	92
5				2.5	87
6				1.5	97
7				5	85
8				4	81
9				2.5	79
10				6	85
11				8	71
12				7	85
13				8.5	80
14				10	78
15				12	70

[a]Reaction conditions:benzene iodide (1 mmol), phenylboronic acid(1.2 mmol), Potassium *t*-butoxide (3 mmol), and H_2O (2 mL).

[b] Isolated yield.



Scheme 2. Bi_2S_3 microspheres catalyzed synthesis of biaryl.



Scheme 3. Model substrates for the ring opening reaction.

Table 3

Optimization of the reaction conditions for the ring opening of 2-phenyloxirane with aniline in the presence of catalytic amounts of Bi_2S_3 microspheres.[a].

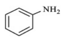
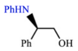
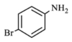
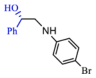
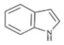
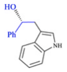
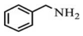
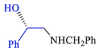
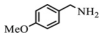
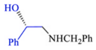
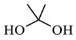
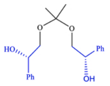
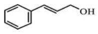
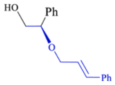
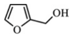
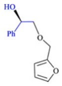
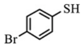
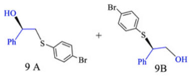
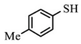
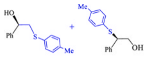
Entry	Solvent	Temp. (°C)	Cat(mg)	Time (h)	Yield(A) (%)[b]
1	None	60	–	24	13
2	None	60	30	1.5	95
3	None	60	20	1.5	75
4	None	60	10	1.5	55
5	None	40	30	1.5	63
6	None	25	30	1.5	48

[a] Reaction conditions: 2-phenyloxirane(1 mmol), aniline(1 mmol), and Catalyst(mg).

[b] Isolated yield.

Table 4

Chemoselective ring opening reaction of epoxides with various nucleophiles.

Entry	Ar-X	product	Time (h)	Yield[b] (%)
1			2	95
2			2.5	92
3			3	90
4			60min	92
5			50min	95
6			4.5	78
7			4.5	82
8			3.5	81
9		 9 A 9B	10min	60:30
10		 10 A 10B	10min	50:50

[a]Reaction conditions: 2-phenyloxirane (1 mmol), nucleophile (1 mmol), and catalyst (30 mg), solvent free.

[b] Isolated yield.

conditions the resulting data summarized in Table 3. In the absence of the catalyst, only trace amount of amino alcohol product obtained in 24 h under solvent-free conditions at 60 °C (Table 3, entry 1). Then we have tested the quantity of catalyst at 60 °C under solvent-free conditions for this reaction (Table 3, entries 3–4). It was observed that the use of 30 mg of catalyst is enough for the completion of the reaction in 2 h with 95 % yield of amino alcohol product (Table 3, entry 1).

With optimal results in hand, the scope of the reaction has been extended further for chemoselective ring-opening reaction of 2-phenyloxirane with different alcohols (including primary and secondary ones), thiol, and aromatic/aliphatic amine (Table 4, Scheme 4). In each case, the catalyst showed reasonable results in term of yield (30–95 %). The product selectivity of the isolated pure product verified by ^{1}H-NMR spectroscopy.

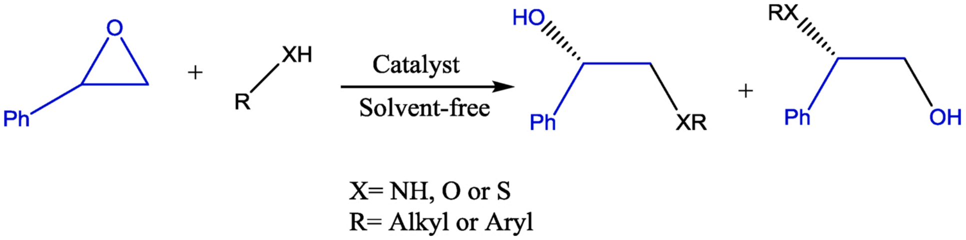
The possibility of catalyst recovery and recyclability is an important object from different aspects such as environmental concerns and commercial applicablity. In this aim, the reusability of the Bi_2S_3 microsphere catalyst has been investigated for the ring opening reaction of 2-phenyloxirane by aniline. As seen from Fig. 7, the catalyst can be efficiently recycled and reused for four consecutive cycles with negligible loss of product yield.

The metal leaching of catalyst was studied using a hot filtration test. Hot filtration technique was done for Suzuki-Miyaura cross coupling reactions. When the reaction preceded to nearly 50 % completion, the catalyst was separated from the reaction mixture and allowed the filtrate to react further in exact conditions. We found that no further reaction occurred after the separation of the catalyst after 3 h; this means that the Bi_2S_3 microspheres catalyst is a heterogeneous catalyst with stable structure.

In order to evaluate the efficiency of Bi_2S_3 microsphere, we compared the catalytic performance of our catalyst for the synthesis of biphenyl with some of the previously reported study (Table 5).

Conclusions

In this research project, we have reported the synthesis of Bi_2S_3 microspheres and its catalytic application in Suzuki-Miyaura cross-coupling reaction for the first time and chemoselective ring opening of epoxides. The notable features of this protocol are the doing reaction under solvent-free conditions, using H_2O as a green solvent, short



Scheme 4. Bi_2S_3 microspheres catalyzed ring opening of epoxides with various nucleophiles.

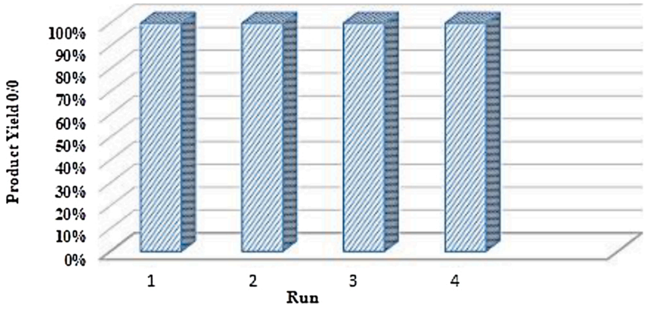


Fig. 7. Catalyst recycling study for the ring opening reaction.

Table 5
Comparison of Bi_2S_3 microspheres for C—C cross-coupling reaction via reaction of phenyl boronic acid and iodobenzene with previously reported procedures.

Entry	Catalyst	Yield (%)[a]	Time (h)	Ref.
1	Pd(II)–NHC complex	99	24	[55]
2	Polymer anchored Pd(II) Schiff ; base	90	5	[56]
3	Pd-MPTAT-1	95	85	[57]
4	Bi_2S_3 microspheres	90	3	This work

[a]Isolated yield.

reaction time, and the high turnover frequency at room temperature, high regio- and chemoselectivity. In addition, catalyst can be easily recovered and reused for the subsequent run for at least 4 times with less deterioration in its catalytic activity.

Experimental

Synthesis of Bi_2S_3 microspheres

In a typical procedure, L-cysteine (1 mmol) was dissolved in 5 mL doubly distilled water, followed by mixing 2 mmol of $Bi(NO_3)_3 \cdot 3H_2O$ in dimethylformamide (20 mL). The mixture of metal and ligand is stirred for 10 min, then transferred into the autoclave at 160 °C for 15 h. The black precipitate was formed. The solid filtrate was washed with ethyl acetate. Finally, the precipitate was dried at 60 °C in the vacuum.

General procedure for the Suzuki reaction

A round-bottom flask was charged with an aryl halide (1 mmol), phenylboronic acid (1.2 mmol), Bi_2S_3 microspheres (60 mg), and potassium *t*-butoxide (3 mmol). The resulting mixture was stirred in H_2O at 100 °C. The reaction was monitored by TLC. At the end of reaction, ethyl acetate (20 mL) was added and filtrated. After concentration, the residue was subjected to column chromatography on silica gel to yield the desired product.

Ring opening of epoxides

In a typical epoxide ring-opening reaction, the catalyst, Bi_2S_3 microspheres (30 mg), was added into a solution of 2-phenyloxirane (1 mmol) and corresponding nucleophie. The solution was stirred at 60 °C under solvent-free conditions and the progress of the reaction was monitored using TLC. After completion of reaction, ethyl acetate (20 mL) was added and filtrated. Finally, the crude product was subjected to column chromatography on silica gel to obtain the pure product.

Selected spectral data

(*R*)-2-Phenyl-2-(phenylamino)ethan-1-ol ^{1}HNMR (400 MHz, $CDCl_3$) (*δ*, ppm): 3.77 (dd, *J* = 4 Hz, *J* = 4 Hz, 1 H), 3.96 (dd, *J* = 4 Hz, *J* = 4 Hz, 1 H), 4.52 (dd, *J* = 4 Hz, *J* = 4 Hz, 1 H), 6.62 (d, *J* = 8 Hz, 2 H), 6.73(t, *J* = 8 Hz, 1 H), 7.15 (t, *J* = 8 Hz, 2 H) 7.32−7.29 (m, 2 H), 7.41−7.39 (m, 5 H).

(1S,1′S)-2,2′-(Propane-2,2-diylbis(oxy))bis(1-phenylethan-1-ol): ^{1}HNMR (400 MHz, $CDCl_3$) (δ, ppm): 0.95 (s, 6 H), 3.98 (dd, *J* = 4 Hz, *J* = 4 Hz, 2 H), 4.18 (dd, *J* = 7.2 Hz, *J* = 7.2 Hz, 2 H), 4.7(s, 2 H), 5.04 (m, 2 H), 7.36−7.32 (m, 5 H), 7.45−7.40(m, 5 H), ^{13}CNMR (100 MHz, $CDCl_3$) (δ, ppm): 21.0, 63.3, 67.9, 77.3, 127.4, 127.7, 128.0, 128.1, 128.4, 128.6, 128.8, 128.9, 129.2, 129.3.

(*R*)-2-(Cinnamyloxy)-2-phenylethan-1-ol:^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 3.78–3.76 (m, 1 H), 4.13–4.15 (m, 3 H), 4.34−4.18(m, 1 H), 6.37–6.39 (m, 1 H), 6.58 (s, 1 H), 6.63−6.43 (m, 1 H), 7.29(d, *J* = 6.8 Hz, 2 H), 7.37(t, *J* = 7.4 Hz, 4 H), 7.43(d, *J* = 7.2 Hz, 4 H), ^{13}CNMR (100 MHz, $CDCl_3$) (δ, ppm): 60.4, 63.7, 82.2, 125.7, 126.1, 126.4, 127.0, 127.7, 128.2, 128.5, 128.6, 129.0, 129.7, 131.1, 132.7, 136.7, 138.5.

(*R*)-2-((4-Bromophenyl)thio)-1-phenylethan-1-ol: ^{1}HNMR (400 MHz, $CDCl_3$) (δ, ppm): 3.17 (dd, *J* = 8 Hz, *J* = 9.2 Hz, 1 H), 3.33(dd, *J* = 4 Hz, *J* = 4 Hz, 1 H), 4.21(s, 1 H), 4.78(dd, *J* = 3.6 Hz, *J* = 3.6 Hz, 1 H), 7.30−7.29 (m, 2 H), 7.38−7.35 (m, 5 H), 7.46(d, *J* = 8 Hz, 2 H), ^{13}CNMR (100 MHz, $CDCl_3$) (δ, ppm): 43.8, 71.8, 120.6, 125.8, 128.0, 128.1, 128.6, 131.6, 132.1, 134.4, 142.0.

(*R*)-1-Phenyl-2-(p-tolylthio)ethan-1-ol: ^{1}HNMR (400 MHz, $CDCl_3$) (δ, ppm): 2.08 (s, 3 H), 2.95(s, 1 H), 3.06 (dd, *J* = 9.6 Hz, *J* = 9.6 Hz, 1 H), 3.33 (dd, *J* = 3.2 Hz, *J* = 3.2 Hz, 1 H), 4.72(m, 1 H), 7.18 (d, *J* = 4.4 Hz, 3 H), 7.35−7.32 (m, 4 H), 7.38(d, *J* = 4.4 Hz, 2 H), ^{13}CNMR (100 MHz, $CDCl_3$) (δ, ppm): 21.0, 44.9, 60.4, 125.9, 127.9, 128.5, 129.9, 130.9, 131.1, 137.1, 142.2.

(*R*)-2-Phenyl-2-(p-tolylthio)ethan-1-ol: 1HNMR (400 MHz, $CDCl_3$) (δ, ppm): 2.08 (s, 3 H), 3.34(s, 1 H), 3.88 (dd, *J* = 6.4 Hz, *J* = 6.4 Hz, 1 H), 3.97(dd, *J* = 6.4 Hz, *J* = 6.4 Hz, 1 H), 4.29 (dd, *J* = 6.8 Hz, *J* = 6.8 Hz, 1 H), 7.10 (d, *J* = 8.4 Hz, 2 H), 7.39−7.27 (m, 5 H), 7.38(d, *J* = 4.4 Hz, 2 H), ^{13}CNMR (100 MHz, $CDCl_3$) (δ, ppm): 21.2, 54.5, 65.0, 127.7, 128.1, 128.7, 129.7, 133.3,137.9, 139.1.

4-Methoxy-1,1′-biphenyl: ^{1}H NMR (400 MHz, $CDCl_3$): (δ, ppm): 3.89 (s, 3 H), 7.04 (d, *J* = 8 Hz, 2 H), 7.36 (t, *J* = 8 Hz, 1 H), 7.47 (t, *J* = 8 Hz, 2 H), 7.60−7.56 (t, *J* = 8 Hz, 4 H).

4-Chloro-1,1'-biphenyl:^{1}HNMR (400 MHz, $CDCl_3$): (δ, ppm): 7.48−7.46(m, 1 H), 7.52−7.50 (m, 2 H), 7.64−7.62 (t, *J*=4.2 Hz, 2 H), 7.76−7.73(m, 4 H).

3′,4′-Difluoro-[1,1′-biphenyl]-4-amine: ^{1}HNMR (400 MHz, $CDCl_3$):

(δ, ppm): 3.48(s, 3 H), 7.69 (d, $J = 8.4$ Hz, 1 H), 7.88 (d, $J = 8.4$ Hz, 1 H), 8.25 (s, 1 H), 8.48–8.45 (m, 4 H).

CRediT authorship contribution statement

Arash Ghorbani-Choghamarani: Supervision, Writing - original draft. **Zahra Taherinia:** Data curation, Methodology.

Declaration of Competing Interest

The authors reported no declarations of interest.

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