

# Silver and copper nanoparticles stabilized on ionic liquids-functionalized polyhedral oligomeric silsesquioxane (POSS): Highly active and recyclable hybrid catalysts



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## ABSTRACT

Two novel heterogeneous hybrid catalysts were successfully synthesized using octa-aminopropyl polyhedral oligomeric silsesquioxane hydrochloride salt (OA-POSS) and ionic liquids, followed by immobilization of Cu and Ag nanoparticles. The obtained hybrid catalysts, Cu@POSS-ILs and Ag@POSS-ILs, were characterized using FT-IR, SEM, EDX, TEM, XRD and TGA. Catalytic studies demonstrated that Cu@POSS-ILs was an excellent catalyst for click reaction in aqueous medium. Furthermore, Ag@POSS-ILs was also exhibited to be an active catalyst for 4-nitrophenol (4-NP) reduction. Simple preparation and easy catalysts recovery and recyclability of Cu@POSS-ILs and Ag@POSS-ILs for at least 3 and 6 runs, respectively, without loss of catalytic activity could be considered as important advantageous from catalytic application point of view.

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## 1. Introduction

Over the past decades, a massive attention has been devoted to the preparation and utilization of metal nanoparticles (NPs) due to their exceptional physical and chemical properties that make them as ideal candidates for a broad range of applications such as sensing, electronics, drug delivery and antibacterial activities [1–5]. Apart from these applications, metal NPs have attracted an extensive interest in catalysis. It is worth mentioning that from practical catalytic application point of view, metal NPs aggregations could be considered as important shortcomings, resulting in a remarkable decrease in their initial catalytic activities. Therefore, utilization of supporting materials for the immobilization of metal NPs is quite substantial. This strategy not only be able to solve the problem of catalysts recycling, but also improve the activity and stability of the catalysts by synergistic interaction between metal NPs and supporting materials [6,7]. Among various solid supports for metal NPs dispersion [3,8–10], there is less attention on the use of polyhedral oligomeric silsesquioxane-ionic liquids (POSS-ILs) as a new type of nanohybrid materials [11,12]. Polyhedral oligomeric silsesquioxanes (POSS) is a new class of organic–inorganic

hybrid materials with the molar ratio of 1.5 for O/Si. POSS structure could be expressed by the typical formula  $T_nR_m$ , where T shows the number of Si atoms and R the organic functional groups [13–15]. Among various types of POSS structures [14,16,17], the cubic structure ( $T_8R_8$ ) with a rigid cage-like core has attracted a considerable attention due to its unique properties, such as good biocompatibility, high mechanical stability and easy surface functionalization, which make POSS as an ideal nano-building for fabricating multifunctional materials with various applications [18–21]. As a novel promising materials, ionic-liquids (ILs), i.e. pure organic salts with low melting temperature, have been vigorously explored by both academic and industrial communities owing to their unique fundamental properties [22,23]. It is worth noting that the preparation of new ILs-based materials with higher performances are still desirable. Recently, POSS hybrid nanostructure was used in order to modulate of ILs properties for utilization in different fields. For example, as a pioneer research group, Chujo et al. synthesized a series of imidazolium based ILs materials containing POSS nanoparticles with high thermal stability and low melting temperature [24–28]. Articles survey showed that there are little reports on the use of polyhedral oligomeric silsesquioxane-ionic liquids (POSS-ILs) as catalysts. For instance, Leng et al. proposed new strategies to prepare amphiphilic polyoxometalate hybrid catalysts using POSS and ionic liquids for epoxidation reaction [12,29,30]. In another interesting report, POSS was functionalized with methyl

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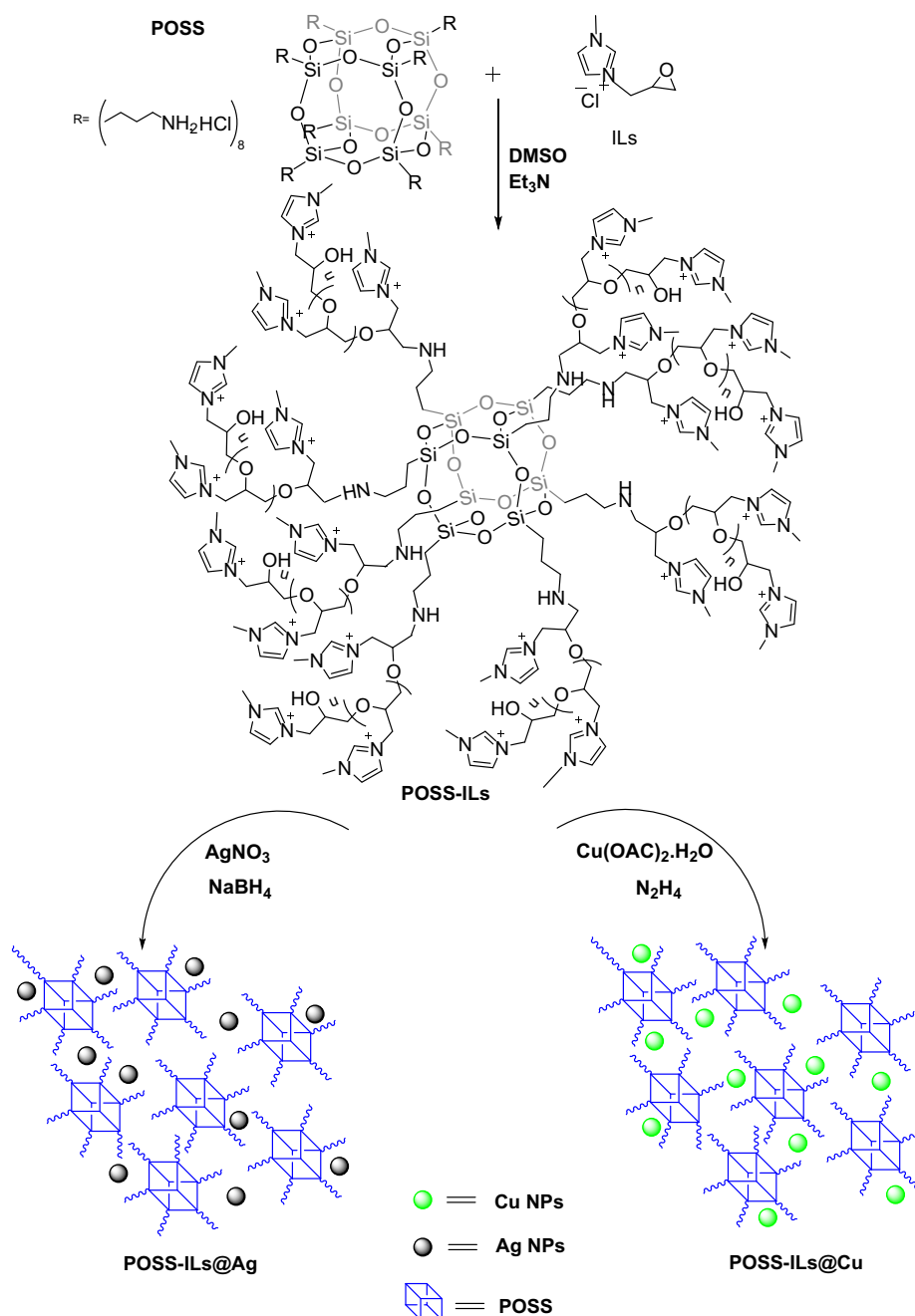
imidazole and used as a novel catalyst for the efficient conversion of CO<sub>2</sub> and epoxides into cyclic carbonates [31]. Taking into account that the embedding of POSS into ILs could create high-tech materials, and in the course of our studies on POSS chemistry [13,14,32] herein for the first time, we developed an innovative exploitation of octa-aminopropyl polyhedral oligomeric silsesquioxane hydrochloride salt (OA-POSS) [33,34] as a nano-building block for constructing new POSS-ILs nanohybrid material. A topic of interest in this context is the use of synthesized POSS-ILs as an appropriate solid support in the preparation of well-dispersed Cu and Ag nanoparticles. The resulting catalysts, Cu@POSS-ILs and Ag@POSS-ILs NPs, were fully characterized by FT-IR, EDX, SEM, TEM, XRD and TGA analysis. Moreover, catalytic experiments have shown that Cu@POSS-ILs and Ag@POSS-ILs NPs

exhibited remarkable catalytic activities and recyclability in click reaction and 4-NP reduction, respectively.

## 2. Materials and methods

### 2.1. Materials

Copper acetate monohydrate, hydrazine hydrate (80%), all benzyl halides (benzyl chloride, benzyl bromide, 2-nitrobenzyl chloride, 4-nitrobenzyl chloride and 2-methylbenzyl chloride) and alkynes (phenyl acetylene, propargyl alcohol and 2-Methylbut-3-yn-2-ol), sodium azide, 3-Aminopropyltriethoxysilane (APTES), 2-(chloromethyl)oxirane and 1-methylimidazole were purchased from Sigma-Aldrich (Germany). All solvents were supplied from



**Scheme 1.** Synthetic approach to prepare of POSS-ILs, Cu@POSS-ILs and Ag@POSS-ILs NPs.

Merck (Germany). Sodium borohydride ( $\text{NaBH}_4$ ), Silver nitrate ( $\text{AgNO}_3$ ) and 4-Nitrophenol (4-NP) were obtained from Sigma-Aldrich (Germany).

## 2.2. Synthesis of octa-aminopropyl polyhedral oligomeric silsesquioxane hydrochloride salt (OA-POSS)

OA-POSS was synthesized according to the previous procedure with hydrolytic condensation of APTES in acidic medium [33]. Briefly, in a 500 ml two-neck round bottom flask equipped with a condenser and a magnetic stirrer, 180 mL methanol and concentrated HCl (15 mL, 35–37%) were added, followed by addition of APTES (7.5 ml, 30 mmol) in drops at 60 °C. Successively, the reaction temperature was increased and refluxed at 90 °C for 16 h with vigorous stirring. After cooling the reaction mixture to room temperature, in order to obtain white precipitate, 300 ml THF was added. The obtained OA-POSS was filtrated and washed several times with THF, then collected, and dried at 40 °C under vacuum for 24 h. finally OA-POSS as a white powder was stored in a sealed vial for further usage (with a yield of 33%). Spectroscopic data are as follows:  $^1\text{H}$  NMR (300 MHz,  $\text{D}_2\text{O}$ ):  $\delta$  2.91 (t,  $\text{CH}_2\text{NH}_3$ , 16H), 1.68 (m,  $\text{SiCH}_2\text{CH}_2$ , 16H), 0.68 (t,  $\text{SiCH}_2$ , 16H) ppm.  $^{13}\text{C}$  NMR (100 MHz,  $\text{D}_2\text{O}$ ):  $\delta$  41.04 (s,  $\text{CH}_2\text{NH}_3$ ), 20.01 (s,  $\text{SiCH}_2\text{CH}_2$ ), 8.55 (s,  $\text{SiCH}_2$ ) ppm. FT-IR (KBr,  $\text{cm}^{-1}$ ): 3224, 3025, 2920, 1604, 1494, 1125, 1107, 935, 705  $\text{cm}^{-1}$ .

## 2.3. Synthesis of 1-methyl-3-(oxiran-2-ylmethyl)-1H-imidazol-3-ium chloride (ILs)

To a 100 ml round bottom flask equipped with a reflux condenser, 3.9 ml (50 mmol) 2-(chloromethyl)oxirane and 4.0 ml (50 mmol) 1-methylimidazole were added. The reaction mixture was stirred at 70 °C for 48 h in order to form a two-phase mixture. The upper layer was decanted and the lower phase was washed with ethyl acetate for three times. Finally, the product was obtained as a brown liquid [35].

## 2.4. Synthesis of ionic liquid-functionalized polyhedral oligomeric silsesquioxane (POSS-ILs)

ILs (51 mg), OA-POSS (50 mg) and triethyl amine (0.5 ml) were charged in a 10 ml round bottom flask containing 2 ml DMSO and equipped with a reflux condenser and a magnetic stirrer. The reaction mixture was stirred vigorously at 90 °C for 24 h in an oil bath. After cooling to room temperature, the reaction mixture was poured into excess acetonitrile ( $\text{CH}_3\text{CN}$ ) under vigorous stirring to precipitate POSS-ILs as a brown solid compound, then washed with DMSO and dried in a vacuum oven at 70 °C for 24 h.

## 2.5. Preparation of Cu@POSS-ILs and Ag@POSS-ILs hybrid materials

25 mg of POSS-ILs was dispersed in 5 ml DMF ultrasonically for 1 h, then 4 mg of copper acetate was added and the mixture was stirred for another 1 h, followed by adding 10  $\mu\text{l}$  hydrazine hydrate (80%). The reaction was kept at room temperature under vigorous stirring for a further 1 h. the product was separated, washed with ethanol and dried under vacuum at 60 °C for 6 h to afford Cu@POSS-ILs. In the case of Ag@POSS-ILs, 70 mg of POSS-ILs was dissolved in 5 ml distilled water, followed by adding 50 mg  $\text{AgNO}_3$  and stirring for 1 h in order to get a milky solution. To reduce the Ag ions to Ag NPs, 5 ml of  $\text{NaBH}_4$  aqueous solution (20 mmol/L) was added dropwise. After separation by centrifuge, the product was washed with ethanol and dried under vacuum at 60 °C for 6 h.

## 2.6. General procedure for click reaction by Cu@POSS-ILs hybrid catalyst

To a mixture of alkyne (1 mmol), the organic halide (1.1 mmol) and  $\text{NaN}_3$  (1 mmol), 7 mg of Cu@POSS-ILs catalyst was added in water. Then the reaction was stirred at 50 °C for 12 h, and the conversion of the starting materials was monitored by TLC. Finally, Cu@POSS-ILs catalyst was separated and the product was extracted with EtOAc ( $3 \times 5$  ml) with no further purification. To optimize, click reaction was carried out in various time (2, 6 and 12 h), different solvents (water, toluene, acetonitrile, acetone and ethanol) with various amount of catalysts (0, 1, 3, 5, 7 and 9 mg).

## 2.7. General procedure for reduction of 4-NP using Ag@POSS-ILs hybrid catalyst

In a typical experiment, aqueous solution of 4-NP (4 mg, 10 ml) and  $\text{NaBH}_4$  (100 mg) were mixed in a 25 ml round bottom flask, followed by adding 7 mg as-prepared hybrid catalyst. The reaction progress i.e. the conversion of 4-NP to 4-AP was monitored by the UV-Vis spectroscopy in a scanning range of 200–700 nm at room temperature.

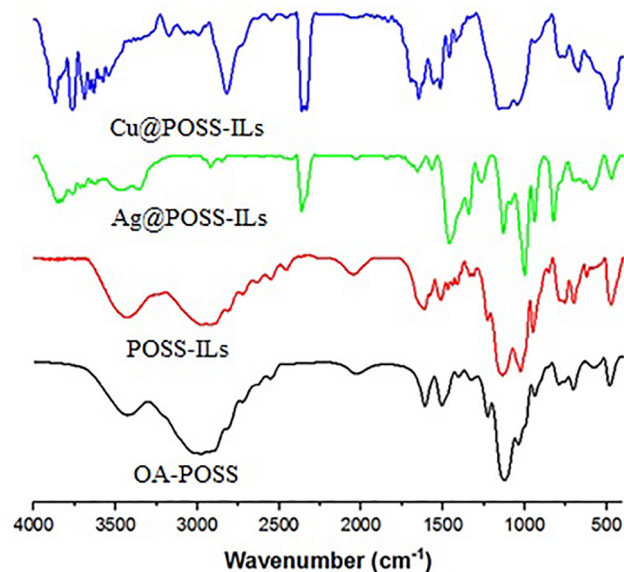


Fig. 1. FT-IR spectra of OA-POSS, POSS-ILs, Ag@POSS-ILs and Cu@POSS-ILs.

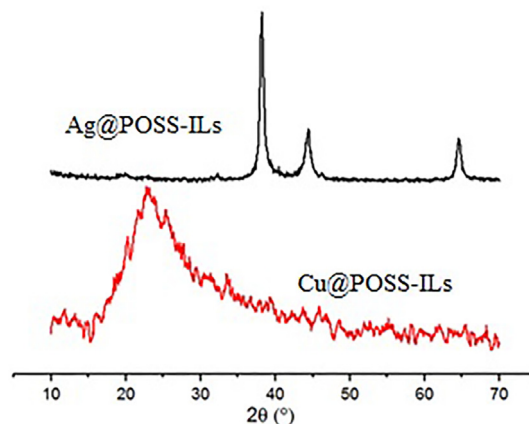


Fig. 2. XRD patterns of Ag@POSS-ILs and Cu@POSS-ILs.

## 2.8. Instrumentation

Fourier transform infrared (FT-IR) spectra were carried out on a Win-Bomem spectrometer, version 3.04 Galactic Industries Corporation over the range of 400–4000  $\text{cm}^{-1}$ . The scanning electron microscopy (SEM) analyses were done by a VWGA3 TESCAN (20.0 KV) microscope field emission scanning electron microscope (FE-SEM) at an accelerating voltage of 20 keV with an energy-dispersive X-ray (EDX) spectroscopy. The XRD diffraction patterns of samples were collected with a Bruker D8 Advance diffractometer using a Cu K $\alpha$  radiation source ( $\lambda = 0.154059 \text{ nm}$ ) at 30 keV in the scan range ( $2\theta$ ) from 4 to 70°. Thermogravimetric (TGA) analyses were performed using a Linseis L81A1750 (Germany) at a heating rate of 10  $^{\circ}\text{C}/\text{min}$  under high purity nitrogen atmosphere from 50 to 800  $^{\circ}\text{C}$ . UV-Vis absorption spectra were recorded on a Shimadzu UV-1800 model spectrophotometer.

## 3. Results and discussion

### 3.1. Synthesis and characterization of hybrid catalysts

The aim of this work was to exploit a simple and facile method in order to synthesize a novel POSS-ILs hybrid solid support for immobilization of Cu and Ag NPs. Scheme 1 showed the synthesis routes of POSS-ILs based catalysts in which octa-aminopropyl polyhedral oligomeric silsesquioxane hydrochloride salt (OA-POSS) functionalized with imidazolium moiety, followed by immobilization of Cu and Ag NPs.

Obtained hybrid catalysts, Cu@POSS-ILs and Ag@POSS-ILs, were used in click reaction and 4-NP reduction, respectively. Excellent catalytic activity of these hybrid catalysts could be explained that

the synthesized POSS-ILs solid support not only facilitated the well dispersion of metal nanoparticles but also the hydrophobicity of inorganic core in POSS has been proved to be helpful in the organic transformations.

Fig. 1 depicts the FT-IR spectra of synthesized POSS based samples. A band at around 1120–1125  $\text{cm}^{-1}$  could be seen in all spectra, which is related to the asymmetric vibration of Si-O-Si on the POSS nanoparticles [34,36]. Furthermore, the bands at 2865 and 2920  $\text{cm}^{-1}$  in the FT-IR spectra proved the existence of propyl chains in OA-POSS [33]. POSS-ILs and hybrid catalysts show characteristic bands at 1425–1630  $\text{cm}^{-1}$  and 2850–2930  $\text{cm}^{-1}$  regions that are corresponded to imidazolium groups and  $\text{CH}_2$  stretching vibrations, respectively, suggesting the coexistence of POSS nanoparticles and ILs moiety [35]. After immobilization of Ag and Cu nanoparticles on the POSS-ILs solid support, the peaks related to Si-O-Si and organic moiety in POSS-ILs are consistent. However, small shifts could be seen in the bands of imidazolium regions, confirming the formation of hybrid catalysts by coordination of Ag and Cu NPs with poly ionic liquid on OA-POSS.

XRD patterns of Ag@POSS-ILs and Cu@POSS-ILs samples were investigated to study the crystalline nature of Ag and Cu NPs present inside the hybrid catalysts. As it could be seen from Fig. 2, the XRD pattern of Ag@POSS-ILs included some sharp peaks at  $2\theta = 38.2^{\circ}$ ,  $44.5^{\circ}$  and  $65.1^{\circ}$  corresponding to (1 1 1), (2 0 0) and (2 2 0) sets of lattice plane, respectively, suggesting the presence of crystalline Ag NPs [37]. In the case of Cu@POSS-ILs, two peaks at  $2\theta = 26.8^{\circ}$  (1 1 1) and  $34.5^{\circ}$  (2 0 0) were characteristic of the face-centered cubic (fcc) structure of Cu NPs. Two weak XRD peaks at around  $2\theta = 43.7^{\circ}$  and  $52.5^{\circ}$  were also observed [38,39].

The cross-section fracture surfaces and the elemental composition of the synthesized hybrid catalysts were investigated by SEM and EDX analysis, respectively. Fig. 3A shows the SEM image of

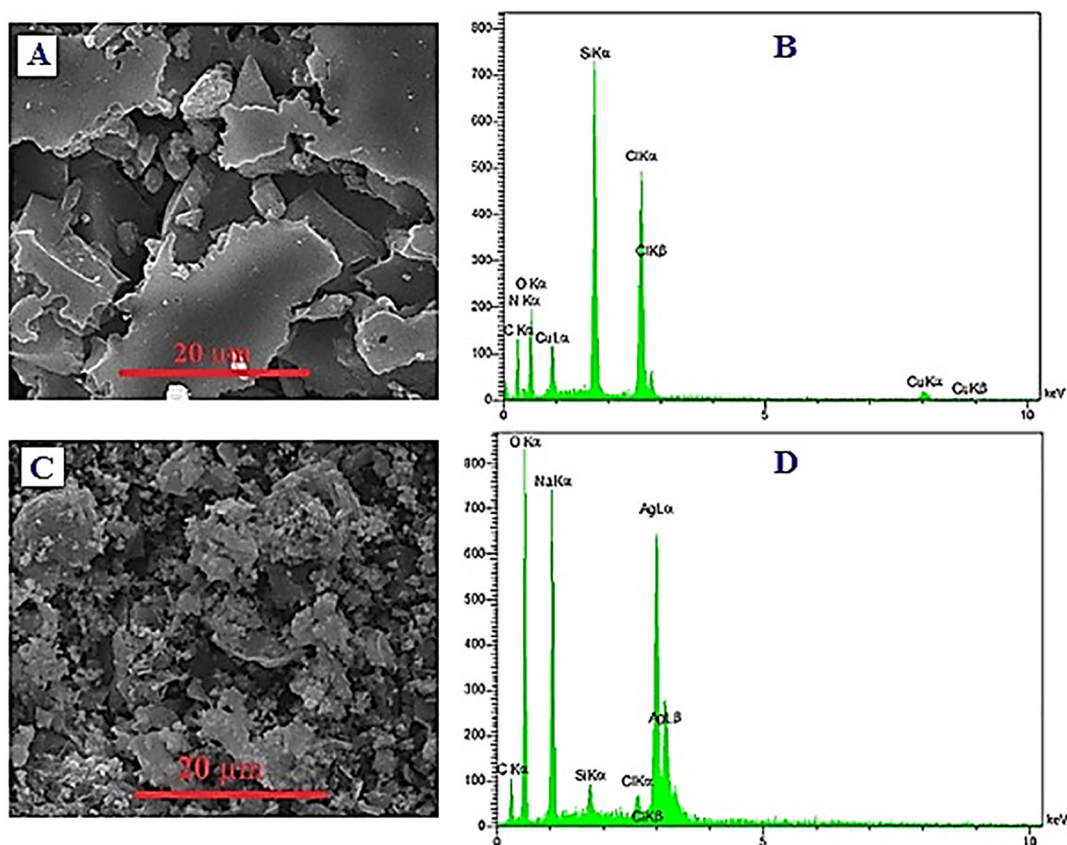


Fig. 3. SEM images (with the magnification of 3.00 kx) of (A) Cu@POSS-ILs, (C) Ag@POSS-ILs and EDX patters of (B) Cu@POSS-ILs, (D) Ag@POSS-ILs.

Cu@POSS-ILs with irregular blocks and smooth surfaces. In the case of Ag@POSS-ILs hybrid catalyst, Fig. 3C, the SEM image depicts a fluffy rough surface composed of aggregated nanoparticles. Moreover, the EDX results is illustrated in Fig. 3B and D, which confirms the existence of Si, Cu and Ag elements in the structure of hybrid catalysts. The content of Ag and Cu was 17.60% and 10.19 wt%, respectively.

TEM images were recorded in order to investigate the size and shape of Cu and Ag NPs fabricated on the surface of hybrid catalysts. Fig. 4 shows TEM images of Cu@POSS-ILs and Ag@POSS-ILs with two different magnifications. In the TEM images of both hybrid catalysts, black aggregated micelles with spherical shapes and size of 50–60 nm are obviously seen, confirming the presence of POSS units (Fig. 4A and C). The same observations were reported by Leng et al. [30] and Bivona et al. [31]. In the high-resolution TEM images, uniformly dispersed dark nanoparticles with small size of 5–10 nm could be seen clearly in Fig. 4B and D, indicating the existence of Cu and Ag NPs in the hybrid catalysts, respectively.

TGA profiles in Fig. 5 demonstrates that the prepared hybrid catalysts have excellent thermal stability with decomposition starting at about 300 °C. The weight loss of 10% before 300 °C could be related to the loss of adsorbed water. The weight loss in 300–500 °C is attributed to the destruction of organic groups.

### 3.2. Catalytic experiments

Referring to TEM images and Scheme 1, the synthesized POSS-ILs solid support enabled us in situ preparation and immobilization

of Cu and Ag NPs with small size and high dispersion in which are favorable and critical from catalytic application point of view. In addition, obtained catalysts possessed both POSS and ILs in their structures, it was considered that the catalysts could facilitate organic transformations [40]. In this regard, we decided to study the catalytic activity of the Cu@POSS-ILs and Ag@POSS-ILs in click reaction and 4-NP reduction, respectively. In the case of Cu@POSS-ILs, to optimize the reaction conditions, the effects of some parameters such as catalyst amount, temperature, reaction time and various solvents were investigated for model reaction of phenyl acetylene, benzyl chloride and sodium azide to synthesize 1-benzyl-4-phenyl-1,2,3-triazole with Cu@POSS-ILs as hybrid catalyst (Table 1).

As it can be seen from Table 1 (entry 1), no product was obtained when the reaction was carried out in the absence of catalyst, demonstrating the need of Cu@POSS-ILs hybrid catalyst to achieve desired product. Entries 2–6 showed the effect of Cu@POSS-ILs amount in the model reaction. By increasing the amount of hybrid catalyst from 1 to 7 mg, the product yield increased from 54 to 72% at 70 °C, respectively. As the reaction temperature has a significant effect on the product yield, we found that no product was obtained at room temperature (entry 7). In contrary, by increasing the reaction temperature (e.g. 40–70 °C), a remarkable increase in the product yield was obtained (entries 9 and 10). According to Table 1 and entry 9, desired product, 1-benzyl-4-phenyl-1,2,3-triazole, was isolated in highest yield (82%) at 50 °C after 12 h. Therefore, in all remaining experiments, 50 °C was selected as the optimum reaction temperature. Also,

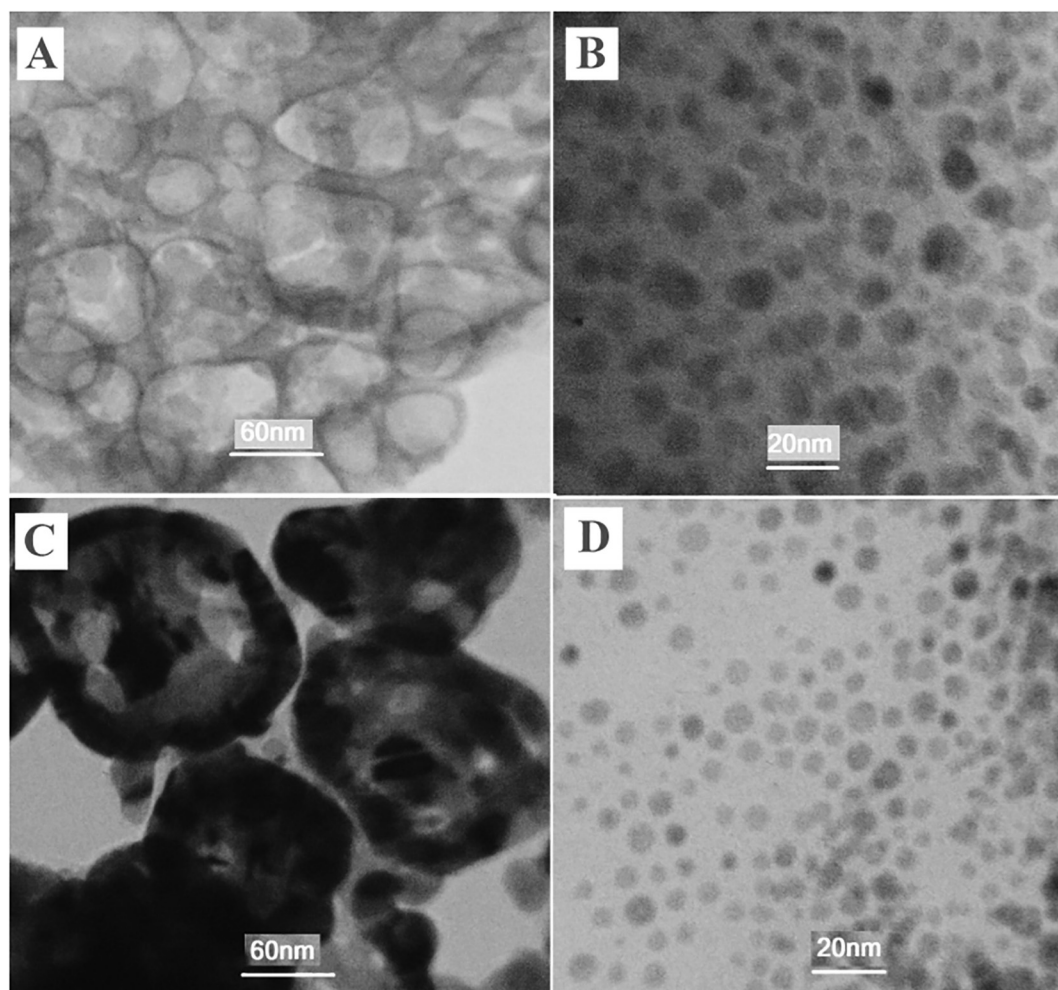
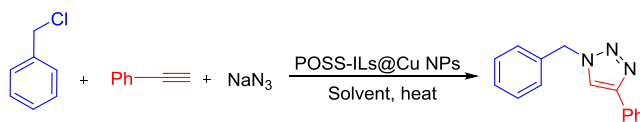


Fig. 4. TEM images of (A and B) Cu@POSS-ILs, (C and D) Ag@POSS-ILs with two different magnifications (60 and 20 nm).

**Table 1**

Selection of click reaction in the presence of Cu@POSS-ILs hybrid catalyst.



Entry	Catalyst amount (mg)	Solvent	T (°C)	Time (h)	Yield (%) <sup>a</sup>
1	0	H <sub>2</sub> O	70	12	0
2	1	H <sub>2</sub> O	70	12	54
3	3	H <sub>2</sub> O	70	12	62
4	5	H <sub>2</sub> O	70	12	67
5	7	H <sub>2</sub> O	70	12	72
6	9	H <sub>2</sub> O	70	12	73
7	7	H <sub>2</sub> O	r.t	12	0
8	7	H <sub>2</sub> O	40	12	48
9	7	H <sub>2</sub> O	50	12	82
10	7	H <sub>2</sub> O	60	12	77
11	7	H <sub>2</sub> O	50	2	35
12	7	H <sub>2</sub> O	50	6	66
13	7	C <sub>2</sub> H <sub>5</sub> OH	50	12	5
14	7	CH <sub>3</sub> CN	50	12	N.R. <sup>b</sup>
15	7	Toluene	50	12	N.R
16	7	Acetone	50	12	N.R

<sup>a</sup> Isolated yield.<sup>b</sup> No reaction.

the time dependence of click reaction was illustrated in Table 1. On the other hand, when the reaction time was less than 12 h, the low amount of product was isolated (entries 11 and 12). Additionally, the catalytic performance of Cu@POSS-ILs was explored in various solvents. As illustrated in Table 1 (entries 14–16), the model reaction was not promoted in acetonitrile, toluene and acetone. In the case of ethanol as a solvent (entry 13), only 5% product yield was achieved. Compared to other solvents, experimental results showed that the click reaction with high yield was carried out in water as a green solvent. Finally, the best optimized conditions were achieved by conducting the model reaction in the presence of 7 mg of Cu@POSS-ILs in water at 50 °C for 12 h (entry 9). Using this optimized condition, to evaluate the scope of general applicability of Cu@POSS-ILs hybrid catalyst, the reaction of different alkynes and substituted benzyl halides was examined. As shown in Table 2, compared to aliphatic alkynes, the click reaction of phenyl acetylene occurred with higher yield (entries 1–5). Benzyl chlorides with electron-withdrawing group are less reactive than those with electron-donating group (entries 3–5). Additionally, due to lack of steric hindrance, benzyl chloride with nitro group at para position was more reactive to the click reaction than the ortho derivative.

The reusability and recoverability of the catalyst are substantial issues from an economic point of view. In this regard, the reusability of Cu@POSS-ILs hybrid catalyst in the click reaction of phenyl acetylene, benzyl chloride and sodium azide to synthesize 1-benzyl-4-phenyl-1,2,3-triazole was tested. For each run, the catalyst was separated from the reaction mixture by centrifugation, washed with distilled water and ethyl acetate, dried and reused in the next run. Fig. 6 showed that after three times recycling the catalyst, the reaction yields slightly decreased due to the loss of catalyst activity.

In addition, leaching experiment demonstrated that the reaction process was heterogeneously catalyzed by Cu@POSS-ILs and the hybrid catalyst was stable during the reaction process.

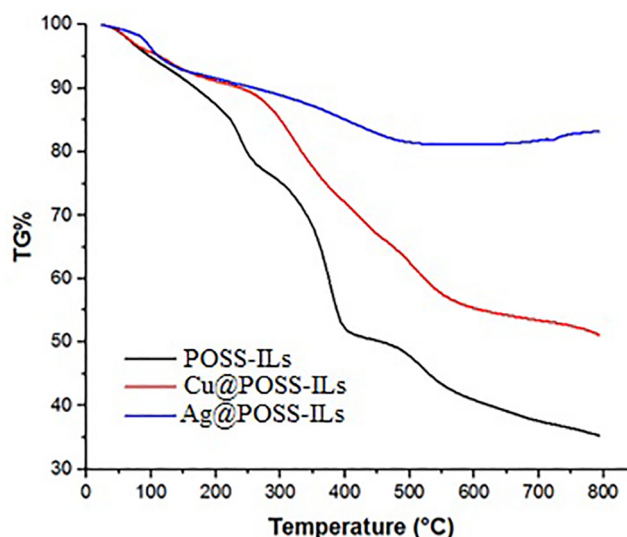
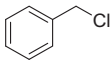
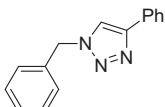
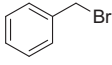
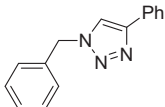
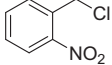
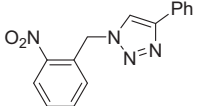
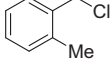
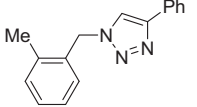
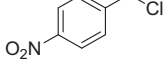
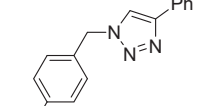
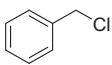
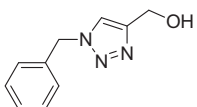
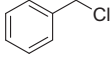
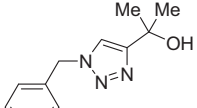
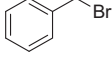
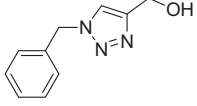
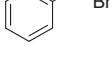
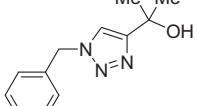
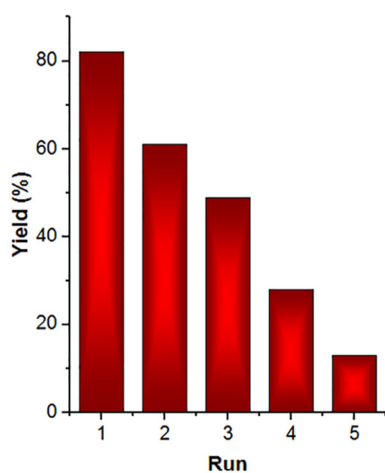


Fig. 5. TGA thermograms of POSS-ILs, Cu@POSS-ILs and Ag@POSS-ILs.

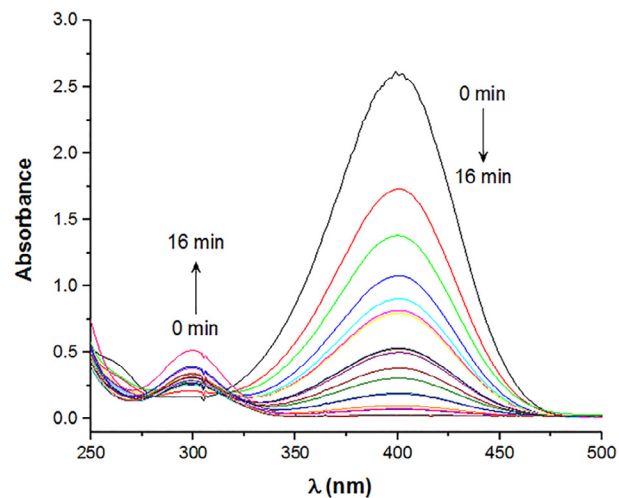
In the present work, the catalytic activity of Ag nanoparticles stabilized on the surface of POSS-ILs solid support, Ag@POSS-ILs, was evaluated in the reduction of 4-NP into 4-amino phenol (4-AP) using sodium borohydride (NaBH<sub>4</sub>) as a reducing agent in aqueous medium. Upon addition of Ag@POSS-ILs, the reaction color changed gradually from yellow to colorless in a period of 0–16 min, demonstrating the successful conversion of 4-NP to 4-AP. This conversion could be easily monitored by UV–Vis spectroscopy. As it could be seen from Fig. 7, the absorbance band at 400 nm relating to nitrophenolate anion remarkably decreased with time and new absorbance peak at 300 nm corresponding to

**Table 2**  
Click reaction of various starting materials in the presence of Cu@POSS-ILs hybrid catalyst.

Entry	Benzyl halide	Alkyne	Product	Yield (%)
1		Ph—C≡C—H		82
2		Ph—C≡C—H		75
3		Ph—C≡C—H		52
4		Ph—C≡C—H		69
5		Ph—C≡C—H		67
6		HO—C≡C—H		6
7		Me <sub>2</sub> C(OH)—C≡C—H		6
8		HO—C≡C—H		10
9		Me <sub>2</sub> C(OH)—C≡C—H		22



**Fig. 6.** Reusability of Cu@POSS-ILs hybrid catalyst in click reaction.



**Fig. 7.** Time-dependent UV-Vis spectral changes in 4-NP reduction by Ag@POSS-ILs.

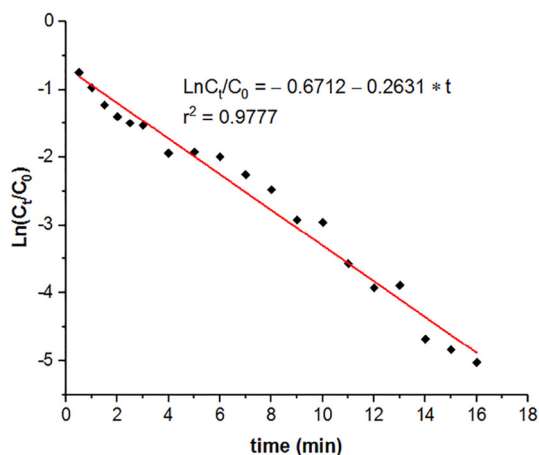


Fig. 8. Linear relationship of  $\ln(C_t/C_0)$  as a function of time.

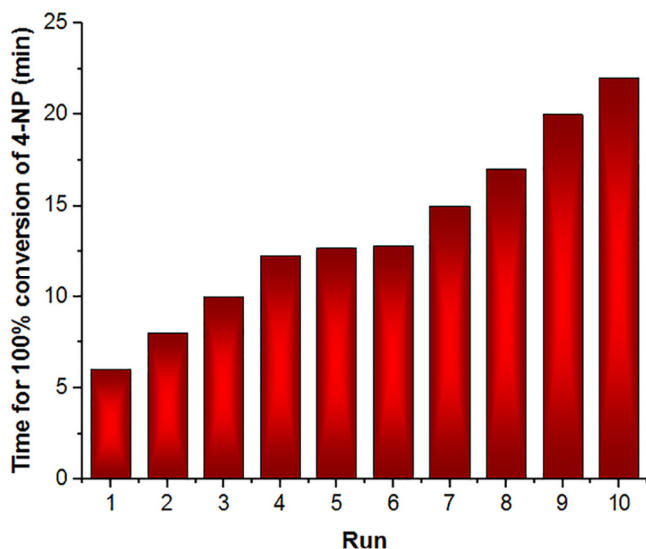


Fig. 9. Reusability of Ag@POSS-IL hybrid catalyst in 4-NP reduction.

4-AP gradually observed. In the absence of catalyst, the absorbance band kept unchanged and the reduction reaction would not carry out over the time.

The catalytic conversion of 4-NP into 4-AP could be expressed using the Eq. (1).

$$(4\text{-NP})\% = \frac{C_0 - C_t}{C_0} \times 100 \quad (1)$$

Whereby,  $C_t$  and  $C_0$  showed the concentration of 4-NP at time  $t$  and 0, respectively.

Moreover, a linear correlation between  $\ln(C_t/C_0)$  and the reaction time at room temperature was depicted in Fig. 8, suggesting that the reduction of 4-NP was expected to be a pseudo-first-order process. The kinetic rate constant ( $k$ ) of the reaction was possible to determine from Fig. 8 and Eq. (2),

$$\ln \frac{C_t}{C_0} = -Kt \quad (2)$$

For Ag@POSS-ILs hybrid catalyst, the kinetic rate constant ( $k$ ) was obtained about  $0.2631 \text{ s}^{-1}$  with the error of  $\pm 0.0096$ . The high catalytic performance could be attributed to the unique structure of as-prepared POSS-ILs solid support, which acted as a platform

for well-dispersion of fabricated Ag NPs with very small sizes. The reusability of the hybrid catalyst was also tested. In this regard, at the end of the reaction, the catalyst was washed repeatedly with ethanol and water in order to remove any reaction byproducts from the previous run. Then the washed catalyst was used in the reaction to confirm the stability of its catalytic activity. As it could be seen from Fig. 9, by increasing the number of reactions runs, the reaction time increased.

#### 4. Conclusion

New hybrid organic–inorganic materials of imidazolium ionic liquids-functionalized polyhedral oligomeric silsesquioxane (POSS) were successfully fabricated and considered as a solid support for in-situ immobilization of Cu and Ag metal nanoparticles (Cu@POSS-ILs and Ag@POSS-ILs). The combination of POSS and ionic liquid not only led to well-dispersion of metal nanoparticles but also facilitated the organic transformation. As-prepared hybrid materials, Cu@POSS-ILs and Ag@POSS-ILs, were used as efficient catalysts in click reaction and 4-NP reduction, respectively. Easy preparation, simple catalyst separation and reusability made the synthesized catalysts (Cu@POSS-ILs and Ag@POSS-ILs) promising catalytic hybrid catalysts for click reaction and 4-NP reduction.

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