

Gold nanoparticles Wells–Dawson heteropolyacid nanocomposite film as an effective nanocatalyst in photocatalytic removal of azo dyes from wastewaters

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Abstract A novel nanophotochromic film consisting of Au nanoparticles and Wells–Dawson-type heteropolyacid, $[\text{H}_6\text{P}_2\text{W}_{18}\text{O}_{62}]$, was prepared by combination of sol–gel and photoreduction method. This film was characterized by UV–visible spectroscopy, particle size distribution, Field emission scanning electron microscopy, and energy dispersive spectroscopy analysis. For the preparation of Au nanoparticles, heteropolyacid, $[\text{H}_6\text{P}_2\text{W}_{18}\text{O}_{62}]$ was used in form of composite film as a green reductant and stabilizer. Au nanoparticles with particle size in the range of 10–20 nm were synthesized and monodispersed in the nanocomposite using dip coating method. The photocatalytic activity of this composite film was studied in the decolorization of methyl orange (MeO) and methyl red (MR) as carcinogenic pollutant dyes using UV irradiation. The pseudo-first order rate constants was established and calculated for these reactions. Comparison of this composite film with the prepared composite by Preyssler heteropolyacid disclosed that the structure of heteropolyacid can affect loading amount of Au nanoparticles.

Keywords Decolorization · Gold nanoparticles · Heteropolyacid · Nanocomposite · Wells–Dawson

Introduction

Au nanoparticles have attracted much attention nowadays mainly due to their exceptional physical and chemical properties. Thus, much effort has been made into their synthesis and characterization [1]. Polyoxometalates (POMs) have been extensively used in the preparation of Au nanoparticles reported in various reports [2–5]. The chemistry of POMs and their salts has been extensively reviewed [6, 7]. They have been defined as a sub-class of inorganic metal oxide clusters, which possess fascinating structures and various properties [8]. Interestingly, when they are submitted to stepwise and multi-electron redox reactions, their structures remain intact. In addition, in their presence it is possible to reduce a compound, electrochemically or photochemically using a suitable reducing agent [9, 10]. Mandal et al. [2] performed a simple process and successfully observed that several metal nanoparticles were formed in the presences of photochemically reduced Keggin heteropolyanions as photocatalysts. Mandal and co-workers demonstrated that the reduction of Ag^+ on the surface of gold nanoparticles can be facilitated in the presence of photochemically generated $[\text{PW}_{12}\text{O}_{40}]^{4-}$ under UV irradiation. In addition, Au nanoparticles were readily prepared via a simple photoreduction mediated by transition metal monosubstituted Keggin heteropolyanions [5]. Although Keggin and its derivatives have been used in the synthesis of Au nanoparticles, the role of Wells–Dawson heteropolyacids (HPAs) has been largely disregarded. A heteropolyacid is a class

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of acid made up of a particular combination of hydrogen and oxygen with certain metals and non-metals. This type of acid is a common re-usable acid catalyst in chemical reactions [5]. Wells–Dawson-type heteropolyacid [H₆P₂W₁₈O₆₂] is remarkable due to its high acidity and outstanding stability both in solution and in the solid state [11]. Literature survey revealed that in spite of these interesting properties the synthesis of nanoparticles using this heteropolyacid in nanocomposite films has been unstudied. We are interested in the chemistry of HPAs [12]. Armed with these experiences and due to the recent interest in the synthesis of nanoparticles in solid matrices [13], we were encouraged to study the preparation of Au nanoparticles incorporated in Wells–Dawson heteropolyacid nanocomposite film. Recently, we have introduced the Preyssler-type heteropolyacid (H₁₄[NaP₅W₃₀O₁₁₀]), as an unique reducing agent and stabilizer for the synthesis of Au nanoparticles in an organic–inorganic nanocomposite film under UV irradiation [13]. To extend our research to other HPAs, we investigated the capability of Wells–Dawson heteropolyacid in the preparation of Au nanoparticles in an organic–inorganic nanocomposite film.

Experimental

Chemicals and instruments

For the synthesis of Dawson acid, at first potassium salt was synthesized and then Wells–Dawson acid, [H₆P₂W₁₈O₆₂], was prepared by passage of potassium salt solution in water through a column of Dowex resin (H⁺ form). The elute was evaporated to dryness under reduced pressure [14].

All chemicals were obtained from commercial sources and used as received. Spin Coater, (S.C.S.86, Japan), Field Emission Scanning Electron Microscope (FESEM) (VEGA\TESCAN-XMU, Czech Republic), Energy Dispersive Spectrometry (EDS) (Mira 3-XMU, Czech Republic), and UV–visible spectrophotometer, (Optizen UV3220, Germany) were used for characterization of samples. The average particle size of Au nanoparticles in the film was measured by SPSS software using Image J program.

Preparation of nanocomposite

Polyvinylalcohol (PVA) 30 wt% was dissolved in deionized water and stirred in an oil bath for 10 min. Then

tetraethylorthosilicate 20 wt% and Wells–Dawson acid solutions were added. This mixture was refluxed at 353 K for 6 h and a clear viscous gel is formed. At the next stage, 250 μL of the obtained transparent gel was used to make films by spin coating method (500 rpm/min) and after reducing, it was dipped in different times including 5, 10, and 30 min into HAuCl₄ solution (25 mL, 3 mM) [13].

Photodegradation experiments

The photo reactor was designed in our laboratory. In a typical reaction, a 250-mL Pyrex glass was equipped with a magnetic stirrer, azo dye solution, and nanocomposite film. The mixture was stirred and purged with nitrogen for 1 h, and then it was irradiated under the high-pressure mercury lamp (Philips, 125 W, wavelength 254 nm) as UV light source. The temperature in the glass reactor was set to 25 ± 2 °C by the circulating water. The experimental procedure is described as follows: a series of 10 mL solutions containing 30 mg L⁻¹ of azo dye solution were prepared and then sample was placed under light irradiation in the presence of nanocomposite film. The progress of reaction was investigated using a UV–visible spectrophotometer.

Results and discussion

Heteropolyacids are well-established as powerful oxidants for the oxidation of a wide range of organic compounds. In this process, the excitation of the O → M charge transfer can occur under UV irradiation [10, 15, 16]. Interestingly, the reduced form of heteropolyacid can act as a strong reducing reagent which can be readily re-oxidized by various chemicals especially as metal ions [3, 15].

In this research, Wells–Dawson acid was used in synthesis of Au nanoparticles through a simple sol–gel and photoreduction process. In this process, Wells–Dawson acid played a dual role (a) photocatalytic reducing agent and (b) stabilizer [13].

The photoreduction of nanocomposite film was confirmed by UV–visible spectroscopy (Fig. 1). The formation of reduced Wells–Dawson in the composite film was confirmed by observation of deep blue color (Fig. 1). In UV–visible spectra (Fig. 1), the reduced Wells–Dawson acid showed absorption peaks at about 300 and 690 nm, which the observed peak in 690 nm is related to the formation of single electron-reduced Wells–Dawson ion. This figure also shows that there is an increase in the intensity up to 60 min, but after that, there is no change. This is a proof that all the Wells–

Fig. 1 UV–Visible spectra of composite film under irradiation at various time intervals: 0 min (a), 10 min (b), 20 min (c), 30 min (d), 40 min (e), 50 min (f), 60 min (g)

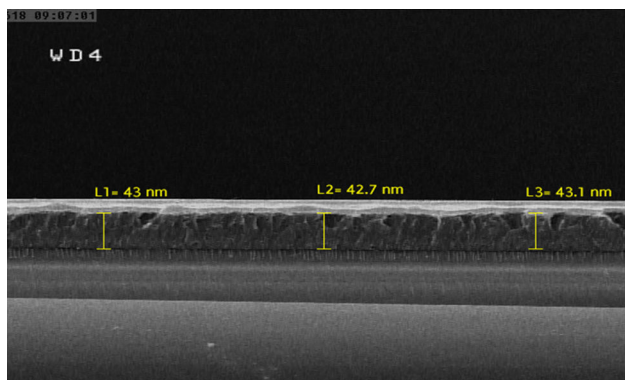
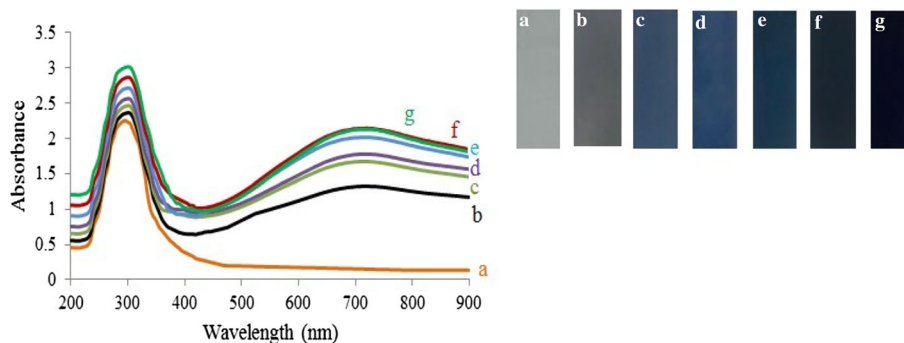


Fig. 2 Thickness of the synthesized nanocomposite film (FESEM image)

Dawson ions in the composite have been reduced. The reduced film was used as reducing medium and host for the formation of Au nanoparticles [17].

With dipping of the reduced nanocomposite film with thickness 43 nm (Fig. 2) into HAuCl_4 solution, a band at 530 nm was appeared which confirms the formation of Au nanoparticles in the composite film (Fig. 3). The formation of Au nanoparticles was further approved by changing the blue film to pink and violet color, respectively.

Fig. 3 UV–Visible spectra of Au-embedded composite film at different dipping time intervals: 0 min (a), 5 min (b), 10 min (c), 20 min (d), 30 min (e)

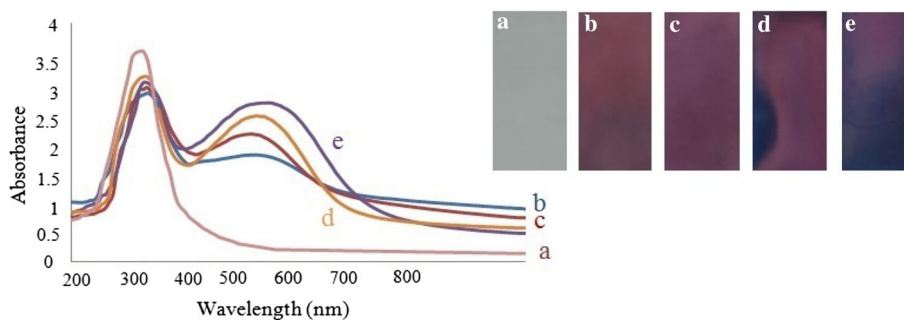


Figure 4 shows the FESEM images of reduced composite film contacted with HAuCl_4 solution at different times. This figure shows when the time of dipping is increased from 5 to 30 min, the average particle size is also increased. The average size of nanoparticles is 10.54, 16.57, and 19.61 in Fig. 3a, b, d, respectively.

The EDS analysis is shown in Fig. 5. It shows the elemental composition of Au nanoparticles and Wells–Dawson in the generated nanofilms. The elemental constitution to control the loading amount of Au nanoparticles confirmed 9.91% w/w in the nanocomposite film. The quantitative results are shown in Tables 1 and 2.

Interestingly, comparison our results with the obtained results in preparation of Au nanoparticles using Preyssler HPA [13], $\text{H}_{14}[\text{NaP}_5\text{W}_{30}\text{O}_{110}]$, showed a higher loading of gold nanoparticles (22%) under similar reaction conditions. Thus, the structure of heteropolyacid can affect the loading amount in this process. The difference can be attributed to the difference between oval and spherical structure of Preyssler and Dawson, respectively [18]. It is suggested that the larger number of H^+ and W atoms in Preyssler may lower the activation barrier, and provides many “sites” on the oval-shaped structure. They are likely to render the loading effectiveness.

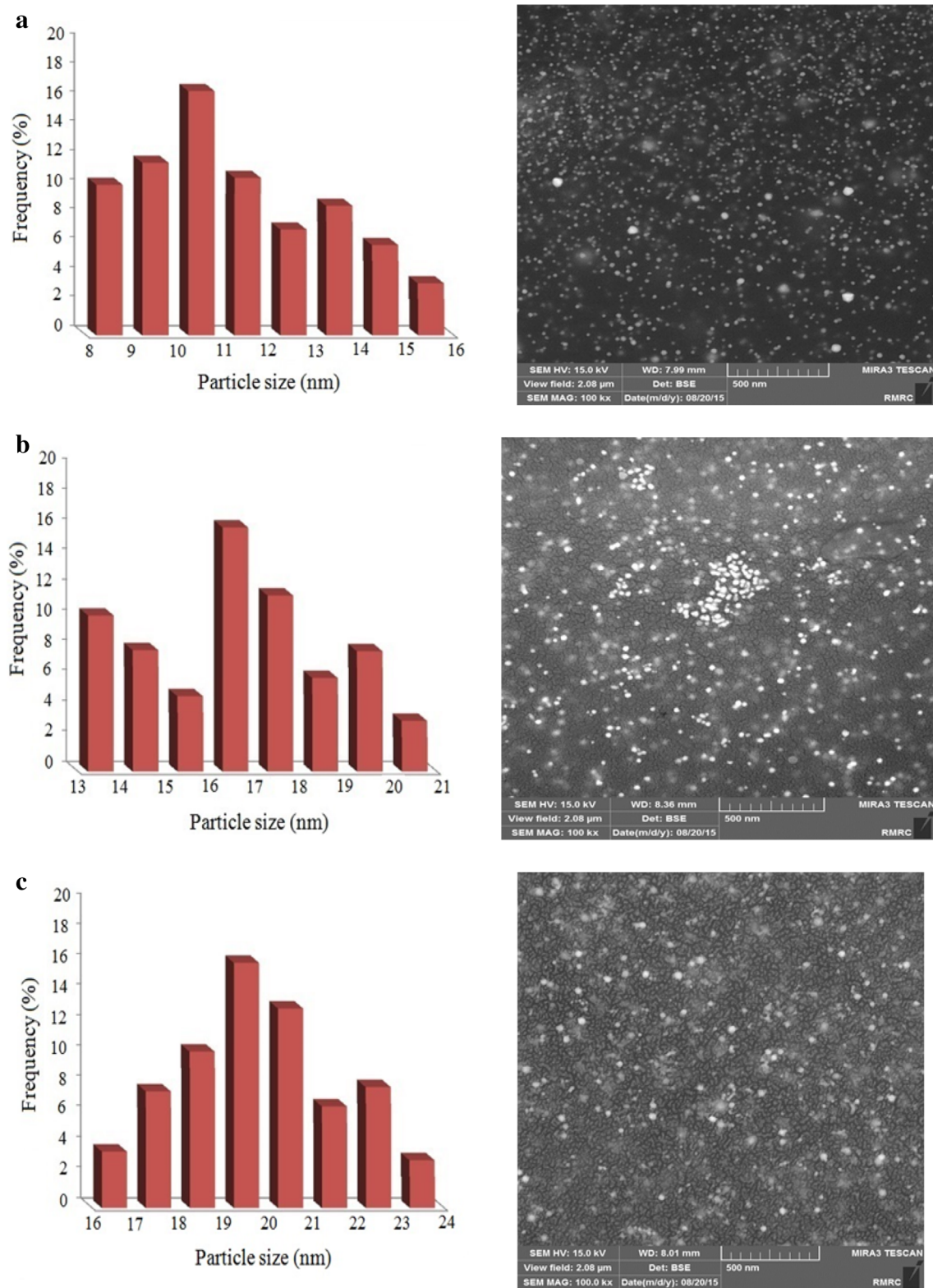


Fig. 4 FESEM images of synthesized gold nanoparticles at different dipping time intervals in 3 mM of HAuCl_4 : 5 min (a), 10 min (b), 30 min (c)



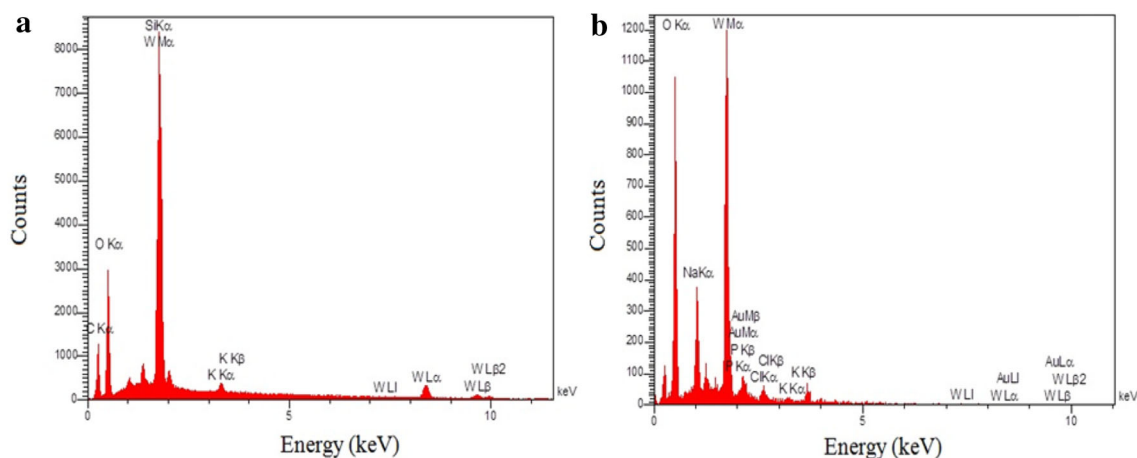


Fig. 5 EDS spectrum of nanocomposite film: before (a), after (b) dipping in HAuCl₄ solution

Table 1 Atomic percentage for Fig. 5a

Elt	Line	Int	Error	K	Kr	W%	A%	ZAF	Formula	Ox%	Pk/Bg
<i>Nanocomposite film</i>											
C	Ka	105.2	41.5241	0.1744	0.0851	23.44	45.82	0.3629		0.00	48.85
O	Ka	263.0	13.8659	0.2172	0.1060	32.84	48.20	0.3227		0.00	56.63
Si	Ka	0.0	0.0000	0.0000	0.0000	0.00	0.00	0.8872		0.00	24.35
K	Ka	27.6	1.0019	0.0144	0.0070	0.83	0.50	0.8443		0.00	3.10
W	La	51.0	0.6128	0.5940	0.2898	42.89	5.48	0.6757		0.00	6.40
				1.0000	0.4879	100.00	100.00			0.00	

Table 2 Atomic percentage for Fig. 5b

Elt	Line	Int	Error	K	Kr	W%	A%	ZAF	Formula	Ox%	Pk/Bg
<i>Nanocomposite film + Au nanoparticles</i>											
O	Ka	162.7	53.9753	0.7160	0.4303	68.07	83.52	0.6320		0.00	275.91
Na	Ka	71.7	13.1083	0.1206	0.0725	15.88	13.56	0.4563		0.00	22.23
P	Ka	2.3	3.1933	0.0042	0.0025	0.32	0.20	0.7737		0.00	3.83
Cl	Ka	11.1	3.1933	0.0255	0.0153	1.91	1.06	0.8019		0.00	4.85
K	Ka	3.3	5.1739	0.0092	0.0055	0.65	0.33	0.8481		0.00	2.97
W	La	0.5	0.7890	0.0324	0.0195	3.26	0.35	0.5983		0.00	2.85
Au	La	0.5	0.7890	0.0922	0.0554	9.91	0.99	0.5591		0.00	4.06
				1.0000	0.6010	100.00	100.00			0.00	

The catalytic activity of the synthesized nanocomposite film was studied in the decolorization of MeO and MR azo dyes. The results are reported in Figs. 6 and 7, and a comparison is reported in Table 3. A significant decrease in the absorbance bands can be observed with a

decolorization degree of 96 and 87.2% after 36 and 43 min for MeO and MR, respectively.

The following equation was used to calculate the degree of azo dye decolorization [19–21]:

$$C = (C_0 - C_e) / C_0 \times 100.$$

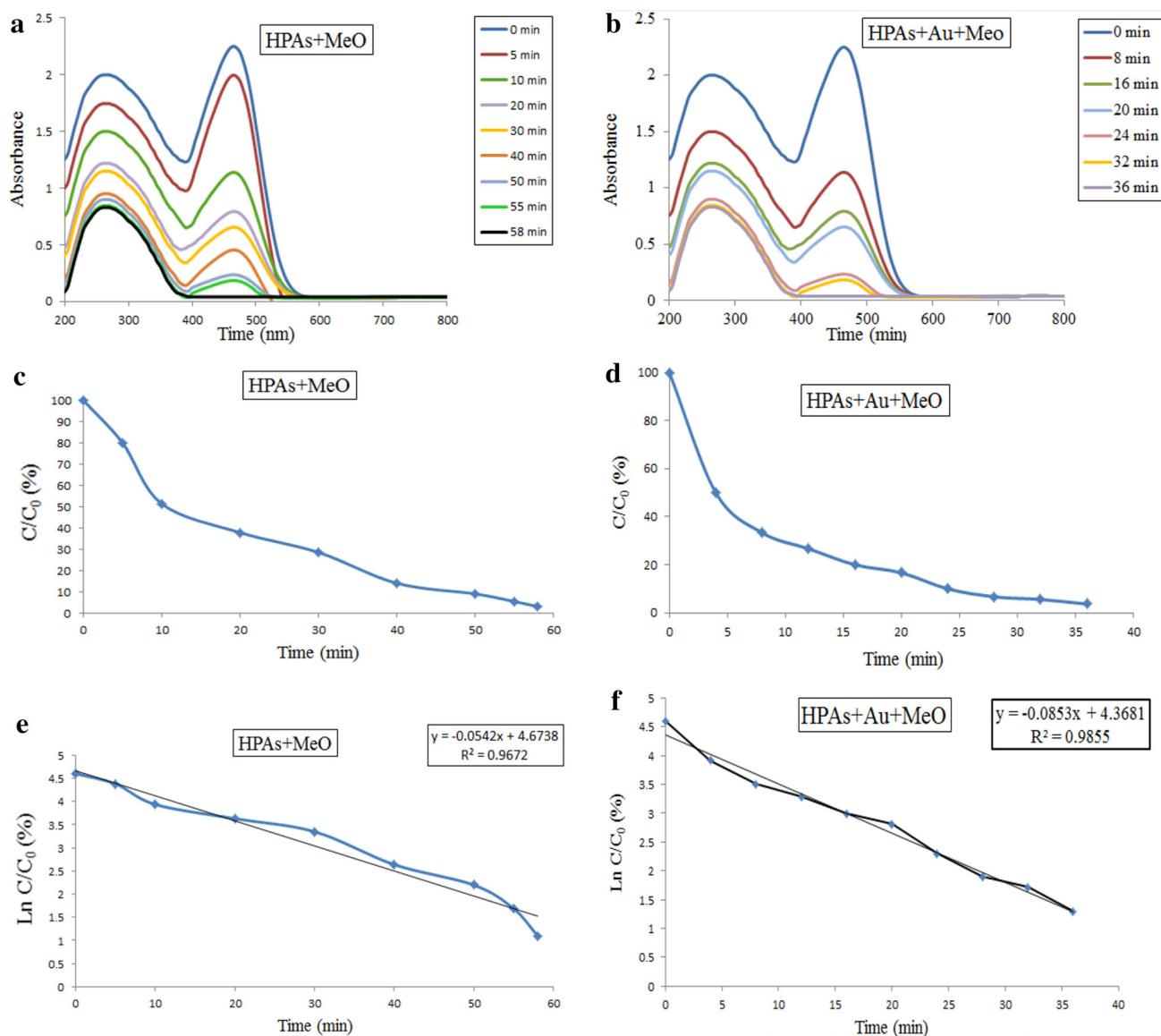


Fig. 6 Catalytic decolorization of MeO: in the absence of Au nanoparticles (**a**, **c**, **e**) and in the presence of Au nanoparticles (**b**, **d**, **f**)

In this equation, C and C_0 are the decolorization degree and the initial absorbance of dyes solution, respectively. C_e stands for the absorbance of the dye solution after photocatalysis. The pseudo-first order rate constants are given by the plot of $\ln(C/C_0)$ versus time.

Conclusions

Dawson acid, $[H_6P_2W_{18}O_{62}]$, can be used as a superior and green-reducing reagent and stabilizer in the preparation of Au nanoparticles in a nanophotochromic film, via a simple

and fast sol–gel procedure and photolysis. The synthesized nano film showed a significant catalytic activity in the decolorization process of MeO with pseudo-first order kinetic behavior.

Interestingly, our findings showed that heteropolyacid structure can control the loading amount of embedded Au nanoparticles up to twice. Further investigation in this field will provide a great opportunity for researches and scientists to develop techniques for the green and controlled synthesis of various nanoparticles in the presence of other heteropolyacids.

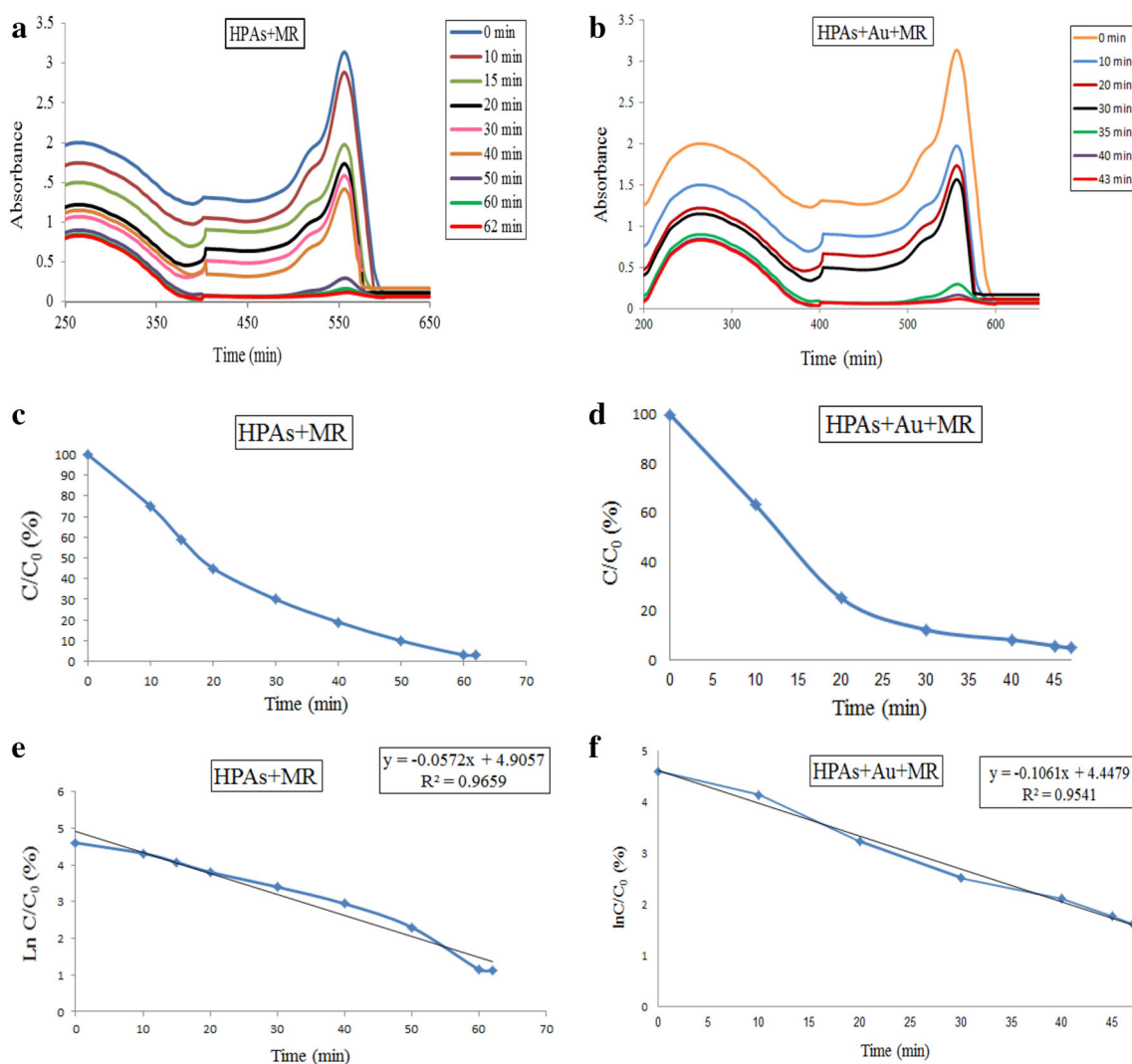


Fig. 7 Catalytic decolorization of MR: in the absence of Au nanoparticles (**a**, **c**, **e**) and in the presence of Au nanoparticles (**b**, **d**, **f**)

Table 3 Comparison for decolorization of MeO and MR

Catalyst	Time for decolorization of Azo dyes (min)	Yield (%)
Dawson film/MeO	58	91.2
Dawson film/Au/MeO	36	96
Dawson film/MR	62	84.4
Dawson film/Au/MR	43	87.2

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