

Catalytic reduction of 4-Nitrophenol by using Fe^{3+} and Ag^+ Co-doped TiO_2 nanoparticles

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Abstract: In this work, a simple sol-gel method was used to prepare magnetic Fe^{3+} and Ag^+ co-doped TiO_2 nanoparticles and their application for the catalytic reduction of 4-nitrophenol to 4-aminophenol by using reductant as NaBH_4 . The prepared catalyst was characterized by XRD, FT-IR, UV-DRS, FE-SEM, EDS and VSM have been applied to investigate the structure, morphology and magnetism of the nanoparticles. The obtained catalyst showed an excellent magnetism and the best catalytic ability than pure TiO_2 . The magnetic nanocatalyst should be extended to various potential applications, such as photo-degradation, separation and purification processes. Since the magnetic particles are readily recovered from the solution phase without centrifugation or filtration. The Fe^{3+} and Ag^+ co-doped TiO_2 nanoparticles prepared in this work has been exploited as solid phase catalysts for the reduction of 4-nitrophenol in the presence of NaBH_4 .

Keywords: TiO_2 , magnetic, Fe and Ag co-doping, 4-nitrophenol, NaBH_4

1. Introduction

Nanocatalysis is a rapidly growing field which involves the use of metal nanoparticles as catalysts for a variety of organic and inorganic reactions [1-3]. Catalysis at the nanoscale has attracted significant attention in the past two decades due to the unique properties of materials that arise at the nanoscale [4]. PNP, as with other nitrophenols and derivatives, is a common byproduct from the production of pesticides, herbicides, and synthetic dyes [5]. PNP is easily reduced by NaBH_4 in the presence of metals in solution [6-7].

Coinage metals, in particular, have been demonstrated to be excellent catalysts for PNP reduction at the nanoscale [8]. One would then suppose that both the activity and the selectivity of suspended catalysts could benefit much from the use of small-sized supports. The separation of solid catalysts from the reaction products simply by filtration or centrifugation necessitates, however, that the catalyst bodies are larger than about 3 μm : Smaller bodies are difficult to be separated out. It is thus highly necessary to develop new catalysts with a nanometer-sized magnetic core and a catalytic shell, which respectively favor the high surface area and convenient magnetic separation. Magnetically recyclable nanometer-sized catalysts allow the catalysts to be recycled conveniently through applying an external magnetic field. Many attempts have been made to synthesize this kind of noble-metal deposited magnetic materials (Fe_3O_4 , c- Fe_2O_3 , etc.) [9–12].

In order to investigate the catalytic activity of the magnetic Fe and Ag co-doped TiO_2 nanoparticles, we have chosen the reduction of 4-nitrophenol by NaBH_4 as a model reaction. 4-Aminophenol finds its application as a photographic developer, corrosion inhibitor, dyeing agent etc. [13]. Due to the significance of 4-aminophenol, there is a demand for direct catalytic reduction of 4-nitrophenol [14]. Indeed, many research groups [15–23] have investigated the reduction of 4-nitrophenol using a number of noble metal nanoparticles as catalysts. In these studies, catalytic metal

nanoparticles were mostly deposited onto dendrimer/polymers or resin beads before conducting the catalytic reduction of 4-nitrophenol with sodium borohydride. In this investigation, we choose silver (Ag) and maghemite (c- Fe_2O_3) nanoparticles as the functional components to construct the magnetically recyclable nanometer-sized catalysts. The Fe and Ag co-doped TiO_2 nanoparticles are in fact found to be efficient nanocatalysts for the reduction of 4-nitrophenol.

2. Experimental

2.1. Materials and Reagents

Nano iron(III) oxide (Spherical, less than diameter 50nm, 99.5%) was purchased from Sigma Aldrich Chemical Co., Ltd., USA. Ammonia solution, isopropyl alcohol and anhydrous ethanol were obtained from Hangzhou High-crystal Fine Chemical Co., Ltd., China. Silver Nitrate (AgNO_3), Tetrabutyl titanate (TBOT), 4-Nitro Phenol and Sodium borohydride were purchased from Merck, China.

2.2. Catalyst Preparation

The Fe_2O_3 nanoparticles (0.50, 0.75, 1.00 and 1.25%) were ultra sonicated for 1h to make them uniformly dispersed in anhydrous ethanol (40mL). Concentrated ammonium hydroxide (4.5mL) was diluted to the above solution and Silver Nitrate (0.50, 0.75, 1.00 and 1.25%) were quickly added under vigorous stirring. The solution was left to stirred for 12h. The product was washed with anhydrous ethanol three times. The resultant product was redispersed in anhydrous ethanol (40mL). Subsequently, a proper amount of TBOT (5.0mL) dissolved in isopropyl alcohol (40.0mL) was introduced to the system drop wise, followed by heating the solution at about 70°C. The whole process was under vigorous stirred for 12h, after that red brown precipitates were washed with deionized water and ethanol five times and dried in a vacuum oven at 80°C for 24h. Finally, the products were calcined in air at 500°C for 2h.

2.3 Catalyst Characterization

UV-Vis absorption spectra were measured using a Shimadzu UV-1601 spectrophotometer. Crystalline structure and crystallinity of the Fe-Ag/TiO₂ nanoparticles were examined by using an X-ray Diffractometer (Shimadzu, XRD-6000) equipped with Cu K α radiation source using Ni as filter at a setting of 45 kV/40 mA. A 2 θ scan range from 10 to 90°C, a scanning step size of 0.01°C and a scintillation counter detector was used. Fourier transform infrared (FT-IR) spectroscopy was carried for Fe-Ag/TiO₂ nanoparticles were obtained in the range 4,000 to 500 cm⁻¹ with an IR-Prestige-21 Shimadzu FT-IR spectrophotometer, by KBr pellet method. The FE-SEM micrographs were obtained by using a JEOL 6335F FE-SEM microscope equipped with a Thermo Noran energy dispersive spectroscopy (EDS) detector. The presence of elemental Iron, Silver, Titanium and Oxygen was confirmed through EDAX. The EDAX observations were carried out in STIC, CUSAT, (JOEL Model JED-2300) and saturation magnetization (Ms) and coercive force (Hc) of the samples were measured by using a vibrating sample magnetometer (VSM, Dexting, Model: 250) with a sensitivity of 10–3 emu.

3. Results and Discussion

3.1. X-ray Diffraction Studies

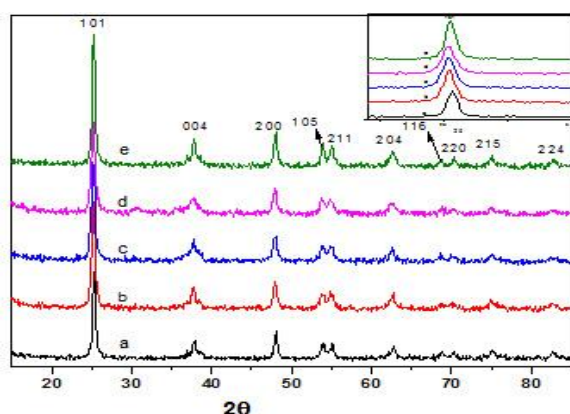


Figure 1: XRD patterns of un-doped TiO₂ (a), 0.50 (b), 0.75 (c), 1.00 (d) and 1.25 wt. percentages of Fe-Ag/TiO₂ nanoparticles, (e). Inset is the enlarged XRD peaks of crystal plane (101)

Fig. 1 shows the XRD patterns of un-doped TiO₂ (curve a), 0.50 wt. % Fe-Ag/TiO₂ (curve b), 0.75 wt. % Fe-Ag/TiO₂ (curve c), 1.00 wt. % Fe-Ag/TiO₂ (curve d) and 1.25 wt. % Fe-Ag/TiO₂ (curve e) powders. It is found that all of the crystal phase is anatase for all of the samples [24]. No diffraction peak corresponding to the Fe and Ag was detected. The reason could be due to the fact that the content of Fe and Ag might be too small to detect. The shape of the diffraction peaks of all the photo catalysts was consistent with that of un-doped TiO₂. The inset in Fig. 1 is the enlarged XRD peaks of crystal plane (101) for all of the samples and compared with the un-doped TiO₂, peak shift of the peak position is observed in inset of Fig. 1. The well-defined diffraction peaks with 2 θ are at about 25°, 38°, 48°, 54°, 54°, 62°, 68°, 70°, 74°, and 82° which are assigned to the (101), (004), (200), (105), (211), (204) (116), (220), (215)

and (224) crystal planes, respectively. This XRD characteristic pattern is consistent with the standard JCPDS values of anatase TiO₂ (JCPDS Card No. 21-1272) [25] with a lattice constants of 'a'='b' is 3.780 Å and 'c' is 9.52 Å, and did not appear in rutile and brookite form.

The diffraction peaks of crystal planes (101), (200), and (004) in the curves are used to determine the lattice parameter and crystal size of the samples, which are summarized in Table 1. It is found that the cell volume of 0.50, 0.75, 1.00 and 1.25 wt. percentages of Fe-Ag/TiO₂ is much larger than that of un-doped TiO₂.

Table 1: Lattice parameters and crystal size of un-doped TiO₂, 0.50, 0.75, 1.00 and 1.25 wt. percentages of Fe-Ag/TiO₂.

Sample	d	Lattice Parameters	Cell Volume (Å ³)	Crystal size (nm)
Un-doped TiO ₂	3.51	a=b=3.78, c=9.48	135.45	18
0.50% Fe-Ag/TiO ₂	3.52	a=b=3.80, c=9.52	137.47	16
0.75% Fe-Ag/TiO ₂	3.54	a=b=3.78, c=9.52	136.02	15
1.00% Fe-Ag/TiO ₂	3.52	a=b=3.78, c=9.52	136.02	13
1.25% Fe-Ag/TiO ₂	3.52	a=b=3.78, c=9.52	136.02	18

The experimental lattice constants 'a', 'b' and 'c' is calculated from the XRD peak 101, 004 and 200 of the XRD pattern 'a'='b' is 3.780 Å and 'c' is 9.52 Å, unit cell volume V=136.02 Å³. Both theoretical and experimental lattice constant 'a', 'b' and 'c' are in very well agreement. The lattice constant 'a', 'b' and 'c' details has been produced in Table.1 and the values in agreement with the literature report (a = b is 3.78 Å and 'c' is 9.52, JCPDS file no. 21-1272). Table 1 presents the results of the lattice parameters and the inter planer spacing's measured in the XRD analysis, the lattice constriction was found.

3.2. Fourier Transform Infrared Spectroscopy

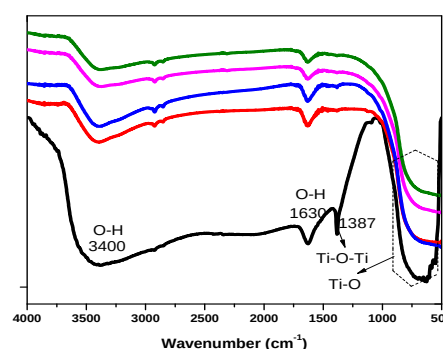


Figure 2: FT-IR spectra of (a) Un-doped TiO₂, (b) 0.50, (c) 0.75, (d) 1.00 and (e) 1.25 wt. percentages of Fe-Ag/TiO₂ nanoparticles.

The FTIR spectra of the all samples in the frequency range of 500–4000 cm⁻¹ are shown in Fig. 2. All the samples show peaks corresponding to the stretching vibration of O–H and bending vibrations of adsorbed water molecules around

3200–3400 cm^{-1} and 1600 cm^{-1} respectively [26-28]. Furthermore, the broadening of $\sim 3400\text{cm}^{-1}$ O-H stretching vibration, the formation of a different -OH group, and most probably as Ti-OH surface group. The broad intense band in the range of 450–700 cm^{-1} is due to the Ti-O stretching and Ti-O-Ti bridging stretching modes [26, 29-30]. Iron and silver co-doped TiO_2 intensity has reduced compared to undoped TiO_2 . No additional peaks are present upon Fe and Ag doping, supporting the efficient dispersion of iron and silver, and it indicates the absence of clusters of iron and silver, which is in good agreement with the XRD analysis result.

3.3. FE-SEM Study

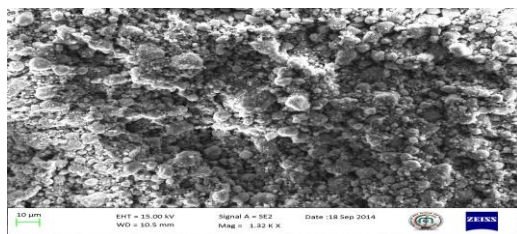


Figure 3: FE-SEM images of 1.00 wt. % of Fe-Ag/ TiO_2 nanoparticles.

According to the FE-SEM, the morphology of the 1.00 wt. % of Fe and Ag co-doped TiO_2 nanoparticles were observed and approximately spherical, in which the Fe and Ag co-doped TiO_2 nanoparticles were in aggregated form. This reveals that the powder particles are slightly agglomerated and the closed view of spherical nanoparticles has shown in Fig. 3.

3.4. Energy Dispersive X-ray (EDX) spectra

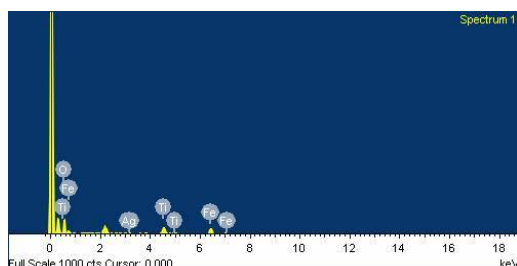


Figure 4: EDS spectra of 1.00 wt. % of Fe-Ag/ TiO_2 nanoparticles

The energy dispersive X-ray (EDX) spectra of the Fe and Ag co-doped TiO_2 are shown in Fig.4 respectively. The peaks corresponding to titanium, oxygen and the respective doped metals of Fe and Ag can be confirmed by Fig. 4. The results of an elemental analysis confirmed by the homogenous distribution of metal nanoparticles in the TiO_2 lattice.

3.5. UV-visible Diffusion Reflectance Spectroscopy:

Fig. 5 shows UV-Vis DRS absorption spectra of un-doped TiO_2 , 0.50, 0.75, 1.00 and 1.25 wt. percentages of Fe-Ag/ TiO_2 samples. Un-doped TiO_2 only exhibits a strong absorption in the UV region that is attributed to the band-to-band transition [24]. Compared with the pure TiO_2 , 1.00 wt. % Fe-Ag/ TiO_2 presents a small hump at around 480 nm tailing the visible-light region. This is mainly due to that

Fe^{3+} inserts into the structure of titanium dioxide, locates at interstices or occupies some of the Ti^{4+} lattice sites because of diffusion and transfer of the ions, and forms impurity interim levels between valence and conduction bands in TiO_2 . The impurity interim levels form impurity energy band, which overlaps with the TiO_2 conduction band as the amount of impurity increases [31].

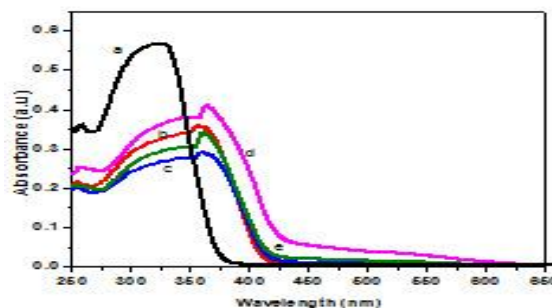


Figure 5: UV-Vis DRS absorption spectra of (a) un-doped TiO_2 , (b) 0.50, (c) 0.75, (d) 1.00 and (e) 1.25 wt. percentages of Fe-Ag/ TiO_2 nanoparticles

The absorption at wavelength of less than 387 nm is caused by the intrinsic band gap absorption of anatase TiO_2 (3.2 eV). The extension of adsorption edge to longer wavelengths for Fe^{3+} & Ag^+ / TiO_2 indicates the existence of good contact between TiO_2 and Fe & Ag grains and promotes the photo catalytic activity of catalysts in the visible light. The lack of absorption bands above 600 nm in all samples indicates the absence of Ti^{3+} ions in the TiO_2 lattice [32].

3.6. VSM

Magnetic measurement on the different size particles

In order to measure the magnetic properties of the nanoparticles we compacted them into pellets that were then cut into suitable sizes. Our measurements were focused on the determination of the magnetization of the nanoparticles as functions of their size and the different parameters of preparation.

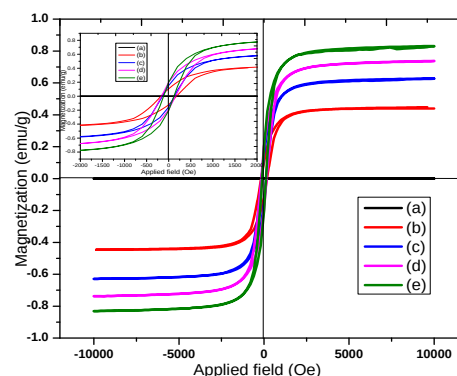
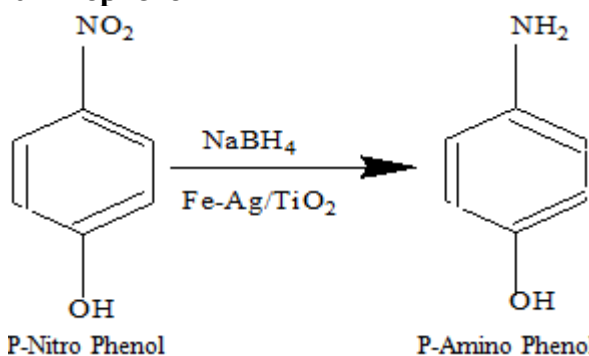


Figure 6: VSM of (a) un-doped TiO_2 , (b) 0.50, (c) 0.75, (d) 1.00 and (e) 1.25 wt. percentages of Fe-Ag/ TiO_2 nanoparticles.

The magnetization was determined. The DC measurements were made using a commercial Vibrating sample magnetometer (VSM). Typical field cycling range was between ± 10 kOe. Since super paramagnetism is very

useful in biotechnology [33], the room-temperature magnetization curves were measured. Fig. 6 show that the saturation magnetization (M_s) values of (a) un-doped TiO_2 , (b). 0.50, (c).0.75, (d). 1.00 and (e). 1.25 wt. percentages of Fe-Ag/ TiO_2 nanoparticles are 0.00, 0.44, 0.63, 0.74 and 0.83, emu/g, respectively, and four samples are essentially super paramagnetic. The M_s increases with increasing percentages of iron doping in TiO_2 could be attributed to the higher magnetic component in the photo catalyst. However, the magnetization curves of all the samples are similar except un-doped TiO_2 .

4. Catalytic reduction of 4-nitrophenol to 4-aminophenol



Scheme 1: Schematic representation of the performance of Fe-Ag/ TiO_2 nanoparticles as catalysts in the reduction of 4-nitrophenol to 4-aminophenol by NaBH_4 .

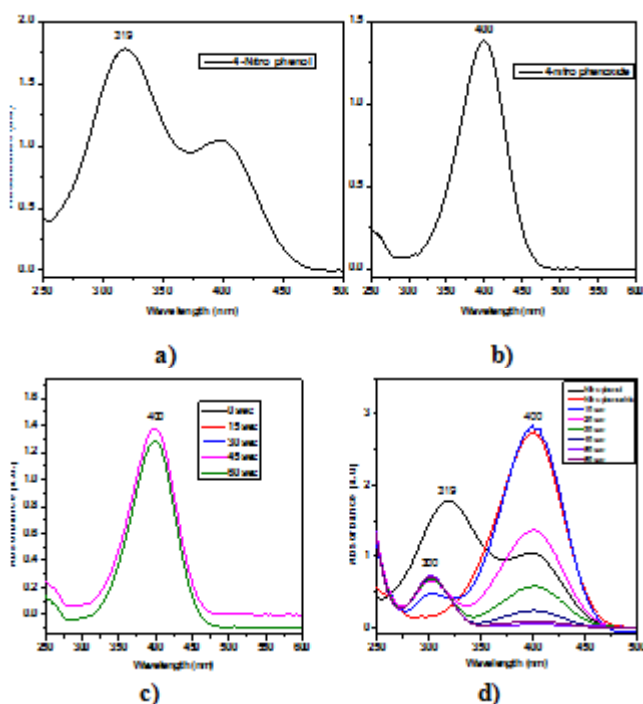


Figure 7: gives UV-Vis absorption spectra of 4-nitrophenol taken (a) before, (b) after immediate addition of NaBH_4 , (c) un-doped TiO_2 and (d). 1.00% Fe-Ag/ TiO_2 .

4.1. Catalytic Activity of Fe-Ag/ TiO_2

Recently, several research groups have investigated the catalytic reduction of 4-nitrophenol with NaBH_4 , using a number of noble metals Ag, Au, Cu, Pt, and Pd nanoparticles [6, 15–23, 34] in different substrates such as

dendrimers, polyelectrolytes, biological cells, and so on [6, 35–36]. Before we investigate the catalytic activity of the Fe-Ag/ TiO_2 , the catalytic ability of the pure TiO_2 nanoparticles was examined. An aqueous solution of 4-nitrophenol (1.5mmol in 100mL) has a maximum absorption at 319 nm, as shown by a trace in Fig. 7a. But it has been observed that, after immediate addition of freshly prepared aqueous solution of NaBH_4 , the peak due to 4-nitrophenol was red shifted from 319 to 400 nm (see Fig. 7b). This peak was due to the formation of 4-nitrophenolate ions in alkaline condition caused by the addition of NaBH_4 [19]. In the absence of proper catalyst, the thermodynamically favorable reduction of 4-nitrophenol (the standard reduction potentials for 4-nitrophenol/4-aminophenol and $\text{H}_3\text{BO}_3/\text{BH}_4^-$ are -0.76 and -1.33 V, respectively) was not observed and the peak due to 4-nitrophenol ions at 400 nm remains unaltered even a couple of days as reported in the literatures [6, 20]. Under alkaline conditions, the decomposition of borohydride is much slower. Borohydride is relatively environmentally friendly because of the low toxicity of borates. The advantage of the catalytic reduction of 4-NP is the easy monitoring of the reactant 4-nitrophenolate anion ($\lambda_{\text{max}}=400\text{nm}$) through spectrophotometry. The 4-nitrophenolate anion formation from 4-NP ($\text{pK}_a=7.15$) in the initial step upon addition of borohydride is indicated when the peak at 319 nm (due to 4-NP) is shifted to 400 nm. The sole product 4-AP ($\lambda_{\text{max}}=300\text{ nm}$) can also be monitored easily, and when required to know whether the reduction is actually taking place. Under certain situations, a significant decrease in absorbance at 400 nm may not be associated with the concomitant evolution of a peak at 300 nm indicating that the process does not involve any reduction, rather it is a mere adsorption of the nitro phenolate ion [36]. The UV-vis absorption spectrum after the addition of pure TiO_2 nanoparticles in the mixture of 4-nitrophenol and NaBH_4 also remains unaltered with time, as shown in Fig. 7c, which means that the pure TiO_2 nanoparticles do not work as catalyst for this reaction.

The addition of small amount of 1.0 wt. % Fe-Ag/ TiO_2 nanoparticles, however, causes fading and ultimate bleaching of the yellow color of the reaction mixture. As shown in Fig. 7d, time dependent UV-vis spectra of this catalytic reaction mixture display the disappearance of 400 nm peak and the gradual development of the new peak at 300 nm which substantiates the formation of the 4-aminophenol [37]. These results indicate that 1.0 wt. % Fe-Ag/ TiO_2 nanoparticles indeed catalyze the reduction process.

In this experiment, the concentration of the borohydride ion, used as reductant, largely exceeds (50 times) that of 4-nitrophenol. As soon as we added the NaBH_4 , the 1.0 wt.% Fe-Ag/ TiO_2 nanoparticles started the catalytic reduction by relaying electrons from the donor BH_4^- to the acceptor 4-nitrophenol right after the adsorption of both onto the particle surfaces. As the initial concentration of sodium borohydride was very high, it remained essentially constant throughout the reaction.

The 1.0 wt.% Fe-Ag/ TiO_2 nanoparticles are very effective for the catalytic reduction of 4-nitrophenol. At the end of the reaction, the catalyst particles remained active and were

easily separated from the product, 4-aminophenol, using a external magnet.

5. Conclusion

The catalytic performance of Fe-Ag/TiO₂ for the reduction of 4- NP to 4-AP was tested as a model reaction with an excess amount of NaBH₄. Accordingly, the reduction rates can be regarded as being independent of the concentration of NaBH₄. After adding NaBH₄ into the aqueous solution of 4-NP, the color of the solution changed from light yellow to dark yellow due to the formation of 4-nitrophenolate ion. Then, the color of the 4-nitrophenolate ions faded with time after the addition of Fe-Ag/TiO₂. The progress of the reaction could be monitored by UV-Vis spectroscopy. The characteristic peak of 4-NP at 400 nm decreased, while at 300nm a new peak appeared which were assigned to 4-AP. The reaction was finished within 60s at room temperature. The reaction did not proceed in this period in the absence of Fe-Ag/TiO₂ catalyst or with un-doped TiO₂ alone.

6. Acknowledgements

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