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Modification of poly (ethylene glycol) with a multifunctional silane ligand, stabilization of Ag nanoparticles and its catalytic activity toward nitro-aromatics reduction

Soghra Fathalipour, Amin Zolali, Behzad Najafpour, Sima Pourbeyram, and Maryam Zirak

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ABSTRACT

The modification of poly (ethylene glycol) (PEG) with (3, 3'-bis-(3-triethoxysilylpropyl)-2, 2'-dithioxo [5, 5'] bithiazolidinylidene-4, 4'-dione) ligand was performed in the presence of Et₃N in toluene (MPEG). With the addition of AgNO₃, MPEG with obtained spherical nanoparticles on the surface could interact with Ag⁺ under ultrasonic. Finally, the MPEG-Ag⁺ complex were reduced with hydrazine under reflux to obtain MPEG-Ag nanocomposite. The structure of MPEG-Ag nanocomposite was characterized by different techniques. The nanocomposite was used as an efficient catalyst for the reduction of nitro-aromatic compounds using NaBH₄ in the water at room temperature. The catalyst was recovered, and applied for subsequent reactions without any substantial loss of efficiency for five runs.

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Introduction

In recent years, an ever-increasing interest has been shown in the synthesis of noble metal nanoparticles (NPs), especially Ag NPs, due to their distinctive properties and potential application in many areas.^[1–8] Ag NPs have a vigorous intensity for aggregation, so it is essential that the particle surface was modified.^[3] The synthesise of Ag NPs in the presence of plants and their extractions,^[6] carbon structures,^[9] polymers,^[10,11] and biomolecules^[12–14] lead to lower aggregation, more stability, and reactivity. Among polymers, PEG is widely used because it is a non-toxic and non-immunogenic polymer, produces biocompatible NPs and able to prevent the aggregation of NPs.^[10]

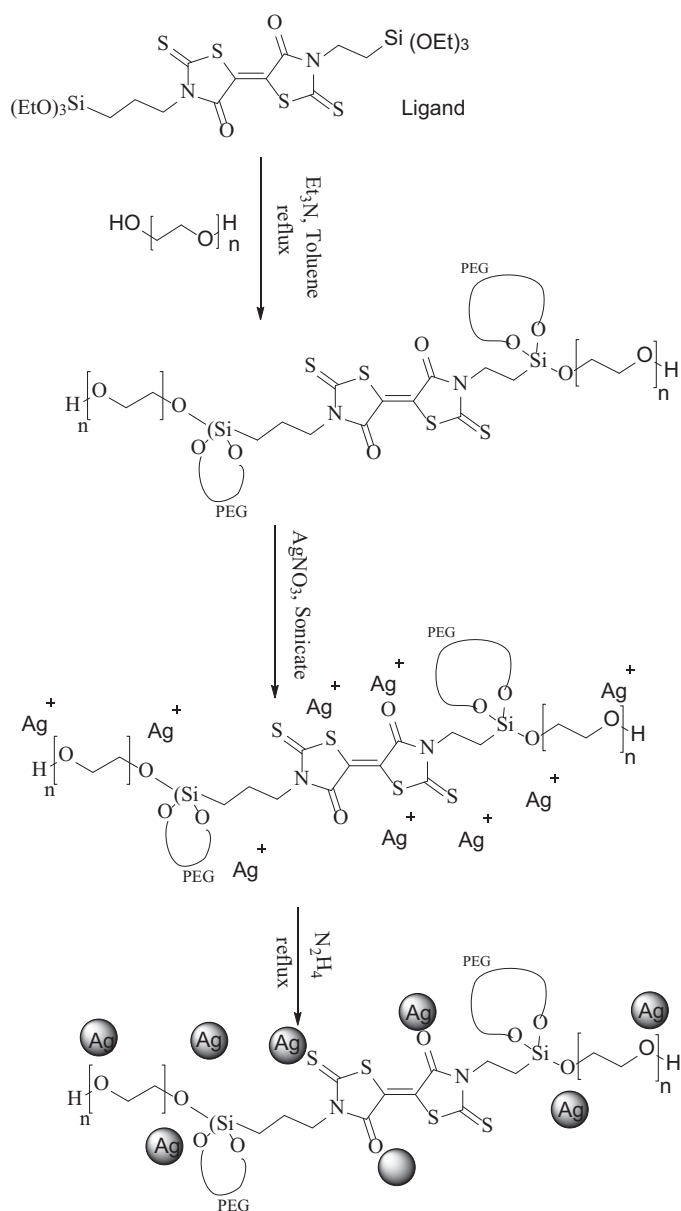
Also, PEG can enhance the stability of Ag NPs due to its high stability in organic solvents and water.^[10,15] The fabrication of Ag NPs in the presence of this polymer was reported by Luo et al.^[15] They displayed that PEG can act as a stabilizer and reducing agent, and the particle size is dependent on the concentration of the precursor and reaction temperature.^[15]

The surface properties of PEG can significantly affect the formation of metal nanoparticles, so the modification of PEG chains with different substrates can change its properties. The surface modification of PEG with chemical treatments such as silane coupling agents can improve the compatibility between the metal particles and polymer.^[16,17] The obtained nanoparticles on modified PEG (MPEG) displayed high dispersity in organic solvents and water media.

Nitro-aromatic compounds and their derivatives are by-products of reactions of pesticides and synthetic dyes.^[18,19] These compounds, especially 4-nitrophenol has a strong

corrosive effect on body tissue (nervous system, liver, and kidneys). So, the elimination of these compounds and converting them to amino compounds as useful intermediates in the manufacturing of dyes, pharmaceuticals, antioxidants, and a wide range of biologically active compounds is essential.^[20,21] Amino compounds were generally synthesized by catalytic hydrogenation that is a messy and environmentally hazardous method, and so using of cheap and safe will be needed. On the other hand, the reduction of nitro groups with Sodium borohydride (NaBH₄) in the absence of any catalyst is highly tedious, and therefore, the use of a suitable catalyst is essential. The reduction with NaBH₄ was used as a model reaction to study the catalyst behavior of metal nanoparticles.^[22] The use of different metal NPs such as Au,^[23] Ag,^[6,7] Pd,^[24] and Ni^[22] was reported for the reduction of 4-NP, but some of these methods have problems in terms of flexibility. This problem have been solved in silicate sol-gel matrix embedded Ag nanostructures.^[25] Therefore, in this work, Ag NPs on modified PEG with silane ligand could effect on catalytic behavior.

The objective of this study is the modification of PEG with a silane coupling ligand (3, 3'-bi's-(3-triethoxysilylpropyl)-2, 2'-dithioxo [5, 5'] bithiazolidinylidene-4, 4'-dione), and the investigation of its effect on its dispersity in organic solvents and stabilizing of Ag NPs. Previous researches have displayed that desired silane ligand can create monodispersed metal NPs with high density.^[26,27] With the coupling of PEG with synthesized silane ligand in the presence of Et₃N in toluene, spherical NPs with high dispersity were created on functional polymer (MPEG). Finally, Ag NPs were loaded on MPEG with the addition of AgNO₃ to MPEG under



Scheme 1. Schematic diagram of the preparation of the MPEG-Ag nanocomposite.

sonication and then the reduction of Ag^+ complex with hydrazine. Functional groups on MPEG stabilized Ag NPs and improved the dispersion stability of obtained nanocomposite in organic solvents (ethanol, toluene, chloroform, DMSO, and THF). The physicochemical properties of nanocomposite were studied with various characterization techniques. XRD and UV-Vis were used to see whether Ag well deposited on MPEG-Ag NPs. Furthermore, the catalytic activity of synthesized nanocomposite toward the reduction of nitro-aromatics was studied. The reduction of nitro compounds was easily monitored by UV-Vis spectroscopy.

Experimental

Materials and instruments

3-aminopropyl triethoxysilane (APTES), carbon disulfide (CS_2), triethylamine (TEA), silver nitrate (AgNO_3),

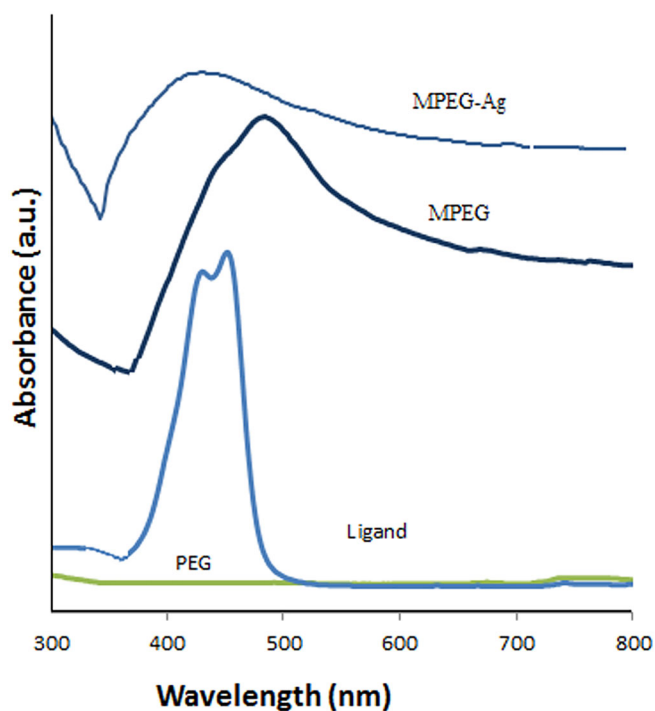


Figure 1. UV-Vis spectra of PEG, ligand, MPEG, MPEG-Ag nanocomposite.

polyethylene glycol (PEG; MW:1000 $\text{g}\cdot\text{mol}^{-1}$), hydrazine monohydrate, sodium borohydride (NaBH_4), 2-nitrophenol (2-NP), 4-nitrophenol (4-NP), 4-nitroaniline (4-NA) and toluene were purchased from Merck as reagent grade.

Instruments

The absorption spectra were studied on a UV-Vis spectrophotometer (PG T80) with a scan range of 200–800 nm. XRD pattern of compounds was examined by EQUINOX 3000 X-ray diffractometer with a Cu K_α radiation source ($\lambda = 1.5406 \text{ \AA}$). ^1H NMR was performed on a 400 MHz Bruker NMR spectrometer using CDCl_3 as the solvent. Fourier Transform Infrared (FT-IR) spectra were recorded using Shimadzu 8400 in the region of $4000\text{--}400 \text{ cm}^{-1}$ using dry KBr. Energy-dispersive X-ray spectroscopy (EDX) analyses were used to identify the chemical components of samples by an EDX detector on a scanning electronic microscope (SEM-TESCANMIRA3). The morphology and the particle size of Ag NPs were also detected with a transmission electron microscopy (TEM, Philips CM30) at an acceleration voltage of 100 kV.

Synthesis of MPEG-Ag nanocomposite

Modification of PEG with silane ligand (MPEG)

Silane ligand was prepared by the reported procedure^[26] and then was reacted with PEG according to the following method to obtain modified PEG (MPEG).

Silane ligand (0.5 g) was added to a solution of PEG (in toluene (2% W/V) in the presence of Et_3N (0.2 mL) and

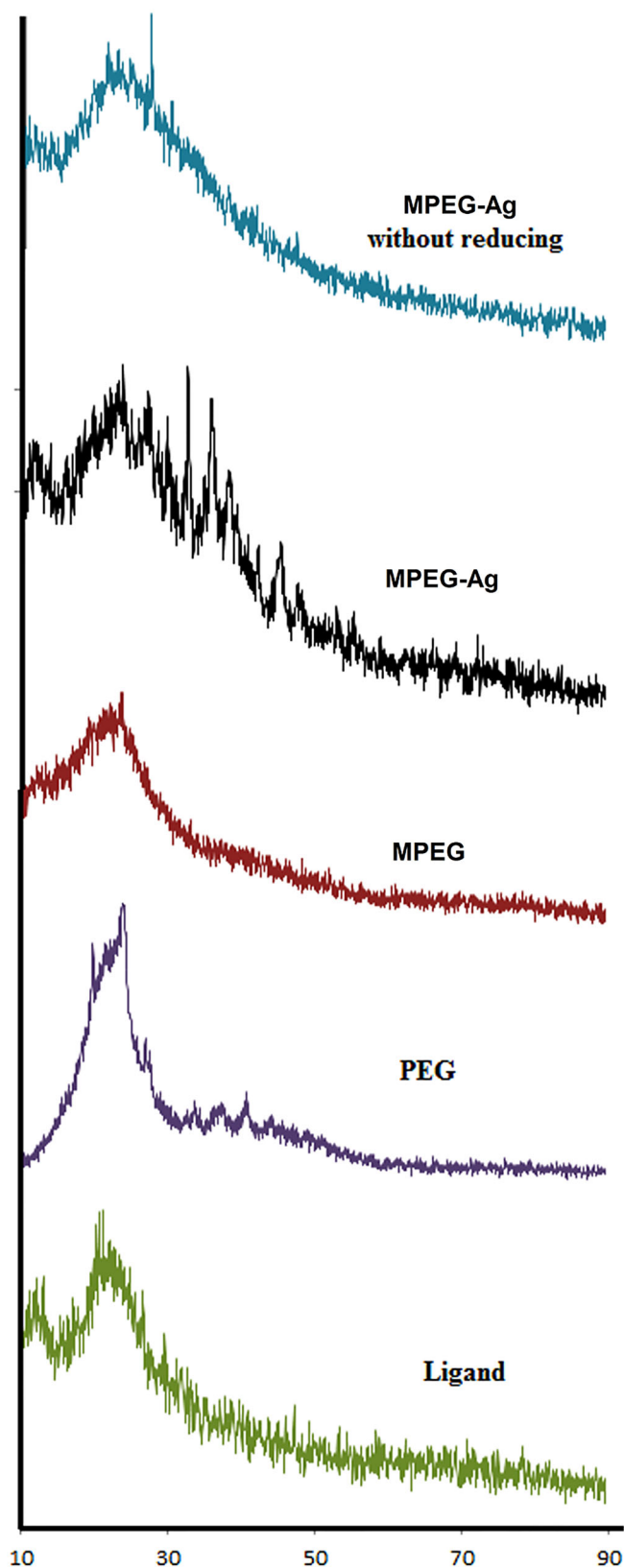


Figure 2. XRD patterns of Ligand, PEG, MPEG, MPEG-Ag nanocomposite and MPEG-Ag without reducing.

heated under reflux for 18 h. Then the obtained mixture was filtered and washed with DI water, ethanol, and acetone subsequently, and then was dried under vacuum.

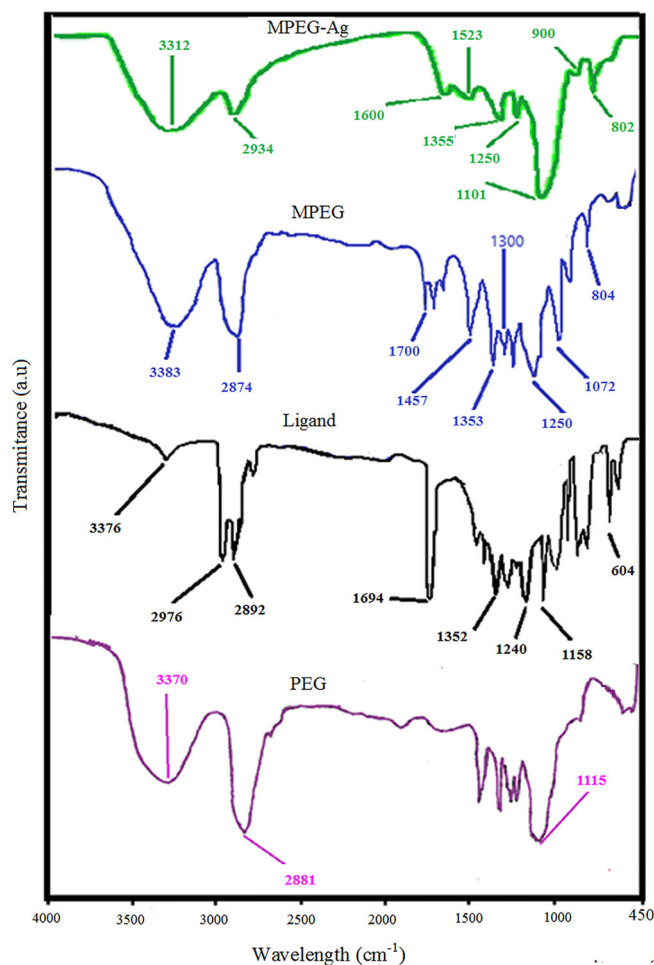


Figure 3. FT-IR of PEG, ligand, MPEG, MPEG, MPEG-Ag nanocomposite.

Synthesis of MPEG-Ag nanocomposite

MPEG-Ag nanocomposite was synthesized by adding the aqueous solution of AgNO_3 (10 mL, 0.001 mM) to the mixture of MPEG (0.025 g) in ethanol (50 mL) under sonication at room temperature for one h, followed by reduction using hydrazine monohydrate (0.01 mL) at reflux for two h. After the filtration, the resultant precipitate was washed with water and ethanol and then dried under vacuum. For comparison, the reaction was carried out in the presence of the mixture of NBH_4 -sodium citrate and the absence of any reducing agent.

The catalytic activity of MPEG-Ag nanocomposite

MPEG-Ag nanocomposite (0.018 g) was added to a mixture of an aqueous solution of nitro- aromatic (1 mL of 0.5 mM) and 1 ml of the freshly prepared aqueous solution of NaBH_4 (80 mM) and then stirred at room temperature for 50 min. Reaction progress was monitored using UV-Vis absorption spectra. After complete reaction, the nanocatalyst was separated from the mixture by centrifugation and then washed with water and ethanol and dried at room temperature for the next cycle to study the reusability of catalyst.

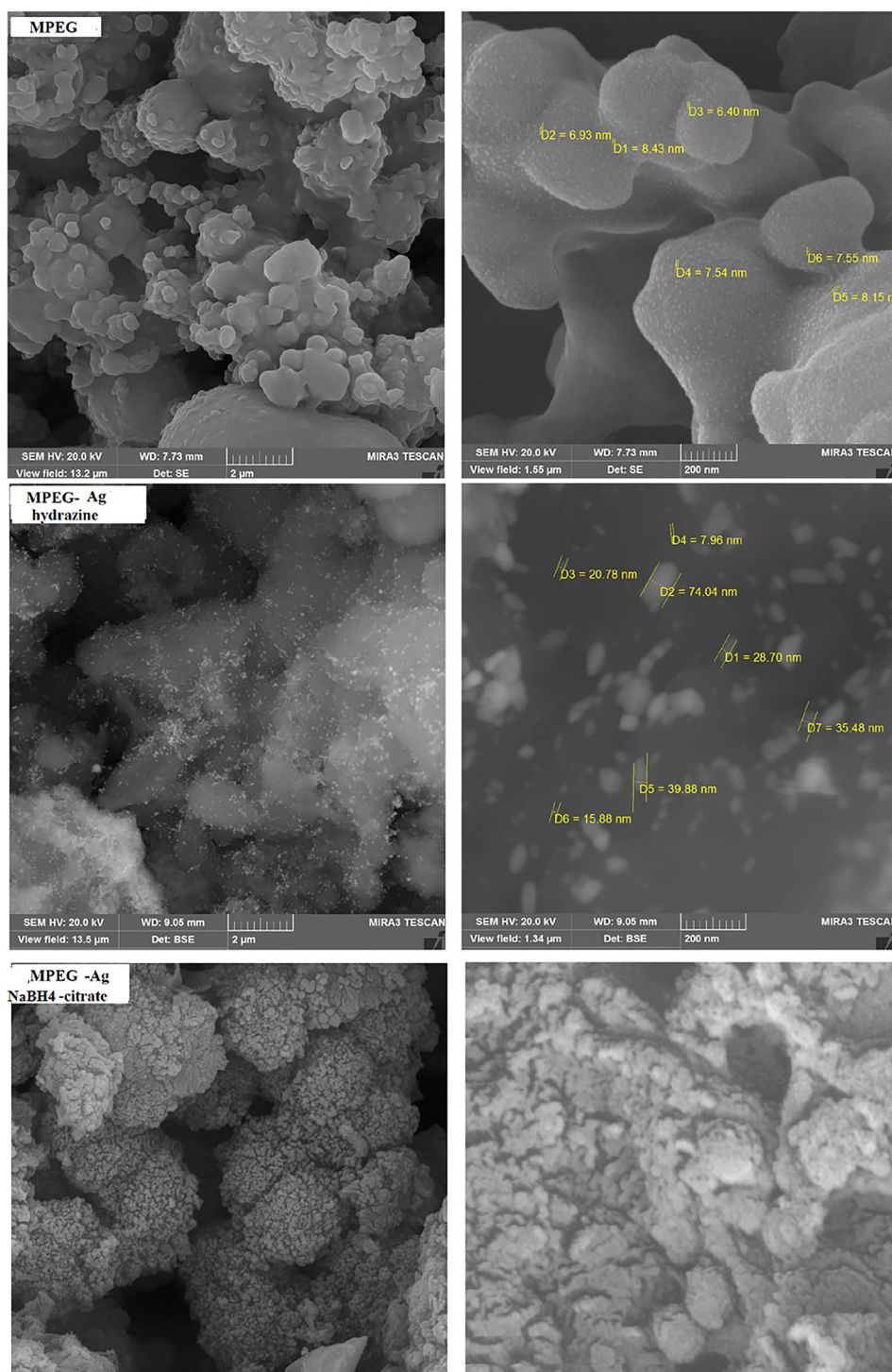


Figure 4. SEM images of MPEG, MPEG-Ag nanocomposite (hydrazine reducing) and MPEG-Ag nanocomposite (NaBH₄ - citrate reducing).

Results and discussion

Modification of PEG with a silane coupling ligand (3, 3'-Bis-(3-triethoxysilylpropyl)-2, 2'-dithio [5, 5'] bithiazolidinylidene-4, 4'-dione) was performed under basic conditions and spherical nanoparticles created on modified PEG. These nanoparticles were formed by the attaching of OH groups of polymer to triethoxysilane groups of the ligand. The nanocomposite was produced by mixing of MPEG and AgNO₃ followed by reduction of Ag⁺ ions using hydrazine. MPEG

having C=S, C=O, and OH groups and spherical NPs could stabilize Ag⁺ ions. The details of the reaction were outlined in Scheme 1.

Figure 1 shows the UV-Vis spectra of ligand, PEG, MPEG, and MPEG-Ag nanocomposite in absolute ethanol. UV-Vis spectra of PEG showed no peak. In UV-Vis of ligand, two electronic bands were appeared at around 436 and 456 nm that could be attributed to the n/π^* transitions of C=S and C=O groups of the ligand.^[28] With the modification of PEG chains with ligand, characteristic peaks of the

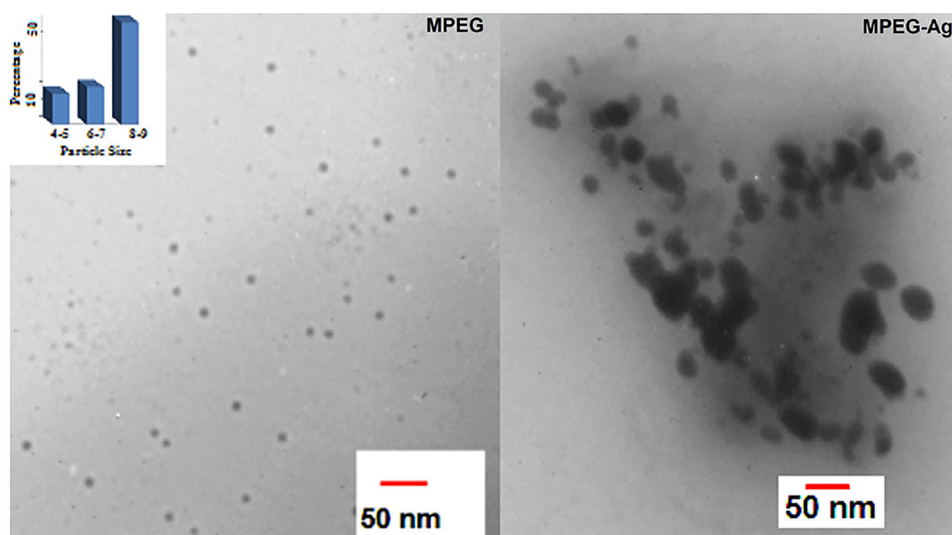


Figure 5. TEM images of MPEG and MPEG-Ag nanocomposite. Size distribution of MPEG (inset).

Table 1. Optimization of the catalyst amount.

Entry	Catalyst	Catalyst amount (g)	Solvent	Temp. (°C)	Time (min)	Yield (%)
1	MPEG-Ag	0.009	H ₂ O	25	60	90
2	MPEG-Ag	0.018	H ₂ O	25	50	95
3	MPEG-Ag	0.036	H ₂ O	25	50	90
4	MPEG-Ag	0.054	H ₂ O	25	45	90

ligand were boarded and shifted to high wavelength due to the presence of PEG chains and obtained interactions. In the UV-Vis spectra of the nanocomposite, the position of peak shifted to the low wavelength (470 nm) due to the surface Plasmon resonance of Ag NPs.

Figure 2 illustrates the XRD results of pure ligand, PEG, MPEG, and MPEG-Ag nanocomposite in the 2θ range 10–80°. In XRD pattern of PEG were appeared reflections at around 2θ : 14, 19, 23, and 27^[29] which with the modification, its lattice structure changed and appeared only a broad peak at around 2θ :24 assigned to the presence of attached silane ligand functional groups. For comparison, the XRD pattern of ligand was appeared in Figure 2, which showed two reflections at around 2θ :11, and 25 due to the lattice structure of ligand.^[28] The formation of Ag NPs on the surface of MPEG was confirmed with the XRD analysis. The four diffraction peaks at 2θ : 38, 44, 55, and 66 correspond to 111, 200, 220, and 311 of faced centered cubic (fcc) Ag planes.^[26] Luo and coworkers used PEG for reducing Ag⁺ at 80 °C,^[15] while in this work, MPEG couldn't reduce Ag⁺ ions to silver nanoparticles at the same condition. This result could approve the elimination of reducing groups (OH) of PEG and its modification with ligand. This result was confirmed with the XRD data (Figure 2).

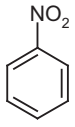
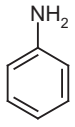
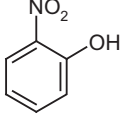
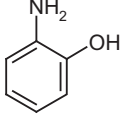
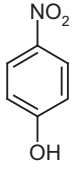
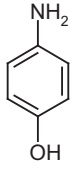
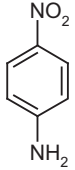
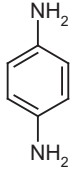
The FT-IR spectra were studied to prove the covalent grafting PEG to the ligand and the changing of the nanocomposite (Figure 3).

In the FT-IR spectra of PEG, centered absorption bands at around 3370 cm⁻¹, 2881 cm⁻¹, and 1115 cm⁻¹ are attributed to the stretching vibrations of –OH, –CH₂ and C–O–C groups, respectively.^[30] The FT-IR spectra of the ligand showed characteristic absorption peaks at around 1694,

1352, 1241, 1158, and 604 cm⁻¹ attributed to the stretching vibrations of C=O, C=S, C–N, C–S, and Si–O–C groups, respectively.^[26] Compared with the ligand, MPEG presented absorption bands of the ligand with shifts in positions of peaks attributed to the presence of polymer chains and their interactions. Furthermore, the presence of a new peak at around 1072 assigned to Si–O–Si confirmed the covalent modification of PEG with silane ligand. In the FT-IR spectra of MPEG-Ag, the intensity of C=O groups and oxygen functional groups decreased due to the interaction with Ag NPs.

Scanning electron equipped with an EDX detector was used to determine the shape, size, and qualitative composition of the resultant nanoparticles in samples. The FESEM images of MPEG and MPEG-Ag nanocomposite are shown in Figure 4. SEM images of MPEG showed attached together microspheres, with high-density monodispersed nanospheres (6–9 nm). Meanwhile, FESEM-EDX was used to determine a suitable reducing agent. The reducing agents such as the mixture of sodium citrate-NaBH₄ and hydrazine were used in the reduction of AgNO₃ on MPEG. The SEM images of the resultant composites are shown in Figure 4. The SEM images demonstrated that in the presence of hydrazine, nanoparticles with small size were obtained, while, with NaBH₄ solution, fused particles were obtained. So, based on the SEM images, hydrazine was chosen as a suitable reducing agent. To demonstrate the composition of the nanocomposite, the EDX analysis was used. The presence of Si and Ag in resultant nanocomposite was proved in the EDX curve (inset Figure 4). On the other hand, a high density of Ag in obtaining composite by hydrazine compared to the NaBH₄, confirmed a suitable reducing agent.

Table 2. MPEG-Ag nanocomposite catalyzed reduction of nitro compound to amino product^a.

Entry	Substrate	Production	Time (min)	Yield (%)
1			30	95
2			45	95
3			50	95
4			80	90

^aReaction conditions: 1 ml of nitro-aromatic (5×10^{-1} mM), 18 mg catalyst, 5 mM of NaBH₄ (1 ml), water, room temperature.

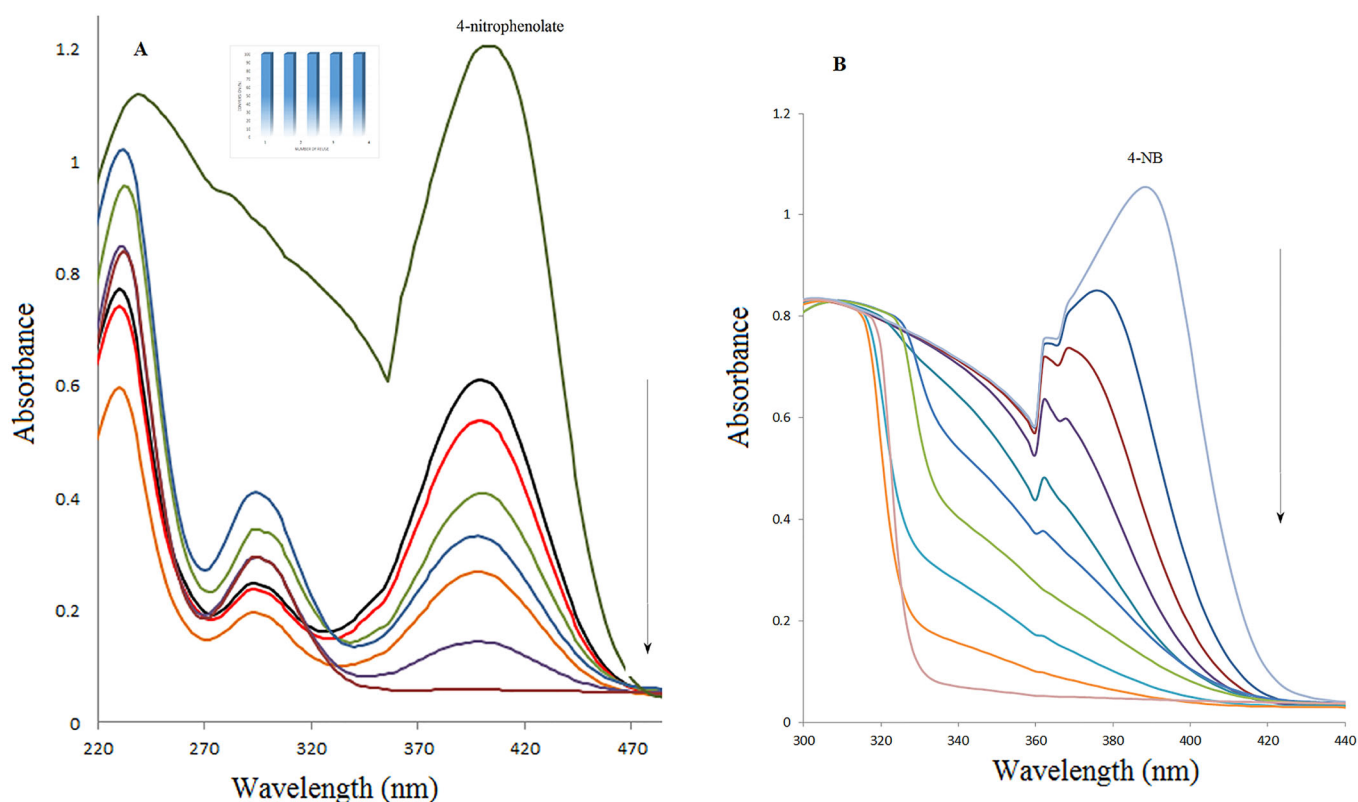


Figure 6. UV-Vis spectra for A: 4-NP and successive reduction of 4-NP catalyzed by MPEG-Ag nanocomposite. Reusability of MPEG-Ag nanocomposite toward 4-NP reduction (inset), and B: successive reduction of 4-NB catalyzed by MPEG-Ag nanocomposite.

Figure 5 shows the TEM images of MPEG and MPEG-Ag nanocomposite. The TEM images of MPEG demonstrated that monodispersed NPs were separated widely on the

surface of modified polymer. The inset of Figure 5, displays the average particle size of nanoparticles attached to the surface of MPEG. The particle size histogram, showed a

Table 3. Comparison of the catalytic activity of MPEG-Ag nanocomposite with other catalysts^a.

Entry	Catalyst system	Conditions	Ref
1	Ag NPs graphite grafted with hyperbranched poly(amidoamine) dendrimer	2/5 mg catalyst, 5mM of NaBH ₄ (1ml), water, rt, 25 min	[5]
2	Synthesized Ag-Polyaniline Using Ionizing Radiation	20 mg catalyst, 5mM NaBH ₄ (1ml), 3 min	[31]
3	Ag/Al ₂ O ₃ Nanocatalyst	5/8 mg catalyst, 5mM of NaBH ₄ (1ml), water, rt, 22 min	[5]
4	Core-shell Ag@Ni magnetic nanocatalyst	75 mg catalyst, isopropylalcohol, 12 min	[4]
5	MPEG-Ag nanocomposite	18 mg catalyst, 5mM of NaBH ₄ (1ml), water, rt, 50 min	[This work]

^aReaction conditions: 1 ml of 4-nitrophenol (5×10^{-1} mM),

narrower range of particle sizes from 4-9 nm with a maximum close to 8 nm. The TEM image of MPEG-Ag nanocomposite displayed Ag NPs with a particle size of around 25 nm on MPEG. The absence of small NPs of MPEG in composite could be attributed to the coverage of these nanoparticles by Ag NPs due to the high interaction between these nanoparticles.

The reduction of 4-nitrophenol carried out in water solvent at room temperature (25 °C) as a model reaction to study the catalytic activity of MPEG-Ag nanocomposite using NaBH₄-catalyst with different amounts (0.009, 0.018, 0.036 and 0.054 g) was added to the reaction mixture (Table 1). 0.018 g was selected as the best result. To monitor the reduction process of nitro-compounds, UV-Vis absorption spectra were recorded with time. In the absence of MPEG-Ag nanocomposite, the corresponding product was not obtained. The reaction was carried out in the water media as a safe and green solvent and other solvents were not tested. With optimized amounts, MPEG-Ag nanocomposite catalyzed the reduction of the various nitro-aromatic compounds in water at 25 °C, and desired amino derivatives were obtained in high yields (Table 2). The yield of reaction was calculated from UV-Vis curves using the following equation:

$$\% = \frac{A_0 - A}{A_0} \times 100$$

where A_0 and A are the absorbance value of the initial concentration and absorbance value after the complete reduction.

The reduction process of 4-NP was investigated by UV-Vis spectroscopy. As shown in Figure 6, before the addition of NaBH₄, the absorption spectrum was observed at 320 nm due to the characteristic peak of NP. After the addition of NaBH₄, the absorption peak shifted to 400 nm, which corresponds to the generation of 4-nitrophenolate ions. In the absence of a catalyst, this peak remained unchanged until 24 h. With the addition of MPEG-Ag catalyst to the reaction mixture, yellow color of the mixture changed to the colorless, the peak height at 400 nm decreased, and a new peak was appeared around 300 nm (Figure 6A). These changes attribute to the reduction of 4-nitrophenol to 4-aminophenol.^[6] The reduction process of 4-NB in the presence of MPEG-Ag catalyst was also shown in Figure 6B. The reduction process of 4-NB was completed after 30 min that it is lower than the reduction time of 4-NP which, this could be related to the presence of hydroxyl groups in 4-NP.

In the proposed reaction mechanism, MPEG-Ag nanocomposite plays a significant role in the transfer of electrons from reducing ions to the nitro groups. The surface of nanocomposite provides adsorption sites for nitro aromatic

compound and BH₄⁻. The catalytic behavior of the synthesized MPEG-Ag nanocomposite was compared with some of the reported catalytic systems (Table 3).

The reusability of the MPEG-Ag nanocomposite for catalytic reduction of 4-NP in the presence of NaBH₄ was displayed in the inset of Figure 6A. It was noticed that the catalytic activity of the nanocomposite has no indicative decrease after five consecutive cycles.

Conclusion

In summary, the loading of Ag NPs on modified PEG with a silane ligand (3, 3'-bis-(3-triethoxysilylpropyl)-2, 2'-dithio [5, 5'] bithiazolidinylidene-4, 4'-dione) was carried out in the presence of Et₃N. First, PEG was modified with the silane ligand in the presence of Et₃N in toluene, and then the MPEG containing spherical nanoparticles was used as a substrate for the synthesizing of Ag NPs. The structure of MPEG-Ag nanocomposite was confirmed by UV-Vis, XRD, FT-IR, SEM, EDX, and TEM analysis. Obtained MPEG-Ag nanocomposite was used as the catalyst for the reduction of the nitro-aromatic compounds in water at 25 °C for 50 min, and corresponding amino compounds were produced in high yield. Also, recoverability of the catalyst was investigated, and show excellent stability and reactivity for five times without any change in catalytic activity. Further studies on the loaded of other Nobel nanoparticles on our modified PEG and electrocatalysis behavior are underway.

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