Photocatalytic removal of methylene blue using titania- and silica-coated magnetic nanoparticles

Sawsan Dagher1, Ahmed Soliman2,4, Aiman Ziout1,5*, Nacir Tit4, Ali Hilal-Alnaqbi1,4*, Saud Khashan6, Fadi Alnaimat1 and Jaber Abu Qudeiri1
1 Department of Mechanical Engineering, UAE University, Al-Ain, UAE
2 Department of Chemistry, UAE University, Al-Ain, UAE
3 Department of Nuclear Fuel Technology, Hot Laboratory Center, Atomic Energy Authority, Cairo, Egypt
4 Department of Physics, UAE University, Al-Ain, UAE
5 Abu Dhabi Polytechnic, ADPoly, Abu Dhabi, UAE
6 Department of Mechanical Engineering, Jordan University of Science and Technology, Irbid, Jordan

*Author to whom any correspondence should be addressed.
E-mail: ziout@uaeu.ac.ae

Keywords: Fe3O4@TiO2, Fe3O4@SiO2, photocatalytic degradation, methylene blue, magnetic nanoparticles

Abstract
The scope of this investigation is the photocatalytic degradation performance of newly synthesized nanoparticles (NPs); namely; Fe3O4; Fe3O4@TiO2 and Fe3O4@SiO2. Non-thermal synthesis methods are used to synthesize the NPs and to explore the ferromagnetic properties of the photocatalysts. The synthesized NPs are characterized using TEM, XRD, FTIR, TGA, VSM, and surface area analysis techniques. The photocatalytic activities of Fe3O4 and Fe3O4@SiO2 NPs, put under solar irradiation, and Fe3O4@TiO2 NPs, put under UV irradiation, are examined. The efficiency in degradation of Methylene Blue (MB) pollutant is shown to be the best for Fe3O4@SiO2 NPs, then in Fe3O4 NPs, and lastly in Fe3O4@TiO2 NPs. The silica (SiO2) coating on Fe3O4 NPs significantly enhances the light absorption and is found to improve the MB degradation rate and the photoinduced charge generation and separation (i.e. it enhances the exciton lifetime). That makes the Fe3O4@SiO2 NPs promising candidates for organic pollutants removal in various environment-related applications.

1. Introduction

Amongst side effects of the industrial revolution is the release of huge amount of wastewater. Wastewater contains several hazardous substances that pollute the environment. For instance, the textile dyes are one of the largest group of chemicals being produced all over the world [1, 2]. Namely, methyl red, methylene blue (MB), methyl orange and malachite green, that cause various kinds of human cancers, coming major challenging concerns for public health safety [3, 4]. However, these dyes show high stability and resistance to biodegradation [5]. Consequently, several physical and chemical methods are undertaken to remove dyes from industrial effluents. Among the attempted methods, one can mention: adsorption, coagulation, flocculation, electrocoagulation [6–8] and photodegradation [9–11]. The methods of wastewater treatment aim usually to adsorb or to head off pollution; but only photocatalytic degradation can transfer organic wastewater into CO2 and H2O without any intermediate [12, 13]. Nonetheless, photocatalyst is collected from the solution by using a magnet, which is a promising green mechanism in environment technology. Hence, producing a new photocatalyst comprising magnetic property, in the form of core–shell structure is of emerging interest. Recently, Magnetite (Fe3O4) nanoparticles (NPs) are discovered to be ideal materials as a core for a photocatalyst, because of many reasons: (i) its low toxicity, and bio-compatibility [14], (ii) high magnetization and high coercivity, (iii) relatively low Curie temperature [15–18], (iv) superior photons’ absorption capability, and (v) strong bonds between the molecules due to the dipole-dipole interactions [19]. Furthermore, it is easy to control the mobility of Fe3O4 NPs through the application of magnetic field.
Natively, titania (TiO₂) is n-type semiconducting material, with a large direct band gap (3.2 eV). TiO₂ absorbs UV radiation (wavelength < 390 nm), while it permits visible light to pass through very slowly, because of its extreme large refractive index in visible region (2.6). In addition to its thermal stability, its other advantages are being nontoxicity, high free hydroxyl production, environmentally-friendly nature, its biological and chemical inertness, and cost-effectiveness [20, 21]. Salamat et al [22] synthesized core–shell titania-coated magnetite NPs using the dusts of electric-arc furnace, synthesized at 180 °C and calcinated at 400 °C, and evaluated its photocatalytic activity for the organic pollutant removal from wastewater. Actually, 96% photodegradation efficiency is obtained, using 1 g L⁻¹ of the photocatalyst, for 90 min, at 30 °C. Kumara et al [23] synthesized magnetically separable porous titanium silicate–Fe₂O₃ hybrid photocatalyst using a hydrothermal method, and the nanocomposite exhibited improved efficiency for MB photodegradation, as it is exposed to UV light. Chanhom et al [24] synthesized Fe₂O₃@SiO₂@TiO₂ NPs and investigated the effect of the thickness of silica (SiO₂) interlayer. Herein, the photo-degradation process is performed by the titania. It is found that 6 nm thickness of silica layer between titania (surface layer) and Fe₂O₃ (core) NPs can prohibit the electron transfer in the inverse direction, and maintain a high efficiency of photocatalytic activity. Other research groups [25] deposited other elements on the surface of TiO₂ NPs such as Pt, Co, Au and noble metal NPs to improve its photocatalytic properties. Notably, TiO₂ can be doped with metal ions to decrease its bandgap energy, and to reach the absorbance of light with higher wavelengths. On the other hand, the photo-generated exciton (electron-hole pair) in a metal-doped TiO₂ has a long lifetime, which leads to photocatalytic activity enhancement [26–28].

Silica-coated materials can form a well dispersed and chemically/thermodynamically stable colloidal solution, as it has a strong affinity with respect to water. Moreover, silica permits light transmission with minimum reflection, possesses high surface-to-volume ratio because of its porous structure. In general, the performance of SiO₂@Fe₂O₃ NPs is characterized by displaying three different trends: (i) Photothermal effect of SiO₂@Fe₂O₃ NPs, where Fe₂O₃ absorbs the infrared light, and transfer it into thermal energy, herein, SiO₂ coating is applied to protect Fe₂O₃ NPs from agglomeration and oxidation, as far as SiO₂ is an inert and chemically stable material. Usually, the coating of Fe₂O₃ NPs serves to increase the negative charge on the molecule surface, that enhance the Coulomb repulsion and leads to shield the dipole–dipole interaction [29]. (ii) Adsorption of pollutants on the porous surface of silica, where, the function of magnetite NPs, after becoming saturated, is to separate the adsorbents from the the mixture using a magnet. SiO₂ can be functionalized with a certain group for selective adsorption [30]. (iii) Photodegradation of pollutants, in which other photoactive components are immobilized on Fe₂O₃@SiO₂ NPs. These components receive photonic energy and interact with the waste intermedia. In this process, Fe₃O₄@SiO₂ NPs serve as a magnetic support in which the silica on the surface can be functionalized with several groups to reach a coating functionalized for photoactive layer. For instance; TiO₂ were coated on Fe₃O₄@SiO₂ NPs (i.e. on the silica) for methylene blue photodegradation. AgBr and AgI were coated on Fe₃O₄@SiO₂ for 4-chlorophenol, azodyes and methylene blue degradation under visible light exposure [31–34]. However, few studies have reported the photodegradation effect of Fe₃O₄@SiO₂ NPs, where no other material has immobilized/passivated on it.

Titania coating of Fe₃O₄ NPs has been applied using diversity of methods; in which heat treatment at high temperatures was considered essential [35]. Heat treatment is critical; since the magnetic characteristics show a deterioration when the magnetic cores experience high-temperature treatments. In addition, heating process involves diffusion of substitutional impurities between the magnetic core and the titania through the vacancies which persist always to exist, that would in turn decrease the photodegradation activity. Therefore, the method of synthesis does affect the structure, size and shape of the Fe₃O₄@TiO₂ NPs, and consequently, the performance of the photocatalyst. To the best of the authors’ knowledge, the photocatalytic activity of Fe₃O₄@TiO₂ NPs and Fe₃O₄@SiO₂ NPs which are synthesized using non-thermal methods, and without further coating will be studied for the first time. Consequently, the objectives of this study are to investigate the photodegradation efficiency of Fe₃O₄@TiO₂ NPs that are synthesized by a non-thermal method, for water purification from organic pollutants. Further aim is, to investigate the photocatalysis effect of Fe₃O₄@SiO₂ NPs for MB dye removal, as induced by solar radiation. Then, a comparison of the photocatalytic performance of the as-synthesized titania-coated Fe₃O₄ NPs, silica-coated Fe₃O₄ NPs, and uncoated Fe₃O₄ NPs is addressed.

2. Experimental methods

2.1. Synthesis and characterization of magnetic photocatalysts

The Fe₃O₄ NPs are prepared separately then coated with either a titania or silica layer. A chemical co-precipitation method is used to synthesize the Fe₃O₄ NPs [36]. Typically, dissolve 0.02 Mole of FeCl₃.6H₂O and 0.01 Mole of FeCl₂.4H₂O in 90 ml H₂O. Keep stirring rigorously and heat the solution up to 80 °C under N₂ gas flow. At that moment, add 11 ml of NH₄OH; consequently, Fe₃O₄ NPs are formed as a black precipitate. Then,
add 11 ml of polyethylene glycol-4000 (PEG) solution dropwise for 1 h. PEG stabilizes the surface of Fe3O4 NPs, thus NPs keep dispersed in the solution, for further coating with titania or silica. Furthermore, PEG plays positive role in the passivation of surfaces of Fe3O4 NPs and provide covalent bonds to suppress and saturate the dangling bonds. Consequently, PEG removes the defect-related gap states and enhances the optical qualities which are, as a matter of fact, needed to enhance the photoreaction and photoconductivity effects [37–40]. Finally, collect the Fe3O4 NPs by a magnet.

Regarding the coating process, TiO2 is applied on the surface of Fe3O4 NPs using a non-thermal method [41]. Typically, disperse 10 mg of the as synthesized Fe3O4 NPs in 25 ml ethanol by ultrasonication for 30 min. Then add TiCl4/ethanol diluted solution (0.5 ml/2 ml). Keep the stirring for 1 h, until the color of the mixture change to gray indicating the formation of Fe3O4@TiO2 NPs. Finally, collect the Fe3O4@TiO2 NPs by a magnet. On the other hand, SiO2 is applied on the surface of Fe3O4 NPs using a modified Stöber method [36]. In brief, disperse 100 mg of the as synthesized Fe3O4 NPs in 75 ml ethanol by ultrasonication, add 6 ml of NH4OH and 200 μl Tetraethyl ortho-silicate dropwise for 2 h. Finally, collect the Fe3O4@SiO2 NPs by a magnet.

The synthesized photocatalysts are characterized using several techniques including transmission electron microscopy (TEM), dynamic light scattering (DLS) by Zetasizer Nano ZS, Fourier transform infrared spectroscopy (FTIR), powder x-ray diffraction (XRD), thermogravimetric analysis (TGA) and UV-visible spectroscopy. Brunauer–Emmett–Teller (BET) method is used to measure the specific surface area of the dried photocatalyst powders. Barrett–Joyner–Halenda (BJH) method is used to measure the pore size distribution. SQUID Vibrating sample magnetometer (VSM) is used to measure the magnetic properties of the photocatalysts. Dynamic light scattering (DLS) technique used to measure the zeta potential of the photocatalysts in H2O suspension, at 25 °C, in which Zeta Sizer Nano ZS machine is utilized.

2.2. Photocatalytic experiments
Kinetics adsorption is investigated in dark before the photocatalytic experiment, using 300 ml of Methylene blue (MB) dye solution, MB concentration is 70 ppm (mg L−1). 40 mg of the synthesized magnetic photocatalyst is added to MB. Thus, Fe3O4/MB, Fe3O4-TiO2/MB and Fe3O4-SiO2/MB containers are kept closed in darkness under continuous shaking. A sample is withdrawn every 20 min, photocatalyst is collected and detached from the sample by a magnet, and the remaining concentration of MB is measured by spectrophotometer.

As the adsorption-desorption equilibrium in the mixture of the photocatalyst and the MB dye is attained, photocatalytic experiments are carried out, under solar radiation in October 2017. The temperature and average solar light intensity at that time and site are 34 °C and 5320 Wh/m²/day, respectively. Samples are kept in closed glass containers and placed under sunlight, except for the Fe3O4-TiO2/MB sample, are placed under UV light of 250 nm wavelength. Then collected at several times. The MB concentration is calculated as the absorbance is monitored at 664 nm wavelength, using a UV–vis spectrophotometer. The experimental measurements are conducted in duplicate and the average of two values is recorded.

3. Results and discussion

3.1. Morphology and structure of the photocatalysts
Figure 1 displays the TEM images of the Fe3O4 NPs without coating and as they are coated with SiO2 and TiO2 layer. The results indicate that all Fe3O4, Fe3O4@TiO2, and Fe3O4@SiO2 NPs have almost a spherical shape. Figure 1 (a) shows that Fe3O4 NPs have sizes in the range between 2 and 10 nm. Figure 1 (b) shows nanoclusters of Fe3O4, successfully coated with a thin layer of titania leading to core–shell structure of Fe3O4@TiO2 NPs, having sizes in the range between 50 and 100 nm. Figures 1 (d)–(f) shows that Fe3O4 NPs clustered into bigger size than the previous particles (figures 1 (b), (c)), then coated with a thin layer of SiO2 leading to core–shell structure of Fe3O4@SiO2 NPs with sizes in the range between 400 and 500 nm. Almost same particles’ sizes distribution data are obtained using DLS technique, where the obtained average size of Fe3O4 NPs, Fe3O4@TiO2, and Fe3O4@SiO2 are 7.8 nm, 73 nm 475 nm, respectively, more details are in [36, 41].

XRD patterns as 2θ in the range of 10°–80° for the Fe3O4 NPs before and after the TiO2 and SiO2 coating are shown in figure 2. The XRD pattern of Fe3O4 demonstrates sharp and intense diffraction peaks, since each plane of the NPs reflects the incident x-ray at certain scattering angle 2θ, each peak at around 2θ is corresponding to one lattice plane of Fe3O4 as follow; 30° for (2 2 0), 36° for (3 1 1), 43° for (4 0 0), 53° for (4 2 2), 57° for (5 1 1), 63° for (4 4 0) and 75° for (533) plane. Indicating a crystallized cubic inverse spinel structure of Fe3O4. The core/shell Fe3O4@TiO2 NPs exhibits diffraction peaks as follow; 25.3° for (1 0 1), 37.8° for (0 0 4), 48.2° for (2 0 0), 54.2° for (1 0 5), 55.3° for (2 1 1), 69° for (116) and 70° for (220) plane of titania [42]. These peaks demonstrate that titania has anatase tetragonal structure, the existence of other few peaks with extremely low intensity are assigned to Fe3O4 cores. The core/shell Fe3O4@SiO2 NPs exhibits a broad diffraction peak at 10°–30° assigned to the amorphous SiO2 [43, 44], in addition to the existence of some peaks from Fe3O4 cores with less intensity than
Fe$_3$O$_4$ diffraction peaks. Owing to the x-ray absorption via the titania and silica shells. The coated samples showed a decrease of the peaks intensity from Fe$_3$O$_4$, which confirms that Fe$_3$O$_4$ NPs are shielded with extremely thin layer of TiO$_2$ or SiO$_2$. It is observed that the decline in the intensity of Fe$_3$O$_4$ peaks is more pronounced for

Figure 1. TEM images of (a) Fe$_3$O$_4$ NPs; (b), (c) Nanocluster of Fe$_3$O$_4$ NPs (core) coated with titania layer (shell); (d)–(f) Nanocluster of Fe$_3$O$_4$ NPs (core) coated with silica layer (shell).

Figure 2. XRD pattern of Fe$_3$O$_4$ NPs, Titania-coated Fe$_3$O$_4$ and Silica-coated Fe$_3$O$_4$ core/shell NPs.
Fe₃O₄@TiO₂ NPs, which reveals that the titania shell on magnetite nanoclusters has more thickness than the silica shell.

FTIR spectra of Fe₃O₄, titania-coated Fe₃O₄ and silica-coated Fe₃O₄ NPs in the range of 4000–400 cm⁻¹ are shown in figure 3. A broad band at around 3600 cm⁻¹ is appeared in all the spectra that corresponds to the O-H group on the surface of the as synthesized NPs and could be attributed to PEG. Fe₃O₄ spectrum exhibits a strong band at 590 cm⁻¹ ascribed to Fe₃O₄ functional group (Fe-O bond), and another peak around 1600 cm⁻¹ exists in Fe₃O₄ and Fe₃O₄@TiO₂ spectra, resulted from water molecules on the surface (H-O-H bending) [45]. Fe₃O₄@TiO₂ spectrum shows peaks at around 2360 cm⁻¹, 1340 cm⁻¹ and 1118 cm⁻¹, which are ascribed to the carbon dioxide from the air, the Ti-O bond and Fe-O-Ti bond, respectively. The combination of stretching vibration of Ti-O-Ti bond and the Fe-O bond at 590 cm⁻¹ leads to a broad band between 500 cm⁻¹ and 700 cm⁻¹ [46], verifying the titania-coated Fe₃O₄ structure. Fe₃O₄@SiO₂ spectrum shows a strong band at 960 cm⁻¹ attributed to Si-OH bond. The peaks at 797 cm⁻¹ and 464 cm⁻¹ resulted from vibrational modes in and out of plane bending of the Si-O-Si, respectively. The band at 570 cm⁻¹ is ascribed to Si-O-Fe bond [47], verifying the silica-coated Fe₃O₄ structure.

Figure 4 shows the TGA curve of the Fe₃O₄ NPs, which gives an approximation of the weight loss of the sample with temperature, to evaluate the mass percentage of PEG on the surface of Fe₃O₄ NPs. The first decomposition stage occurs at 30 °C up to ≈150 °C, where a steep weight loss of 2% is observed, owing to the release of any remaining water and alcohol on the particles’ surface. The second stage shows a major weight loss with 6% change over a wide range of temperature between 150 °C and 450 °C. The weight loss at this stage is due to the PEG decomposition, which indicates a very thin layer of PEG on Fe₃O₄ NPs surface. At temperatures in
the range of 450 °C–700 °C polyethylene glycol is completely dehydrated leading to about 1% weight loss, then no further weight reduction is noticed because of the high thermal stability of Fe3O4.

Figure 5(a) shows UV–vis light absorption spectra of the prepared photocatalysts. Obviously, Fe3O4 and Fe3O4@TiO2 NPs exhibit absorption in UV light region. However, Fe3O4@SiO2 exhibit absorption in the full light spectrum (i.e., no clear absorption peak). According to the band theory, the optical band gap can be estimated using the Tauc’s formula [48]:

\[ (\alpha h\nu)^n = B(h\nu - E_g) \]  

(1)

Where \( \alpha \) is the absorption coefficient (cm\(^{-1}\)), \( B \) is a characteristic constant and \( n \) is a parameter identifying the electronic transition type (e.g., \( n = 2 \) for direct transition), \( h\nu \) is the photon energy (eV), \( E_g \) is the energy band gap (eV). The \( E_g \) can be calculated by extrapolating the straight line fit of the graphical representation of \((\alpha h\nu)^2\) versus \(h\nu\) to \(h\nu\)-axis, as shown in figures 5(b), (c). The linearity of the curves usually confirms the existence of direct band gap transitions.

The measureable \( E_g \) for Fe3O4 NPs and Fe3O4@TiO2 NPs are 3.3 eV and 4.1 eV, respectively, as shown in figures 5(b), (c). The \( E_g \) values of these NPs are much larger than the \( E_g \) of their bulk, which is attributed to the quantum confinement effects, thus, as crystal size decreases the band gap energy increases. Additionally, a very low amount of titania on the surface of Fe3O4 NPs can lead to the difference in energy levels of the energy molecular quantum states within Fe3O4. In addition to quantum-confinement effects, PEG and titania possess energy levels close to the interface states.

### 3.2. Surface area analysis

Specific surface areas of the photocatalysts are measured using the BET method, by measuring the amount of the adsorbed N\(_2\) gas on the surface of the NPs [49]. Figure 6(a) shows the N\(_2\) adsorption/desorption isotherms of the Fe3O4, Fe3O4@TiO2 and Fe3O4@SiO2 NPs. The isotherms exhibit type IV, indicates the mesoporous (i.e. 2–50 nm pore size) character of the synthesized photocatalysts. Figure 6(b) shows their corresponding pore-size distributions which are measured using the BJH method [50]. The values of BET surface area, BJH cumulative pore volume and average pore size are shown in table 1.

Fe3O4@SiO2 NPs shows the highest surface-to-volume ratio and largest pore size whereas the Fe3O4@TiO2 shows the least surface-to-volume ratio with poor pore size. Furthermore, Fe3O4 NPs exhibit surface area of 111 m\(^2\), which is less than the surface area of the silica-coated Fe3O4 (138 m\(^2\)). These results confirm that the silica coating increases the specific surface area of the NPs which is, in turn, beneficial for the photodegradation process.

### 3.3. Magnetic properties

Figure 7(a) shows the magnetic hysteresis loops of the Fe3O4 and Fe3O4@TiO2 NPs at 2 K and 300 K. Herein, zero-field-cooling (ZFC) is carried out to obtain Magnetization (M) versus applied magnetic field (H) curves. In the ZFC measurements the temperature of the NPs is set at a particular temperature. At 2 K the saturation magnetization (\( M_s \)) at the maximum applied field of 70 000 Oe (not shown here), remanent magnetization (\( M_r \)) and coercivity (\( H_c \)) of the Fe3O4 NPs are 75 emu g\(^{-1}\), 22 emu g\(^{-1}\) and 331 Oe, respectively. Fe3O4@TiO2 NPs exhibit \( M_s \), \( M_r \) and \( H_c \) of 28 emu g\(^{-1}\), 7 emu g\(^{-1}\) and 328 Oe, respectively. At 300 K no hysteresis loops are observed, where the Ms of Fe3O4 and Fe3O4@TiO2 NPs are 65 and 23 emu g\(^{-1}\), respectively. Thus, no obvious \( M_s \) or \( H_c \) is observed for the NPs, indicating the superparamagnetic behavior at 300 K. Superparamagnetic NPs exhibit excellent magnetic properties. Therefore, they can be separated easily from solution with the use of an external magnet.

---

**Figure 5.** (a) UV–visible absorption spectra of the of Fe3O4, Titania-coated Fe3O4 and Silica-coated Fe3O4 NPs dispersed in H\(_2\)O, (b) Tauc plot of the Fe3O4 NPs, (c) Tauc plot of the Titania-coated Fe3O4 NPs.
However, it is evident that the $M_s$ values at 300 K is less than the $M_s$ at 2 K due to thermal agitations of the NPs' magnetic moments. Furthermore, the $M_s$ values are considerably reduced compared to the $M_s$ for bulk Fe$_3$O$_4$ (around 90 emu g$^{-1}$ at 300 K) [51]. The decrease in $M_s$ of magnetic NPs is due to disorder of the surface spin and finite size effects. The NPs have much higher surface-to-volume ratio than the bulk material. That leads to the residence of a huge fraction of the total number of atoms on the surface of the particle. However, the environments of the atoms in core are different than those on the surface of the particle. The surface of the particle can experience several defects resulting in spin canting or disordered surface spins and spin-glass behavior, due to changes in the (i) atomic coordination, (ii) lattice disorder, (iii) dangling bonds [52]. Thus, the net magnetization of the NPs are smaller than that of the bulk material.

Figure 7(b) shows the ZFC and field-cooled (FC) magnetization–temperature ($M-T$) measurements, conducted on the NPs. In the FC measurements, the NPs are heated up to 300 K, then the temperature is cooled again from 300 K to 2 K at a constant applied magnetic field of 50 Oe. The ZFC/FC curves of the Fe$_3$O$_4$ and

Table 1. BET and BJH experimental results of the Photocatalysts.

| Photocatalyst     | BET- surface area (m$^2$.g$^{-1}$) | BJH- Cumulative pore volume (cm$^3$.g$^{-1}$) | Average pore size (nm) |
|-------------------|-----------------------------------|----------------------------------------------|------------------------|
| Fe$_3$O$_4$       | 111                               | 0.14                                         | 5.0                    |
| Fe$_3$O$_4$@TiO$_2$ | 76                                | 0.13                                         | 6.9                    |
| Fe$_3$O$_4$@SiO$_2$ | 138                               | 0.42                                         | 10.2                   |

Figure 6. (a) Nitrogen adsorption–desorption isotherms and (b) BJH pore size distribution curves of Fe$_3$O$_4$, Titania-coated Fe$_3$O$_4$ and Silica-coated Fe$_3$O$_4$ NPs.

Figure 7. (a) Hysteresis loop of the as-synthesized Fe$_3$O$_4$ and Fe$_3$O$_4$@TiO$_2$ NPs measured at 300 K and 2 K. (b) Zero-field-cooled (ZFC) and field-cooled (FC) curves for the as-synthesized Fe$_3$O$_4$ and Titania-coated Fe$_3$O$_4$ NPs under an applied magnetic field of 50 Oe.
Fe₃O₄@TiO₂ show that as the temperature increases from 0 to 300 K, the ZFC magnetization increases first and then decreases after reaching a maximum at 300 K, which corresponds to the blocking temperature (TB). This result further proves that the as-synthesized NPs show a superparamagnetic behavior at room temperature. Whereas the FC magnetization increases as the temperature decreases to 200 K. A small dep is noticed around 200 K, then the magnetization becomes nearly constant as the temperature decreases to 2 K, which is an evident on the existence of super or surface spin-glass structure [52–56]. The super-spin-glass behavior is resulted from the large interparticle interactions whereas the surface spin-glass behavior can be caused by frozen disordered surface spins [54, 55].

M–H and M–T curves show that the magnetization values of Fe₃O₄@TiO₂, considerably smaller than those of Fe₃O₄ because of the nonmagnetic titania coating which surrounding the Fe₃O₄ cores. Additionally, this reduction of magnetization in the coated sample can be attributed to super-spin-glass structures; each agglomerate of Fe₃O₄ NPs of sizes around 7 nm is coated with TiO₂. This huge number of the Fe₃O₄ NPs (core) leads to a strong interparticle interaction which forms super-spin-glass structures. Similar magnetic properties for Fe₃O₄@SiO₂ are expected, since the Fe₃O₄ NPs are synthesized the same way, and the nonmagnetic silica coating is surrounding an agglomerate of a huge number of Fe₃O₄ NPs (cores). However, the as-synthesized NPs exhibit strong responsive to an external magnet in which they can be collected easily from the solution, washed and reused for another purification cycle. Once the magnet is removed, the NPs do not retain any net magnetization, indicating the superparamagnetic characters.

### 3.4. Adsorption performance

Adsorption kinetics is a more pronounced mechanism in the absence of light. Adsorption of a model pollutant (i.e. MB dye) onto Fe₃O₄, Fe₃O₄@TiO₂, and Fe₃O₄@SiO₂ NPs is investigated. By collecting a portion of MB solution for each 20 min and analyze it for the residual concentration of MB. Herein, the samples are kept in dark for 300 min. The Fe₃O₄@TiO₂ NPs results showed an insignificant change in the concentration of MB after 5 h shaking in darkness, which indicates the chemical stability and a non-porous structure of the titania layer. These are shown in figure 8(b). Fe₃O₄ NPs and Fe₃O₄@SiO₂ NPs results show a significant adsorption within the first 300 min. subsequently, the pores are saturated and equilibrium is reached as displayed in figures 8(a), (c). Figure 8(d) shows a graph for the ratio of MB concentration at certain times to its initial concentration (Cₜ/C₀) versus time utilizing the Fe₃O₄@SiO₂ NPs. MB concentration decreases by about 11% in the first 3 h then remains constant. This phenomenon proves the adsorption process taking place in SiO₂.

![Figure 8. Degradation UV–vis spectra of MB dye using photocatalysts](image)
3.5. Photocatalytic activity

As the adsorption-desorption equilibrium is attained among the particles and the dye, the photoactivity of the as-synthesized NPs is investigated by photodegradation of MB. After reaching the equilibrium adsorption state in the dark, Figures 8(a)–(c) show the UV–vis spectra for MB with Fe₃O₄, titania-coated Fe₃O₄ and silica-coated Fe₃O₄ NPs, respectively. The solutions are kept under solar radiation, and the solution with Fe₃O₄@TiO₂ is kept under UV light for 140 min, where photocatalytic degradation is the dominant mechanism. Figure 8(d) shows that the concentration of MB decreases significantly by about 97% within 140 min.

The performance of Fe₃O₄@TiO₂ is evaluated under solar irradiation for 5 h. However, unnoticeable change in the solution colour is observed, hence insignificant change in the MB concentration is obtained. That can be attributed to the fact that TiO₂ (on the surface) is a wide band gap semiconductor that can be excited by light of high energy (i.e., UV, short wavelength). Furthermore, the reduction of the particles’ size to the nanoscale increases the band gap value, consequently, the elaboration of the excitation energy, due to quantum-confinement effects. When the band gap becomes larger, electrons require more energy to be excited to the conduction band.

Photocatalytic experimental results of MB degradation on Fe₃O₄, Fe₃O₄@TiO₂ and Fe₃O₄@SiO₂ NPs are fitted to three models, to understand the controlling mechanism of the degradation processes as shown in Figure 9.

(i) The zero-order kinetic model can be expressed by [57]

\[
\frac{C_t}{C_0} = 1 - \frac{k_0}{C_0} t
\]

Where, \(C_0\) is the initial MB concentration, \(C_t\) the concentration of MB at time \(t\), and \(k\) is the degradation rate coefficient. \(C_t/C_0\) vs \(t\) plot gives a straight line, and its slope is \(-k/C_0\), as shown in figure 9(a).

(ii) The linear form of first-order kinetic model can be stated by [57]

\[
Ln \frac{C_t}{C_0} = -k t
\]

\(k\) is determined from the slope of the straight line of \(-Ln(C_t/C_0)\) vs \(t\) plot, as shown in figure 9(b). (iii) The second order kinetic model can be stated by [57]

\[
\frac{1}{C_t} - \frac{1}{C_0} = k_2 t
\]

\(k\) is indicated by the slope of the straight line of \((1/C_t - 1/C_0)\) vs \(t\) plot, as shown in figure 9(c). The determined values of \(k\) for the three tested photocatalysts with their respective coefficient of determination \(R^2\), are shown in Table 2. As observed from the results, the kinetics of the degradation of MB for Fe₃O₄ and Fe₃O₄@SiO₂ NPs photocatalysts are best described by the zero-order model, with \(R^2\) values close to unity, \(k\) value for Fe₃O₄@SiO₂ NPs (0.01 min⁻¹) is higher than \(k\) value for Fe₃O₄ NPs (0.008 min⁻¹). Degradation of MB by Fe₃O₄@TiO₂ NPs

| Photocatalysts | Zero-order model | First-order model | Second-order model |
|---------------|------------------|-------------------|-------------------|
|               | \(K_0\) (min⁻¹)  | \(R^2\)           | \(K_1\) (min⁻¹)  | \(R^2\)           | \(k_2\) (min⁻¹)  | \(R^2\)           |
| Fe₃O₄        | 0.0085           | 0.97              | 0.0142           | 0.92              | 0.0328           | 0.75              |
| Fe₃O₄@TiO₂   | 0.0073           | 0.92              | 0.0066           | 0.97              | 0.0063           | 0.99              |
| Fe₃O₄@SiO₂   | 0.0102           | 0.99              | 0.0182           | 0.87              | 0.0649           | 0.53              |

Figure 9. Photodegradation of MB by Fe₃O₄, Fe₃O₄@TiO₂ and Fe₃O₄@SiO₂ NPs under irradiation for 140 min, based on kinetic models; (a) Zero-order model; (b) First-order model; (c) Second-order model.
can be fitted by the first order model, with \( k \) value of \( \sim 0.0066 \, \text{min}^{-1} \). However, MB degradation by Fe\(_3\)O\(_4@\)TiO\(_2\) NPs as a photocatalyst is best described by the second order model, with \( k \) value of 0.0063 \( \text{min}^{-1} \) being the least, which indicate that the degradation rate of MB is boosted by using Fe\(_3\)O\(_4@\)SiO\(_2\) NPs.

The removal efficiency (E) or de-colouration rate is calculated using the following formula [58]:

\[
E = \frac{C_0 - C_t}{C_0} \times 100
\]

Under solar light irradiation, Fe\(_3\)O\(_4\) photocatalyst could decompose 89% of MB after 140 min irradiation time. When Fe\(_3\)O\(_4\) NPs coated with silica layer and used as a photocatalyst, an increase of MB photodegradation efficiency is observed (97%). However, as Fe\(_3\)O\(_4\) NPs coated with titania layer the exhibited MB photodegradation efficiency is 56%, under UV irradiation as shown in figure 10(a).

The photocatalytic experiments reveal that the silica coating could importantly improve the photocatalytic performance of Fe\(_3\)O\(_4\) photocatalyst. The Fe\(_3\)O\(_4@\)SiO\(_2\) yield the highest MB degradation efficiency, which is about 1.7 times the degradation efficiency of the Fe\(_3\)O\(_4@\)TiO\(_2\). TEM images show that Fe\(_3\)O\(_4\) nanocluster surface is completely shielded with titania layer. Which is confirmed by the high reduction of the Fe\(_3\)O\(_4\) XRD peaks in Fe\(_3\)O\(_4@\)TiO\(_2\) pattern (figure 3). Thus, the photodegradation activity is mainly obtained by TiO\(_2\) layer that absorbs UV light. Conversely, in Fe\(_3\)O\(_4@\)SiO\(_2\) photocatalyst, the photocatalytic degradation is attained by the core of the particles (Fe\(_3\)O\(_4\)) and the silica coating serve as a protective layer to enhance the stability of the photocatalyst in the aqueous solution and, furthermore, to enhance the optical absorption.

Recyclability is the main advantage of the magnetic photocatalysts. The reusability evaluation is carried out for four times as shown in figure 10(b). The photocatalytic efficiency of the recycled Fe\(_3\)O\(_4\) NPs after four cycles reduced from 89% to 62%, this is can be attributed to the Fe\(_3\)O\(_4\) NPs’ tendency to agglomerate, due to the magnetic dipole interaction, that leads to the reduction of the surface area, and the degradation efficiency.

However, the recycled Fe\(_3\)O\(_4@\)TiO\(_2\) and Fe\(_3\)O\(_4@\)SiO\(_2\) NPs showed insignificant change in the degradation efficiency for four cycles, demonstrating their stability and effectiveness in the photodgradation of organic pollutants from water. The high efficiency obtained by Fe\(_3\)O\(_4@\)SiO\(_2\) for four cycles indicates that Fe\(_3\)O\(_4@\)SiO\(_2\) is a promising photocatalyst.

Furthermore, the stability of the photocatalysts are checked by measuring the surface charge of the NPs. The measured zeta potential values are about +7, −43 and −54 mV for Fe\(_3\)O\(_4\), Fe\(_3\)O\(_4@\)TiO\(_2\) and Fe\(_3\)O\(_4@\)SiO\(_2\) NPs, respectively. The small positive charge on the surface of Fe\(_3\)O\(_4\) indicates their affinity to agglomerate into clusters and their low stability. Whereas, the huge negative charge on the silica and titania surface generates coulomb repulsion among the particles to boost the inter-particle spacing. Leading to a high stable and homogenous colloidal solution. Thus, the high reusability of of the Fe\(_3\)O\(_4@\)TiO\(_2\) and Fe\(_3\)O\(_4@\)SiO\(_2\) NPs is promising.

Figures 11(a), (b) shows MB aqueous solution before and after solar irradiation, respectively. The fading of the dark blue color indicates the degradation of the MB dye, where the Fe\(_3\)O\(_4@\)SiO\(_2\) magnetic photocatalysts are collected by the external magnet to be used for another purification cycle. Figure 8(c) demonstrates the mechanism of MB degradation, using Fe\(_3\)O\(_4@\)TiO\(_2\) as a photocatalyst. First, titania layer absorbs photons (UV radiation) with energy larger than its bandgap, so electron-hole pairs (excitons) are generated. Then the electron and hole in the exciton separate apart, the free electrons transfer towards the conduction band and the holes to the valence band at the interface (PEG layer), where electric field exists, due to depletion zone of core–shell interface. Thus, the existence of an extremely thin layer of PEG with a large bandgap insulating material,
prevents electrons transfer between titania and Fe₃O₄ and decreases electrons (e⁻) and holes (h⁺) recombination process.

Consequently, e⁻ and h⁺ transfer to the photocatalyst surface. The e⁻ reduce O₂ to superoxide radicals (O₂⁻·). Simultaneously, the h⁺ oxidize H₂O to form hydroxyl radicals (OH·*), that works on MB degradation or h⁺ directly oxidize MB. The formed reactive species, O₂⁻·, OH·*, and h⁺ initiate the redox reactions and degradation of MB into CO₂, H₂O, or inorganic ions. As shown in figure 8(c). Finally, the photocatalyst is extracted from the media by an external magnet [46, 59].

Similar mechanism of MB degradation using Fe₃O₄@SiO₂ as photocatalyst, the silica layer enhances the transfer of the photoinduced charge to the photocatalyst surface, and improves the light harnessing ability of Fe₃O₄, which could be beneficial for photocatalytic performance. This mechanism is most effective when photocatalytic oxidation is conducted in the presence of water (as it is done in our experiment). Furthermore, photodegradation is boosted by enhancing the transportation of e⁻ and h⁺, to increase the effectiveness of charge separation and to increase the lifetime of the photo-generated excitons.

4. Conclusions

Magnetic photocatalysts, namely Fe₃O₄@TiO₂ NPs and Fe₃O₄@SiO₂ NPs, are synthesized using a non-thermal method and a modified Stöber method, respectively. Their photocatalytic degradation performance is investigated using MB dye. The as synthesized NPs have a spherical shape with core/shell characteristic, and the typical size of Fe₃O₄@TiO₂ NPs (73 nm) is smaller than Fe₃O₄@SiO₂ NPs (475 nm). TiO₂ and SiO₂ are fine-coated on the surface of Fe₃O₄ NPs with thickness of few tens of nanometers. However, TiO₂ layer is thicker than SiO₂ layer, which affects their photodegradation mechanism. The as synthesized NPs show perfect superparamagnetic behavior, hence they are believed to be promising for wide range of engineering applications. The photocatalytic activity results show that Fe₃O₄@SiO₂ NPs, under solar irradiation, exhibit a distinguished degradation efficiency of MB as high as 97%. This later efficiency is higher than Fe₃O₄ NPs (89%), and is much higher than the degradation efficiency obtained by Fe₃O₄@TiO₂ NPs (56%) under UV irradiation. The improved photocatalytic performance of Fe₃O₄@SiO₂ NPs can be attributed to the increased surface area, enhanced optical absorption, the effective generation of excitons in the Fe₃O₄ core, dissociation of the photo-generated charges, then the separation of the e⁻ and h⁺ at the core/shell interface, and the enhancement of exciton’s life time. Moreover, the kinetics of degradation of MB for Fe₃O₄@SiO₂ NPs photocatalyst is fitted by the zero-order model, and exhibit the highest degradation rate of MB. Therefore, the Fe₃O₄@SiO₂ NPs can be extensively used in several environmental applications for organic contaminant treatment.

Acknowledgments

The authors acknowledge the financial support received from United Arab Emirate University (UAEU) research fund, Startup Grants no. 31N233 and 31N256.

ORCID iDs

Aiman Ziout https://orcid.org/0000-0002-2355-3084
Ali Hilal-Alnaqbī https://orcid.org/0000-0003-3382-3540
References

[1] Chequer F M D, Gisele Oliveira A R, Ferraz E R A, Cardoso J C, Zanoni M V B and Oliveira D P 2013 Textile dyes: dyeing process and environmental impact Eco-Friendly Textile Dyeing and Finishing (Rijeka: InTech) 151–76 ch 6

[2] Lee K M, Lai C W, Ngai K S and Juan J C 2016 Recent developments of zinc oxide based photocatalyst in water treatment technology: a review Water Res. 88 428–48

[3] Modwia A, Abhbo MA, Hasand E A, Al-Duaija O K and Houas A 2017 Adsorption kinetics and photocatalytic degradation of malachite green (MG) via Cu/ZnO nanocomposites Journal of Environmental Chemical Engineering 5 5954–60

[4] Saikia L, Bhuyan D, Saikia M, Malakar B, Dutta D K and Sengupta P 2015 Photocatalytic performance of ZnO nanomaterials for self-sensitized degradation of malachite green dye under solar light Applied Catalysis A: General 490 42–9

[5] Lembikiwi W, Khaled S, Mecerri M, Lounici H and Drouiche N 2012 Degradation of dispersed red 167 azo dye by bipolar electrocoagulation Separation Science and Technology 47 1682–8

[6] Lembikiwi W, Drouiche N, Belaicha N, Oubagha N, Bazzir A and Meceri M O 2015 Kinetic study of the adsorption of textile dyes on synthetic hydroxyapatite in aqueous solution Journal of Industrial and Engineering Chemistry 23 352–7

[7] Chenna M, Chemal R, Drouiche N, Messaoudi K and Lounici H 2016 Effectiveness of a physicochemical coagulation/flocculation process for the pretreatment of polluted water containing Hydroben Blue Dye Desalinization and Water Treatment 57 27003–14

[8] Mayoufi A, Niub M F and Houas A 2014 Doping level effect on visible-light irradiation W doped TiO2-anatase photocatalysts for Congo red photodegradation Comptes Rendus Chimie 17 818–23

[9] Umar M and Aziz H A 2013 Photocatalytic degradation of organic pollutants in water In Organic Pollutants—Monitoring, Risk and Treatment (Rijeka: InTech)

[10] Shoua M, Niafa M F, Rayes A, Swaminathan M and Houas A 2017 TiO2–PANI/Cork composite: a new floating photocatalyst for the treatment of organic pollutants under sunlight irradiation J. Environ. Sci. 60 3–13

[11] Shoua M, Niub M F, Rayes A, Ochis T and Houas A 2017 Application of solar light for photocatalytic degradation of Congo red by a floating salineic acid-modified TiO2/palm trunk photocatalyst Comptes Rendus Chimie 20 181–9

[12] Fujishima A, Zhang X and Tryk D A 2008 TiO2 photocatalysis and related surface phenomena Surf. Sci. Rep. 116 515–82

[13] Chong M N, Jin B, Chow C W K and Saint C 2010 Recent developments in solar water technology: a review Water Res. 44 2997–3027

[14] Rosman R, Saifullah B, Maniam S, Dorniani D, Hussein M Z and Fakurazi S 2018 Improved anticancer effect of magnetite nanocomposite formulation of GALLIC Acid (Fe3O4–PEG–GA) against lung, breast and colon cancer cells Nanomaterials 8 83–97

[15] Deng H, Li X, Peng Q, Wang X, Chen J and Li Y 2005 Monodisperse magnetic single-crystal ferrite microspheres Angewandte Chemie International Edition 44 2782–5

[16] Yang D P, Gao F, Cui D X and Yang M 2009 Microwave rapid synthesis of nanoporous Fe3O4 magnetic microspheres Current Nanoscience 5 485–8

[17] Li C, Wei Y, Liata V, Zhu Y and Zhu J 2013 Microwave–solvolothermal synthesis of Fe3O4 magnetic nanoparticles Mater. Lett. 107 23–6

[18] Jiang W, Yang H C, Yang S Y, Horng B H, Hung J C, Chen Y C and Hong C Y 2004 Preparation and properties of superparamagnetic nanoparticles with narrow size distribution and biocompatible J. Magn. Magn. Mater. 283 210–4

[19] Hu J, Wang H, Dong F and Wu Z 2017 A new strategy for utilization of NIF from solar energy–Promotion effect generated from photo-thermal effect of Fe3O4@SiO2 for photocatalytic oxidation of NO Applied Catalysis B: Environmental 204 384–92

[20] Wu J M, Hayakawa S, Tsuru K and Osaka A 2002 In vitro bioactivity of anatase film obtained by direct deposition from aqueous titanium tetrafluoride solutions Thin Solid Films 414 275–80

[21] Fujishima A, Rao T N and Tryk D A 2000 Titanium dioxide photocatalysis Journal of Photochemistry and Photobiology C: Photochemistry Reviews 1 1–21

[22] Salamat S, Younesi H and Bahramifar N 2017 Synthesis of magnetic core–shell Fe3O4@TiO2 nanoparticles from electric arc furnace dust for photocatalytic degradation of steel mill wastewater RSC Advances 7 19391–405

[23] Kumara A A, Rajinia A and Venkatathri N 2017 Synthesis and characterization of magnetically separable porous titanium silicate nanocomposite catalyst for environmental applications Materials Today: Proceedings 4 19–24

[24] Chanthorn P, Charoenlap N, Tomapatanaget B and Insin N 2017 Colloidal titania-silica-iron oxide nanocomposites and the effect from silica thickness on the photocatalytic and bactericidal activities J. Magn. Magn. Mater. 427 54–9

[25] Hernandez J V, Coste S, Murillo A G, Romo F C and Kasabia A 2017 Effects of metal doping (Cu, Ag, Eu) on the electronic and optical behavior of nanostructured TiO2–Allays Compd. 710 355–63

[26] Zangeneh H, Zinatizadeh A A L, Habibi M, Akia M and Hasnain M I 2015 Photocatalytic oxidation of organic dyes and pollutants in wastewater using different modified titanium dioxides: a comparative review Journal of Industrial and Engineering Chemistry 26 1–36

[27] Carp O, Huisman C L and Reller A 2004 Photoinduced reactivity of titanium dioxide Prog. Solid State Chem. 32 33–177

[28] Dong H, Zeng G, Tang L, Fan C, Zhang C, He X and He Y 2015 An overview of limitations of TiO2-based particles for photo-catalytic degradation of organic pollutants and the corresponding countermeasures Water Res. 79 128–46

[29] Hu J, Wang H, Dong F and Wu Z 2017 A new strategy for utilization of NIF from solar energy—promotion effect generated from photothermal effect of Fe3O4@SiO2 for photocatalytic oxidation of NO Applied Catalysis B: Environmental 204 584–92

[30] Farmany A, Shim S and Mahdavi M H 2016 Ultrasound-assisted synthesis of Fe3O4@SiO2 core/shell with enhanced adsorption capacity for diazinon removal J. Magn. Magn. Mater. 416 75–80

[31] Guo F, Ma B W, Yin A Y, Fan K N and Dai W L 2011 Photodegradation of rhodamine B and 4-chlorophenol using plasmonic photocatalyst of Ag-Fe3O4@SiO2 magnetic nanoparticle under visible light irradiation Applied Catalysis B: Environmental 101 580–6

[32] Li G T, Wang K H, Zhang X W, Hu C, Yu I C, Chan B C Y and Wong P K 2009 Degradation of acid orange 7 using magnetic AgBr under visible light: the roles of oxidizing species Chemosphere 76 1185–91

[33] Liu J, Zuoa S, Yua L, Yua Y, Lia B and Chen P 2013 Visible light photodegradation of methylene blue by AgBr–TiO2/SiO2@Fe3O4 magnetic photocatalysts Particuology 11 728–31

[34] Wysocka I, Kowalska E, Trzcińska K, Łapińska M, Nowaczyk N and Zielińska-Jurek A 2018 UV–vis-induced degradation of phenol over magnetic photocatalysts modified with Pt, Pd, Cu and Au nanoparticles Nanomaterials 8 28–48

[35] He Q, Zhang Z, Xiong J, Xiong Y and Xiao H 2008 A novel biomaterial: Fe3O4@TiO2 core–shell nanoparticle with magnetic performance and high visible light photocatalytic activity Opt. Mater. 31 380–4

[36] Khoshan S, Dagher S, Al Omarti S, Tit N, Elnahaj E, Mathew B and Hilal-Allaqabi A 2017 Photo-thermal characteristics of water–based Fe3O4@SiO2 nanofluid for solar–thermal applications Material Research Express 4 055701
[37] Shen J, Zhu Y, Yang X, Zong J, Zhang J and Li C 2012 One-pot hydrothermal synthesis of graphene quantum dots surface-passivation by polyethylene glycol and their photoelectric conversion under near-infrared light New J. Chem. 36 97–101
[38] Shameli K, Bin Ahmad M, Jazayeri S D, Sadaghat S, Shahnazadeh P, Jahangirian H, Mahdavi M and Abdollahi Y 2012 Synthesis and characterization of polyethylene glycol mediated silver nanoparticles by the green method International Journal of Molecular Sciences 13 66 39–50
[39] Pan H, Xia Y, Qin M, Cao Y and Wang W 2015 A simple procedure to improve the surface passivation for single molecule fluorescence studies Phys. Biol. 12 045006
[40] Luo N, Weber J K, Wang S, Luan B, Yue H, Xi X, Yang Z, Wei W, Zhou R and Ma G 2017 PEGylated graphene oxide elicits strong immunological response despite surface passivation Nat. Commun. 177 14 537
[41] Khashan S, Dagher S, Tit N, Alazzam A and Obidat I 2017 Novel method for synthesis of Fe3O4@TiO2 core/shell nanoparticles Surface & Coatings Technology 322 92–8
[42] Hasanpour A, Niyaifar M and Amighian M H J 2012 A novel non-thermal process of TiO2-shell coating on Fe3O4-core nanoparticles Journal of Physics and Chemistry of Solids 73 1066–70
[43] Liu X, Tao Y, Mao H, Kong Y, Shen J, Deng L and Yang L 2017 Construction of magnetic-targeted and NIR irradiation-controlled drug delivery platform with Fe3O4@Au@SiO2 nanospheres Ceram. Int. 43 5 061–7
[44] Injumpa W, Ritprajak P and Insin N 2017 Size-dependent cytotoxicity and inflammatory responses of PEGylated silica-iron oxide nanocomposite size series J. Magn. Magn. Mater. 427 60–6
[45] Xu J, Yang H, Fu W, Du K, Sui Y, Chen J, Zeng Y, Li M and Zou G 2007 Preparation and magnetic properties of magnetite nanoparticles by sol-gel method J. Magn. Magn. Mater. 309 307–11
[46] Abbas M, Rao B P, Reddy V and Kima C G 2014 Fe3O4/TiO2 core/shell nanocubes: single-batch surfactant less synthesis, characterization and efficient catalysts form ethylene blue degradation Ceram. Int. 40 11 177–86
[47] Du G H, Liu Z L, Xia X, Chu Q and Zhang S M 2006 Characterization and application of Fe3O4/SiO2 nanocomposites J. Sol-Gel Sci. Technol. 39 285
[48] Dagher S, Haik Y, Ayesh A I and Tit N 2014 Synthesis and optical properties of colloidal CuO nanoparticles J. Lumin. 151 149–54
[49] Gelb L D and Gubbins K E 1998 Characterization of porous glasses: simulation models, adsorption isotherms, and the Brunauer–Emmett–Teller analysis method Langmuir 14 2 097–111
[50] Luisa Ojeda M, Marcos Esparza J, Campero A, Cordero S, Kornhauser I and Rojas F 2003 On comparing BJH and NLDFT pore-size distributions determined from N2 sorption on SBA-15 substrata Physical Chemistry Chemical Physics 5 1859
[51] Cullity B D and Graham C D 2009 Introduction to Magnetic Materials 2nd edn (Hoboken, NJ, USA: Wiley-IEEEPress)
[52] Kodama R H 1999 Magnetic nanoparticles J. Magn. Magn. Mater. 200 359–72
[53] Suzuki M, Fullem S I, Suzuki I S, Wang L and Zhong C J 2009 Observation of superspin-glass behaviour in Fe3O4 nanoparticles Phys. Rev. B 79 024418
[54] Kodama R H, Berkowitz A E, McNiff E J and Foner S 1997 Surface spin disorder in ferritin nanoparticles (invited) J. Appl. Phys. 81 5 552–7
[55] Mørup S, Brok E and Frandsen C 2013 Spin structures in magnetic nanoparticles Journal of Nanomaterials 2013 720829
[56] Mørup S, Madsen M B, Franck J, Villadsen J and Koch C J W 1983 A new interpretation of Mossbauer spectra of microcrystalline goethite: ‘super-ferromagnetism or super-spin-glass behavior?’ J. Magn. Magn. Mater. 40 163–74
[57] Atkins P and de Paula J 2006 Physical chemistry The Rates of Chemical Reactions 8th edn (New York: Oxford University Press) pp 791–829 ch 22
[58] Soltiman A M, Eluuccary S A, Alic I M and Ayesh A I 2017 Photocatalytic activity of transition metal ions-loaded activated carbon: degradation of crystal violet dye under solar radiation Journal of Water Process Engineering 17 245–55
[59] Haque F, Daeneke T, Kalantar-zadeh K and Ou J Z 2018 Two-dimensional transition metal oxide and chalcogenide based photocatalysts Nano-Micro Letters 10 23