Visible Light-Driven Photocatalytic Activity of Magnetic Recoverable Ternary $\text{ZnFe}_2\text{O}_4/\text{rGO}/\text{g-C}_3\text{N}_4$ Nanocomposites

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Abstract

$\text{ZnFe}_2\text{O}_4/\text{rGO}/\text{g-C}_3\text{N}_4$ ternary nanocomposite photocatalysts with different $\text{ZnFe}_2\text{O}_4/\text{g-C}_3\text{N}_4$ weight ratio (0.5, 0.75, 1) were prepared by a stepwise solvothermal method using ethylene glycol as the solvent. Physicochemical methods such as X-ray diffraction, UV-Vis diffuse reflectance spectroscopy and photoluminescence spectroscopy were applied in order to characterize the composites. The formation of a meso-/macroporous structure with specific surface area between 67 and 77 $\text{m}^2 \text{g}^{-1}$ was confirmed by N_2 adsorption/desorption. The bandgap of the composites was found to be lower (2.30 eV) than that of $\text{g-C}_3\text{N}_4$ (2.7 eV). In contrast to pure $\text{g-C}_3\text{N}_4$, the composites showed no fluorescence, i.e. no recombination of e^-/h^+ took place. All samples, including pure $\text{g-C}_3\text{N}_4$ and ZnFe_2O_4 , were tested for adsorption and photocatalytic degradation of aqueous malachite green model solutions (10^{-5} M) under visible light irradiation ($\lambda > 400 \text{ nm}$). The results show that the prepared nanocomposites have higher absorption and photocatalytic activity than the pristine $\text{g-C}_3\text{N}_4$ and ZnFe_2O_4 and can be successfully used for water purification from organic azo-dyes.

Keywords: Graphitic carbon nitride; reduced graphene oxide; zinc ferrite; photocatalysis; malachite green decomposition.

1. Introduction

Synthetic organic dyes are severe water pollutants causing environmental problems. They are typically aromatic compounds with structural variations, many of them resistant to degradation.¹ Among them, malachite green is an organic water pollutant known to be harmful for living creatures because of its potential carcinogenicity, mutagenicity and teratogenicity in mammals.² Depending on the polluted water composition, different methods have been applied in order to solve water contamination problems, including biological reactions,³ sedimentation,^{4–6} coagulation,^{7,8} adsorption,⁵ reverse osmosis,^{9,10} membrane filtration,¹¹ ion exchange,¹² etc. Photocatalytic processes have also been applied, and much effort has been spent on the development of different semiconductors as photocatalysts among which TiO_2 and its modifications is well known.^{13–18}

The aim of the research presented here is to develop new photocatalysts and to overcome the main limitation of TiO_2 , i.e. its wide band gap (3.2 eV) that makes it active

under UV light irradiation only (about 5% of sunlight). Recently the graphite analogue, graphitic carbon nitride, $\text{g-C}_3\text{N}_4$, raised interest due to its unique electronic structure. It is a non-metallic polymer with n-type semiconducting behavior and unique electrical, optical, structural and physicochemical properties. Like graphite, $\text{g-C}_3\text{N}_4$ has a two-dimensional planar π conjugation structure, able to enhance the electron transfer processes due to its excellent electronic conductivity.¹⁹ With its medium-sized band gap and its thermal and chemical stability in ambient environment, it has become one of the most promising photocatalytic materials.¹⁹ The interest in its application as a photocatalyst increased after its photocatalytic properties were discovered by Wang et al.²⁰ However, $\text{g-C}_3\text{N}_4$ also has some disadvantages such as a small specific surface area, a small number of active centers, quick recombination of the photo-induced e^-/h^+ , low mobility of photoinduced e^-/h^+ ²¹ and an wide band gap (2.7 eV).²² These shortcomings can be avoided by adding a co-catalyst to $\text{g-C}_3\text{N}_4$ to pre-

pare nanocomposites. In recent years, particular interest has appeared in composites of g-C₃N₄ and reduced graphite oxide, rGO, due to the large specific surface area of rGO and its ability to efficiently separate photo-induced charges.²³ The above effect can also be achieved by combining g-C₃N₄ with multi-wall carbon nanotubes.²⁴ However, these nanocomposites can only solve two of the above disadvantages of g-C₃N₄ as a photocatalyst. The wide band gap of 2.7 eV limits the application of visible light. In order to use g-C₃N₄ as a photocatalyst with visible light, it may be combined with other semiconductor materials with a narrower forbidden zone. Due to its narrow band gap of 1.9 eV, ZnFe₂O₄ as a co-catalyst can absorb a wider range of visible light wavelengths. It may also show improved separation of photogenerated electron-hole pairs. Its magnetic properties facilitate the removal of the composites from the reaction mixture, so they can be reused.²⁵ In the literature available, there are publications presenting studies on triple nanocomposites such as CoMoS₂/rGO/C₃N₄ with visible light photocatalytic activity for hydrogen evolution,²⁶ C₃N₄/rGO/TiO₂^{27,28} for decomposition of methyl orange, rhodamine B, and phenol under visible light, and C₃N₄/rGO/WO₃ for degradation of methylene blue.²⁹ Both the studies mentioned and our experience with ZnFe₂O₄ as photocatalyst suggested that ZnFe₂O₄/rGO/g-C₃N₄ would be a promising composition to study, as it potentially could overcome g-C₃N₄ shortcomings as photocatalyst as well as take advantage of rGO for the separation of photo-induced charges. The photocatalytic properties of the nanocomposites ZnFe₂O₄/rGO/g-C₃N₄ were tested for removal of malachite green as representative pollutant under visible light irradiation, showing better activity than the individual semiconductors. The work presented here on the preparation and the properties of ZnFe₂O₄/rGO/g-C₃N₄ can contribute both to the knowledge of inorganic synthesis of such composites and to the improved photocatalytic removal of organic dyes from water.

2. Experimental

2. 1. Materials

Chemicals such as urea (puriss. p.a., Fluka, Switzerland), graphite, Zn(NO₃)₂ · 6H₂O, Fe(NO₃)₃ · 9H₂O, and CH₃COONa · H₂O (all p.a., Sigma-Aldrich, USA) were used in this study.

2. 2. Synthesis of the Samples

2. 2. 1. Synthesis of Graphitic Carbon Nitride, g-C₃N₄

Thermal polycondensation of urea in a closed crucible at 550 °C for 5 h was applied. The powder was dispersed in water and homogenized by stirring for 1 h, followed by filtering, washing and drying at 50 °C overnight. The successful synthesis was confirmed by XRD and TEM analyses.

2. 2. 2. Synthesis of Reduced Graphene Oxide, rGO

Graphene oxide was prepared by using the modified Hummer's method starting from graphite flakes.³⁰ In a typical procedure, 0.5 g of graphite was dispersed in 50 mL mixture of conc. H₂SO₄ and conc. H₃PO₄ (volume ratio 9:1) and then ultrasonicated for 1 hour. After that, 6 g of KMnO₄ was added and magnetically stirred for 5 h followed by 12 h stirring at 50 °C. The so prepared mixture was cooled to room temperature and transferred in a beaker containing 100 g of ice. After stirring and melting of the ice, 20 mL of 30% H₂O₂ solution was added dropwise in order to remove the unreacted KMnO₄. The suspension immediately changed its color from purple to yellow, indicating the formation of graphene oxide. The solid phase was separated by filtration and then dispersed in 100 mL of 5% HCl solution in order to remove all the metal cations and then separated again by centrifugation and washing with water until a pH = 7. The GO obtained was reduced further to rGO by hydrothermal treatment in a PTFE-lined autoclave at 180 °C for 12 h using hydrazine as a reducing agent.

2. 2. 3. Synthesis of the Composites ZnFe₂O₄/rGO/g-C₃N₄

A solvothermal method was used to prepare the composites. The metal salts Zn(NO₃)₂ · 6H₂O and Fe(NO₃)₃ · 9H₂O were dissolved in 50 mL of ethylene glycol, EG, with ratio n(Zn²⁺):n(Fe³⁺) = 1:2. The rGO was added and dispersed by 30 min magnetic stirring and 2 h of sonication. After g-C₃N₄ was added, the suspension was stirred for 30 min by magnetic stirring, followed by 30 min sonication in an ultrasonic bath. After adding 3 g of CH₃COONa · 2H₂O and stirring for 30 min, the metal ions were precipitated. The mixture was transferred to a 75 mL PTFE autoclave and kept at 180 °C for 24 h. By varying the ZnFe₂O₄/g-C₃N₄ mass ratio (0.5, 0.75, 1), three ZnFe₂O₄/rGO/g-C₃N₄ composites containing 5 wt% rGO were prepared. They are mentioned further in the text as CN50 (ZnFe₂O₄ : g-C₃N₄ = 0.5), CN75 (ZnFe₂O₄ : g-C₃N₄ = 0.75), and CN100 (ZnFe₂O₄ : g-C₃N₄ = 1).

2. 3. Methods for Characterization of the Samples

X-Ray Diffraction to determine the crystal structure of the materials was performed using a PANalytical Empyrean X-ray diffractometer in the 2θ range of 15–80° using CuKα radiation (λ = 0.15405 nm) for the nanocomposites and in 2θ range of 10–80° for the individual components, steps of 0.01° and 20 seconds exposure time at each step. The average crystallite size was calculated using the well-known Scherrer's equation.³¹ The microstructural information of the ZnFe₂O₄ was extracted by

full profile Rietveld method using the FullProf Suite software.³² UV-Vis absorption spectroscopy was applied using an Evolution 300 UV-Vis spectrometer (Thermo Scientific) for measuring the absorption of the samples in the range of 200–900 nm. Bandgap energies were calculated from the UV-Vis absorption spectra in the range from 200 to 400 nm according to Tauc's equation $ah\nu = A(h\nu - E_g)^{n/2}$, where A is a constant independent of $h\nu$, E_g is the semiconductor bandgap and n depends on the type of transition.³³ Textural characteristics such as specific surface area, total pore volume, and pore size distribution were determined at -196°C using a TriStar II 3020 apparatus (Micromeritics). The total pore volume was estimated at a relative pressure P/P_0 0.989. Transmission electron microscopy (TEM): a JEOL JEM 2100 microscope was used at 200 kV and up to 100k magnification for characterization of the morphology of the samples. Particle size distribution analysis was performed by using ImageJ software.³⁴

2. 4. Photocatalytic Tests

The photocatalytic tests were performed using a slurry of 0.5 g catalyst L^{-1} and a 10^{-5} M aqueous solution of Malachite Green oxalate (MG), (Chroma GmbH) as a model pollutant. The equipment and the procedure applied were similar with those used in our previous studies.^{14–18,35,36} For illumination 15W white LED (manufactured by V-TAC), 418–700 nm, situated at 10 cm distance above the slurry was used.

3. Results and Discussion

3. 1. Characterization of the Samples

3. 1. 1. Characterization of the Phase Composition by X-ray Diffraction

The phase composition, cell parameters and crystallite size of the samples were determined using the X-ray diffrac-

Figure 1. XRD patterns, from bottom to top (a) of the initial samples r-GO, $\text{g-C}_3\text{N}_4$, ZnFe_2O_4 and (b) of the nanocomposites CN50, CN75, CN100

Figure 2. Experimentally observed (dots), Rietveld calculated (continuous line) and difference (continuous bottom line) profiles, obtained after Rietveld analysis of the XRD data (a) ZnFe_2O_4 and (b) the composite CN100. Peak positions are shown at the base line as small markers.

tion analysis. The composition of the initial substances r-GO, g-C₃N₄ and ZnFe₂O₄ were confirmed (Fig. 1, a). The strong diffraction peak observed at 27° 2theta in the pure g-C₃N₄ can be assigned to the (002) diffraction plane of layered g-C₃N₄ (JCPDS 87-1526) (Fig. 1, a). It corresponds to the characteristic interlayer stacking of aromatic segments.³⁷ The nanocomposites mainly show the presence of ZnFe₂O₄ (Fig. 1, b). The presence of g-C₃N₄ in the composites is detected below 30° 2theta shown by an inverted “Δ” (Fig. 1, b).

Rietveld analysis of the XRD data of ZnFe₂O₄ and the composite CN100 was performed (Fig. 2, a, b). The information obtained by the Rietveld refinement was the crystallite size and microstrains as both are related (to extend) to the catalytic properties of the materials.^{38,39}

This is also proven by the BET measurements as it can be seen later in the text (Part 3.1.3). On the other side, the microstrains are related to the density of the defects in the crystal structure. The defects, known as active centres in catalysis, are places (especially on the surface) with lower potential energy where the reaction between solid/liquid (or solid/vapor) occurs. Although this is not always true in context of photocatalysis as defects can also act as recombination centres for photogenerated e⁻/h⁺ pairs leading to lower activity.

The lattice parameters, crystallite size, and the microstrain of the composites and the pure ZnFe₂O₄ are shown in Table 1. It can be seen that the increasing content of ZnFe₂O₄ in the composites is causing changes in all the parameters mentioned. All the values are getting closer to those of the pure ZnFe₂O₄. The microstrain is decreasing in the line 0.0177 (CN50), 0.0147 (CN75), 0.0116 (CN100), and 0.0053 for the pure ZnFe₂O₄, respectively. The structure of the composites is more defective at lower zinc ferrite content. The latter can be observed in the reduction of the unit cell volume as a result of the microstrains.

3. 1. 2. Characterization of the Sample Morphology by TE

The morphology and the structure of as-synthesized samples observed by TEM are shown in Figure 3. The layered structure of the individual g-C₃N₄ can be seen in Fig. 3, a. The ZnFe₂O₄ particles are flower-shaped on the surface of g-C₃N₄ (Fig. 3, b). The electron diffraction of the samples g-C₃N₄ and ZnFe₂O₄ is shown in Fig. 3, c, d, respectively. It is used as supplementary analysis to the XRD and approves the successful preparation of ZnFe₂O₄ and g-C₃N₄.

With increasing ZnFe₂O₄ content in the composites, polydispersed agglomerates are formed. The particle size distribution for CN50 is between 5–10 nm (Fig. 3, e), in accordance with the XRD data.

3. 1. 3. Textural Characterization

Nitrogen adsorption – desorption isotherms measured at –196 °C on powdered samples (Fig. 4, a) showed that the samples are of type IV, which is the typical characteristic of mesoporous materials according to the IUPAC classification.⁴⁰ The isotherm of ZnFe₂O₄ with H1 loop is typical for well-defined cylindrical pores or agglomerates of approximately uniform spheres (Fig. 4, a). The H3 loop for the g-C₃N₄ and the composites are distinctive for non-rigid aggregates of plate-like particles with slit-shaped pores. The hysteresis loops observed are characteristic of mesoporous solids and their shape exhibits a change in the pore structure. Macropores may be present as well, based on the shape of the hysteresis loops near P/P₀ = 1.⁴¹ The average pore size is rather close for the samples g-C₃N₄, CN50 and CN75 (Table 2), while that of ZnFe₂O₄ is larger and that of CN100 smaller. The composites show a maximum in the pore size distribution at about 25–50 nm,

Table 1. Lattice parameters, crystallite size and microstrain; CN50 (ZnFe₂O₄ : g-C₃N₄ = 0.5), CN75 (ZnFe₂O₄ : g-C₃N₄ = 0.75), and CN100 (ZnFe₂O₄ : g-C₃N₄ = 1).

Sample	Unit cell, Å	Crystallite size, nm	Microstrain, %	R _{wp} , %	χ ²
CN50	8.4312 ± 0.0007	8 ± 0.2	1.77	9.1	1.74
CN75	8.4321 ± 0.0005	9 ± 0.4	1.47	8.4	1.71
CN100	8.4325 ± 0.0003	11 ± 0.4	1.16	7.9	1.68
ZnFe ₂ O ₄	8.4342 ± 0.0002	23 ± 0.3	0.53	7.2	1.53

Table 2. Textural characteristics of the samples studied.

Sample	Specific surface area, S _{BET} , m ² g ⁻¹	Total pore volume, V _{total} , cm ³ g ⁻¹	Average pore size, D _{average} , nm
g-C ₃ N ₄	88	0.47	22
ZnFe ₂ O ₄	34	0.27	32
CN50	72	0.44	25
CN75	77	0.44	23
CN100	67	0.23	14

Figure 3. TEM micrographs of (a) g-C₃N₄ and (b) CN50 presented along with the electron diffraction (c) and (d), respectively. The particles size distribution for CN50 is shown in (e).

while CN100 shows a broad polydispersed pore size distribution (Fig. 4, b).

The pure g-C₃N₄ sample has the largest specific surface area, 88 m² g⁻¹, while pure ZnFe₂O₄ with 34 m² g⁻¹ has the lowest one among the samples tested (Table 2). In spite of the statement that g-C₃N₄ exhibits low S_{BET} ,⁴² 88 m² g⁻¹ is a reasonably good value, comparing for example with

9.6 m² g⁻¹ reported in ref.⁴² for g-C₃N₄ obtained by the same hydrothermal method for 48 h/180 °C (12 h/180 °C in present work). Apparently, the duration of the hydrothermal treatment is influencing the agglomeration of the sample. The addition of rGO and ZnFe₂O₄ caused a reduction of the specific surface area leading to composites with 77, 72, and 67 m² g⁻¹ surface area, which could be due to

Figure 4. Adsorption-desorption isotherms of the pure $g\text{-C}_3\text{N}_4$ and ZnFe_2O_4 , and the composites CN50, CN75, CN100 (a) and BJH pore diameter distribution, determined from the desorption branch of the isotherm (b); V – pore volume, D – pore diameter.

their deposition on the pores of carbon nitride. Quite likely the presence of $g\text{-C}_3\text{N}_4$ inhibits the agglomeration of ZnFe_2O_4 particles and makes them uniformly dispersed.

3. 2. Optical and Photocatalytic Properties

3. 2. 1. Optical Properties

The UV/Vis spectra of $g\text{-C}_3\text{N}_4$, ZnFe_2O_4 and the composites are presented in Fig. 5, a, clearly showing enhanced light absorption of the composites, probably due to interfacial interaction between $g\text{-C}_3\text{N}_4$ and ZnFe_2O_4 .⁴³ It can be expected that the enhanced light absorption could lead to higher photocatalytic activity by generating more photoinduced charge carriers under visible light. Based on these UV/Vis spectra, the band gap energy was calculated for all the samples (Fig. 5, b). The values for the similar band gaps of the composites with energy of 2.30–2.31 eV (538–536 nm), between the values of $g\text{-C}_3\text{N}_4$, 2.7 eV (458

Figure 6. Typical photoluminescence of $g\text{-C}_3\text{N}_4$, compared with the absence for CN50.

Figure 5. (a) UV/Vis spectra and (b) the energy of the forbidden zone, E_g , for all the samples studied

nm) and ZnFe_2O_4 , 2.06 eV (600 nm), confirm their prospective for photocatalytic activity higher than that of $\text{g-C}_3\text{N}_4$.

Such a prospective is also indicated by the absence of fluorescence in the composites, which provides evidence for efficient inhibition of radiative recombination of photogenerated e^-/h^+ (Fig. 6). The strong fluorescence of the pure $\text{g-C}_3\text{N}_4$ related to strong e^-/h^+ recombination (Fig. 6), may explain the low photocatalytic activity of the pristine sample.

3. 2. 2. Degradation of Malachite Green Under Visible Light Irradiation

The photocatalytic performance of the samples for degradation of malachite green under visible light illumination is shown in Fig. 7. In the given range of reaction conditions, adsorption of malachite green on the catalyst surface cannot be neglected (Table 3). However, this was well considered in the subsequent interpretation of collected experimental data. The relevant data for the rate constants are summarized in Table 3.

The rate constant obtained for the photolysis was $0.6 \times 10^{-3} \text{ min}^{-1}$. The pure samples $\text{g-C}_3\text{N}_4$ and ZnFe_2O_4

Figure 7. Photocatalytic performance of as-prepared samples for degradation of malachite green under visible-light illumination.

showed low values for their rate constants: 2.9 and $4.6 \times 10^{-3} \text{ min}^{-1}$, respectively. The rate constants of the composites were higher, and showed increasing values with increasing $\text{ZnFe}_2\text{O}_4/\text{g-C}_3\text{N}_4$ ratio (0.5, 0.75, 1), i.e. 4.0×10^{-3} , 5.1×10^{-3} and $7.7 \times 10^{-3} \text{ min}^{-1}$, respectively. Apparently, ZnFe_2O_4 and $\text{g-C}_3\text{N}_4$ show a synergetic effect, which is best demonstrated for the composite CN100. The highest degradation of malachite green achieved was 63 % for 150 min illumination with visible light. In Table 3, the data for the ratio k/S_{BET} ($\text{min}^{-1} \text{ g m}^{-2}$) are presented, showing the best activity for ZnFe_2O_4 , followed closely by the composite CN100.

The observed photocatalytic activity may be correlated to the physical properties of the catalysts, such as: (i) Surface area: the largest S_{BET} surface area of $\text{g-C}_3\text{N}_4$ among the samples tested could provide more active sites to adsorb and convert MG molecules in comparison with the ZnFe_2O_4 and the composites. However, this is not observed; $\text{g-C}_3\text{N}_4$ may be less active than expected because of its strong e^-/h^+ recombination shown by the fluorescence (Fig. 6). Among the composites, CN100 has less than average S_{BET} but showed the best photocatalytic activity. (ii) Large pore volume: it would favor the diffusion of MG molecules within the pores towards the active sites on the surface of the photocatalysts. However, $\text{g-C}_3\text{N}_4$ with the largest pore volume shows the lowest activity. (iii) Pore size distribution: The composite CN100 has a very broad pore size distribution showing best activity i.e. positively influencing the activity (Fig. 4, b). (iv) Bandgap energy: among all samples tested, the composites have the lowest and equal value for E_g but show different activity. Thus the band gap energy alone cannot explain all differences; the activity is determined by a combination of factors. From this it can be concluded that the most active composite CN100 has an optimum combination of band gap value, $\text{ZnFe}_2\text{O}_4/\text{g-C}_3\text{N}_4$ ratio and absence of e^-/h^+ recombination. The rGO, being present in equal amounts for all the composites, has the function of solid-state electron mediator,^{28, 29} adsorbent, photosensitizer and electron acceptor.²⁸

For the discussion of the mechanism of the photocatalytic reaction, the values of the band edges i.e. the potentials of the current band (CB) and the valence band (VB) of the semiconductors ZnFe_2O_4 and $\text{g-C}_3\text{N}_4$ should be considered. Some of the literature data are summarized

Table 3. Rate constants and extent of malachite green removal based on adsorption on the catalyst surface and degradation.

Sample	Rate constant, $\times 10^{-3} \text{ min}^{-1}$	Rate constant to S_{BET} , $\times 10^{-4}, \text{ min}^{-1} \text{ g m}^{-2}$	Adsorption, %	Degradation after 150 min, %
$\text{g-C}_3\text{N}_4$	2.9	0.395	47	35
ZnFe_2O_4	4.6	1.353	63	44
CN50	4.0	0.556	76	41
CN75	5.1	0.66	78	48
CN100	7.7	1.149	86	63

Table 4. Potentials of current band (CB) and valence band (VB) of ZnFe₂O₄ and g-C₃N₄.

№	ZnFe ₂ O ₄			g-C ₃ N ₄			Ref.
	CB, eV	VB, eV	E _g , eV	CB, eV	VB, eV	E _g , eV	
1	0.29	2.35	2.06	-1.08	1.54	2.62	Present work
2	0.41	2.38	1.97	–	–	–	45
3	-0.06	1.8	1.76	-1.03	1.64	2.67	42
4	-1.54	0.38	1.92	-1.26	1.34	2.60	40
5	–	–	–	–	1.54	–	43

and presented in Table 4 along with data from our study. It can be seen that in the literature for g-C₃N₄ similar values were reported, i.e. CB -1.03 and VB 1.64 eV⁴⁴ as well as -1.26 and 1.34 eV⁴². This is in good agreement with the value for the VB of g-C₃N₄ (1.54 eV) determined by X-ray photoelectron spectroscopy.⁴⁵ The literature data for ZnFe₂O₄ are less consistent: values observed include -0.06 and 1.8 eV⁴⁴ as well as -1.54 eV and 0.38 eV.⁴² Taking into account the literature data for the current and valence band it should be mentioned that the CB and VB values for ZnFe₂O₄ are lying over those for g-C₃N₄ according to ref.⁴⁴ but under values of g-C₃N₄ according to ref.⁴² i.e. inconsistency in the data is observed. This can lead to a different way of the interpretation of energy transfer during the photocatalytic process, particularly the migration of electrons and holes between the current band and the valence band of the semiconductors ZnFe₂O₄ and g-C₃N₄.

For the samples synthesized ZnFe₂O₄ and g-C₃N₄ the band edge positions were evaluated applying the simple equations $E_{VB} = X - E_0 + 0.5E_g$ and $E_{CB} = E_{VB} - E_g$. The symbols used E_{CB} , E_{VB} , and X are showing the potentials of the conduction band, of the valence band and the electronegativity of the semiconductors ZnFe₂O₄ or g-C₃N₄ defined as the geometric average of the absolute electronegativity of the constituent atoms.⁴⁶ According the literature data the energy of the free electrons on the hydrogen scale E_0 is about 4.5 eV.⁴⁶ For the semiconductors ZnFe₂O₄ and g-C₃N₄ the X values were calculated to be 5.82 and 4.73 eV, respectively. Following this, the bottom of current band and the top of valence band were calculated to be -1.08 eV and 1.54 eV for g-C₃N₄, and 0.29 eV and 2.35 eV for ZnFe₂O₄, respectively (Table 4). The data for ZnFe₂O₄ are in good agreement with data in ref.⁴⁷ in spite of the different synthetic method used, influencing the value.

Based on these results, a mechanism for photodegradation of MG over ZnFe₂O₄/r-GO/g-C₃N₄ composites can be proposed (Fig. 8). When ZnFe₂O₄/r-GO/g-C₃N₄ composites are exposed to visible light, both ZnFe₂O₄ and g-C₃N₄ are excited. The photogenerated holes and electrons are in the valence band and conduction band, respectively. g-C₃N₄ can effectively absorb visible light to form photoexcited charge carriers.

Because the current band of g-C₃N₄ is more negative than that of ZnFe₂O₄, the electrons migrate into the current

Figure 8. Illustration of the mechanism of the photocatalytic activity of as prepared ZnFe₂O₄/GO/g-C₃N₄ samples.

band of ZnFe₂O₄; holes in the valence band of ZnFe₂O₄ simultaneously migrate to the VB of g-C₃N₄. By this the photogenerated electrons are accumulated on ZnFe₂O₄ and holes accumulated on g-C₃N₄. This in turn with water-dissolved oxygen and adsorbed water molecules causes the formation of radicals. These are well known as oxidizing species and as a result MG degradation takes place. The rGO is improving the photocatalytic properties of the composites obtained by efficient separation of photo-induced charges.²³

4. Conclusions

Nanocomposites of the type ZnFe₂O₄/r-GO/g-C₃N₄, based on coupling of two semiconductors, were successfully prepared by applying solvothermal synthesis, where ethylene glycol was used as a solvent. All of the composites, including the stand alone components, were tested and showed activity for photocatalytic degradation of malachite green in aqueous solution under visible light irradiation. The composites show better activity than the pristine g-C₃N₄ and ZnFe₂O₄, with the CN100 sample in which g-C₃N₄ and ZnFe₂O₄ were present in equal amount showing the highest activity. The improved photocatalytic activity was due to the synergy and the charge transfer between g-C₃N₄ and ZnFe₂O₄ as well as the efficient separa-

tion of photo-induced charges by rGO. More research has to be done to find the optimum $\text{ZnFe}_2\text{O}_4/\text{g-C}_3\text{N}_4$ ratio. The examined composites show potential for degradation of water-dissolved organic pollutants.

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Povzetek

Nanokompozitni fotokatalizatorji $\text{ZnFe}_2\text{O}_4/\text{rGO}/\text{g-C}_3\text{N}_4$ z različnimi masnimi razmerji $\text{ZnFe}_2\text{O}_4/\text{g-C}_3\text{N}_4$ (0,5; 0,75; 1) so bili pripravljene z večstopnejsko solvothermalno metodo ter uporabo etilen glikola kot topila. Za karakterizacijo kompozitov so bile uporabljene različne metode, kot so rentgenska difrakcija, UV-Vis spektroskopija in fotoluminiscenčna spektroskopija. Nastanek mezo-/makroporozne strukture s specifično površino med 67 in 77 $\text{m}^2 \text{g}^{-1}$ je bil potrjen z adsorpcijo/desorpcijo N_2 . Ugotovljeno je bilo, da je v primerjavi z $\text{g-C}_3\text{N}_4$ (2,7 eV) širina prepovedanega pasu kompozitov manjša (2,30 eV). V nasprotju s $\text{g-C}_3\text{N}_4$, kompoziti niso izkazovali fluorescence, torej ni prišlo do rekombinacije e^-/h^+ . Vsi vzorci, vključno s $\text{g-C}_3\text{N}_4$ in ZnFe_2O_4 , so bili testirani za adsorpcijo in fotokatalitično razgradnjo vodnih raztopin zelenega malahita (10^{-5} M) pri obsevanju z vidno svetlobo ($\lambda > 400 \text{ nm}$). Rezultati kažejo, da imajo pripravljene nanokompoziti večjo absorpcijo in fotokatalitično aktivnost kot nemodificirana $\text{g-C}_3\text{N}_4$ in ZnFe_2O_4 in so zato potencialni kandidati za razgradnjo organskih azobarvil v vodi.

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