INFLUENCE OF TiO_2 MODIFICATION BY MWCNTs ON ITS ACTIVITY IN ANTICANCER DRUG REMOVAL FROM WATER

[1]Patrycja WILCZEWSKA, [2]Patrycja PARNICKA, [3]Aleksandra BIELICKA-GIEŁDOŃ, [4]Ewa Maria SIEDLECKA

University of Gdansk, Poland, EU, [1]patrycja.wilczewska@phdstud.ug.edu.pl, [2]patrycja.parnicka@phdstud.ug.edu.pl, [3]a.bielicka-gieldon@ug.edu.pl, [4]ewa.siedlecka@ug.edu.pl

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Abstract

Cytostatic drugs are a broad group of chemotherapy compounds mainly applied for tumor, skin diseases and infections treatments. Anticancer pharmaceutics are exhibited carcinogenic, mutagenic and teratogenic activity and have been recognized as low biodegradable so their concentration would increase in the environment. Effective removal of pharmaceuticals in municipal wastewater treatment plants plays a critical role in preventing them from getting into the aquatic environment. Presented work focuses on the photocatalytic removal of poor biodegradable actual micropollutant - Imatinib (IMA) from aqueous solution. The 2.5 wt. % multi-walled carbon nanotubes (MWCNTs) modified TiO_2 nanocomposite was synthesized by two methods: sol-gel (s-g) and hydrothermal (hyd). The anatase as a photocatalysts' structure was confirmed by using X-day diffraction technique. Photoluminescence and UV-vis tests were used for investigation of photocatalysts optical properties. The scanning electron microscopy techniques used for morphology investigation showed the various location of MWCNTs in composites depending of synthesis method applied. Good photocatalytic properties of both 2.5% MWCNTs/TiO_2 for imatinib degradation under UVA, and artificial solar light irradiation was showed. Imatinib was also removed and mineralized under visible light irradiation by 2.5% MWCNTs/TiO_2(s-g). The study showed that MWCNTs contributed in increasing photocatalytic activity of TiO_2 in solar and/or visible light due to retardation of electron-hole recombination and visible light absorption by modification of band-gap and/or sensitization.

Keywords: TiO_2, multiwalled carbon nanotubes, photocatalysis, cytostatic drugs

1. INTRODUCTION

Carbon nanotubes, especially multi-walled carbon nanotubes (MWCNTs) show the potential to contribute in increasing photocatalytic activity of photocatalysts due to high-surface area and high quality active sites, retardation of electron-hole recombination and visible light absorption by modification of photocatalyst band-gap and/or its sensitization [1]. Over the past decade the number of studies seeking to develop CNTs-TiO_2 composites with enhanced photocatalytic activity or CNTs used as a promising material for environmental treatment has been increased. All the reports have revealed that modification semiconductors by CNTs could enhance the performance of such obtained photocatalysts. It was observed that the method of synthesis affects the physicochemical properties and morphology of MWCNTs/TiO_2 nanocomposite, which in turn influences on the photocatalytic activity [2]. The introduction should provide a clear statement of the study, the relevant literature on the study subject and the proposed approach or solution.

Cytostatic drugs (antineoplastic/anticancer drugs) are a broad group of chemotherapy compounds mainly applied for tumor, skin diseases and infections treatments [3]. These drugs and their human metabolites can directly enter into the water cycle from the hospital effluent, household and industrial wastewater, and drug waste disposal [3-5]. Cytostatic pharmaceutics are exhibited carcinogenic, mutagenic and teratogenic activity and have been recognized as low biodegradable so their concentration would increase in the environment [5]. Effective removal of pharmaceuticals in municipal wastewater treatment plants plays a critical role in

preventing them from getting into the aquatic environment [3]. Imatinib (IMA) is one of cytostatic drugs with the high consumption all over the world. Starting in 2003, IMA was gradually introduced for use in newly-diagnosed chronic myeloid leukemia patients [23]. Up till now, there are no reports relative about the concentration of IMA in wastewater and aquatic environment [6]. Presented work focuses on the photocatalytic removal of poor biodegradable actual micropollutant - IMA from aqueous solution. In this study, the photocatalysts MWCNTs/TiO_2 with 2.5%wt. of MWCNTs and pristine TiO_2 were synthesized by sol-gel and hydrothermal methods. The influence of synthesis method and the presence of MWCNTs on the structure, morphology and optical activity of TiO_2 photocatalyst were studied by XRD, SEM, UV-vis/DRS and PL. The photocatalytic activity was tested to IMA degradation under UV, solar and visible light irradiation.

2. MATERIALS AND METHODS

2.1. Hydrothermal synthesis of MWCNTs/TiO_2 nanocomposite

MWCNTs (diameter - 8 - 15 nm, length - 10 - 50 μm, purity - > 95%wt.), contents of COOH groups - 0.49%wt. were added in amount of 200 mg to a 250 mL one neck flask containing 7.5 mL of 65 % concentrated nitric acid and 142.5 mL deionized water. Then after being refluxed at boiling point for 45 min, the suspension was cooled down to room temperature and subsequently centrifuged. The received supernatant was removed by decantation. Black precipitates were washed several times using deionized water followed by successive decantation until the pH value reached to 6.0-6.5. The powders of MWCNTs were dried in an oven at 80 °C overnight and then stored in a vial for use. The amounts of 31 mg as-prepared MWCNTs were added to a mixture of 9 mL ethanol and 18 mL deionized water, and sonicated for 1 h to obtain homogeneous dispersion. Then a solution of 1.7 mL tetrabutoxide titanium in 9 mL ethanol was added dropwise into the above suspension of MWCNTs, while stirred by a magnetic stirrer. After another 3 h stirring, the resultant suspension was transferred into a 50 mL Teflon-sealed autoclave and the hydrothermal treatment was conducted at 180 °C for 12 h. The product was centrifuged and washed with water several times, followed by a rinse with ethanol. The sediments were dried at 60 °C in an electric oven. Moreover, pure TiO_2 were prepared by following the same procedures as stated above. Samples prepared via this method were labeled as TiO_2(hyd) and MWCNTs/TiO_2(hyd)

2.2. Sol-gel synthesis of MWCNTs/TiO_2 nanocomposite

The preparation was performed at room temperature as following: 4.25g of $Ti(OC_4H_9)_4$ was dissolved in 40 mL of ethanol and 10mL of deionized water. 0.09375g of functionalized MWCNTs described in section 2.1 was dispersed in 16.5 mL ethanol, 10 mL deionized water and 1mL 36.5 % concentrated hydrochloride and sonicated for 15 min to reach a uniform suspension. Next, a mixture of $Ti(OC_4H_9)_4$ and ethanol were added dropwise into the as-prepared MWCNTs solutions under vigorous stirring at room temperature for 5 h. After 5 h stirring, the sample was undergoes centrifuged and rinsed with ethanol. The powder was dried in an oven at 80 °C overnight and undergoes further heat treatment in air at temperature of 450 °C for 2 h. Pure TiO_2 were prepared by following the same procedures as stated above. Samples prepared via this method were labeled as TiO_2(s-g) and MWCNTs/TiO_2(s-g).

2.3. Photocatalytical activity

The photocatalytic activities of MWCNTs/TiO_2 were evaluated by performing IMA solution degradation experiments under UV light lamp, the solar and visible light irradiation. Photocatalytic reactions were carried out in a glass reactor and with a magnetic stirrer. Before turning on lamps, the solutions mixed with composites were kept in the dark for 30 min to allowing the adsorption-desorption equilibrium to be reached. In the test with UV light Heraeus Mercury Medium Pressure Lamp 150 W were used. The lamp emitted radiation in the range from 200 nm to 400 nm, with the maximum intensity at the wavelengths in the UVA range. The

photocatalytic activity of nanocomposites in the solar and visible light irradiation were tested in ATLAS SUNLEST XLS+ solar light simulator without and with cut-off filter (λ> 420nm). The source of radiation was a 1700 W Xenon lamp (430 W/m^2). The concentration of the photocatalyst was 0.5 gL^{-1} MWCNTs/TiO_2 and 20 mgL^{-1} IMA aqueous solution. The solutions were irradiated for 150 min (UV) or 180 min (solar, visible light). The volume of the solutions were 15 ml, 75 ml and 75 ml for irradiation under UVA, solar and visible light, respectively. During all the experiments, the specimens of both drugs solutions were collected in appropriate time carefully by a plastic pipe, and filtered through 0.22 μm syringe filters to remove photocatalyst particles. Drug removal was analyzed using an HPLC chromatography (LIQUID CHROMATOGRAH LC - 20 ADXR Shimadzu with detector UV-Vis/DAD). Parameters of analytical methods are shown in our previously article [6].

3. RESULTS

3.1. Photocatalysts characterization

All sample prepared both methods: 2.5% MWCNTs/TiO_2 and pristine TiO_2 had patterns corresponding to bare anatase suggested only surface modification TiO_2 by MWCNTs. No significant difference in morphology of TiO_2 materials obtained by sol-gel and by hydrothermal method was found, and the morphological structure of studied photocatalysts were consistent with previous reports [7]. In contrast to this fact, MWCNTs/TiO_2 samples prepared by different methods characterized the different arrangement of MWCNTs on the TiO_2 surface. In the case of hydrothermal method, nanotubes are deposited on the surface and wrapped around the TiO_2 particles, while in material prepared by sol-gel method nanotubes seemed to be placed between TiO_2 particles (**Figure 1**).

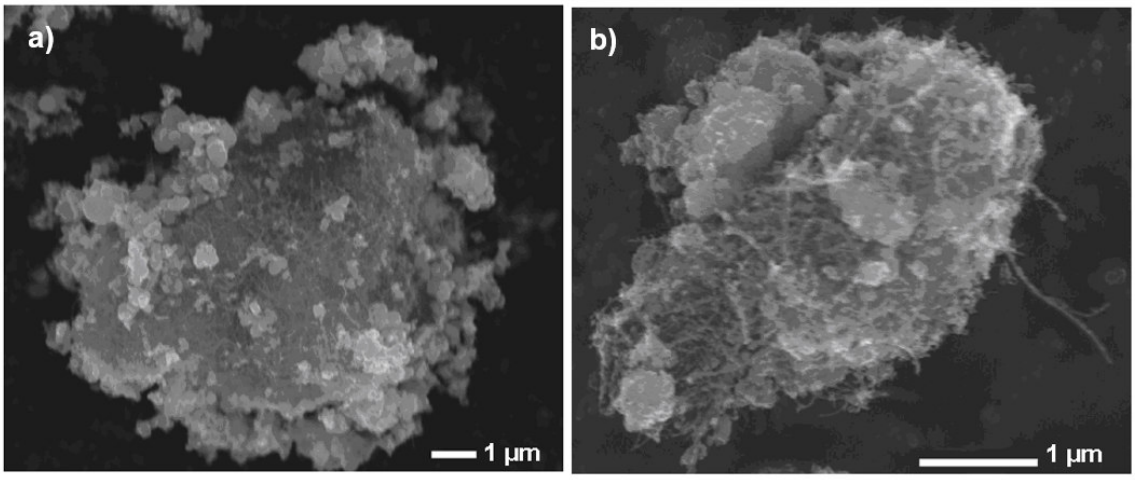

Figure 1 SEM images of a) MWCNTs/TiO_2 (s-g) and b) MWCNTs/TiO_2 (hyd)

All samples presented the typical absorption with an intense transition in the UV region, which can be assigned to the intrinsic bandgap absorption of TiO_2. Both pristine TiO_2 samples showed no absorption above absorption edge (385 nm). The MWCNTs/TiO_2(hyd) sample exhibited strong absorption in the λ < 400 nm region of visible light. Improvement of the absorption in visible light range by a MWCNTs/TiO_2(hyd) nanocomposite is due to the contribution of presented on the TiO_2 surface MWCNTs absorption. MWCNTs/TiO_2(s-g) synthesized via sol - gel method exhibited much lower improvement in light absorption than nanocomposite made by hydrothermal method. A fluorescence decrease was observed for the both MWCNTs/TiO_2 nanocomposites compare to appropriate pristine TiO_2. It can be explained by the electron transfer from excited TiO_2 to MWCNTs and reduction the charge carriers e^-/h^+ recombination.

3.2. Photocatalytic studies

The photocatalytic activity of prepared photocatalysts was examined in three wavelength of light and the results were shown on **Figure 2.**

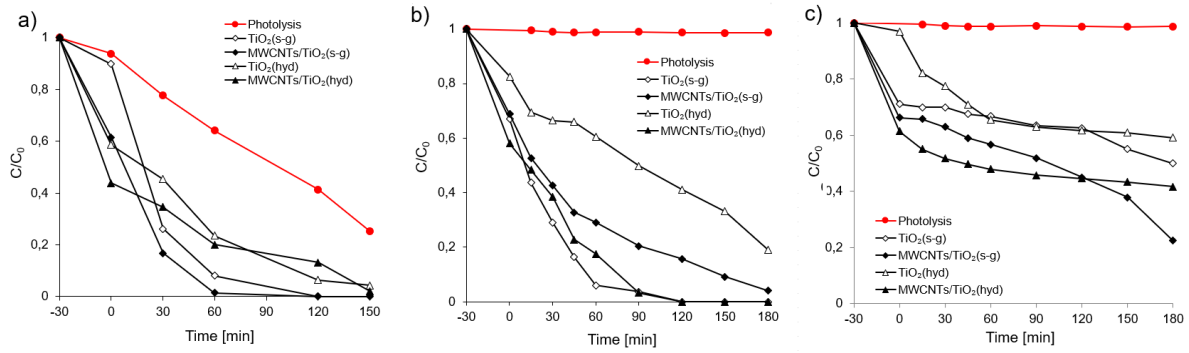

Figure 2 Photocatalytic decomposition of IMA under a) UVA, b) solar and c) visible light irradiation in presence of prepared photocatalysts

3.2.1. UVA irradiation

IMA was characterized the 75 % degradation efficiency in photolysis process and 25 - 27 % adsorption ability on all studied photocatalysts surface. The presence of MWCNTs with the high specific surface, increase the adsorption of drug on the MWCNTs/TiO_2 composites up to 48 - 56 % **(Figure 2a)**. Moreover a difference in adsorption capacity of MWCNTs/TiO_2 prepared by hydrothermal and sol-gel method was found. This fact can be explain the presence of more easily accessible MWCNTs on the surface of photocatalyst prepared by hydrothermal method. Furthermore, it was found that degradation of IMA over MWCNTs/TiO_2(s-g) achieved the highest almost 100 % removal efficiency after 60 min while IMA was decay over MWCNTs/TiO_2(hyd) in 100 % after 150 min. In both cases modification by MWCNTs of TiO_2 increased photocatalytic removal of IMA from water solution. TOC and TN removal achieved the values of 58 % and 21 % respectively for TiO_2 modified by MWCNTs prepared via sol-gel. The highest TOC and TN removal values reached 62 % and 37 % for MWCNTs/TiO_2(hyd).

3.2.2. Solar and visible light irradiation

Photolysis of IMA under simulated solar and visible irradiation in the absence of a photocatalyst showed negligible time-dependent changes in the drug concentration **(Figures 2b,c)**. The introduction of MWCNTs by hydrothermal method significantly enhanced the degradation efficiency compared to TiO_2(hyd) sample from 82 to 100 % in 180 min reaction. On the other side the MWCNTs/TiO_2(s-g) composite revealed lower photocatalytic activity (96 %) compared to TiO_2(s-g) (100 %). The comparison of photocatalytic activity of prepared by us samples of MWCNTs/TiO_2 and previously synthetized and studied photocatalysts is difficult due to the ubiquitous use of dyes for the evaluation of the samples photocatalytic activity. MWCNT/TiO_2 samples were more efficient in IMA mineralization than pure TiO_2 samples obtained in the appropriate method. Furthermore, the best mineralization reaching approximately 51 % after 180 min photocatalytic process was in presence of MWCNTs/TiO_2(s-g). The TiO_2 and the nanocomposite prepared by sol - gel method compared to TiO_2 and MWCNTs/TiO_2 obtained by hydrothermal method showed much higher TOC removal, while TN removal was not observed.

3.2.3. Visible light irradiation

TiO_2 and MWCNTs/TiO_2 prepared by sol-gel method seems to be more active in IMA decomposition under visible light than those prepared by hydrothermal method. The highest value TOC removal observed for

MWCNTs/TiO_2(s-g) may have be caused by both processes the adsorption of the drug on the surface of photocatalyst and its activity in visible light. TN removal was not showed in any experimental conditions.

4. CONCLUSION

MWCNTs/TiO_2 nanocomposite photocatalysts with different TiO_2 morphologies on the surface of MWCNTs were prepared successfully by hydrothermal and sol-gel processes. The MWCNTs distribution in nanocomposite MWCNTs/TiO_2 was proposed to be the critical factor for the efficiency photocatalytic activity these group of photocatalyst. The enhanced light absorption of the MWCNTs/TiO_2 composites may led to the increase of photogenerated charge carriers production and to result in improved photocatalytic performance. However, fluorescence quenching can also be caused by reduced generation of electron hole pairs which can be observed during photocatalytic activity tests. The nanocomposite catalyst prepared by the sol-gel system has higher efficiency in cytostatic drug photodegradation than that prepared by the hydrothermal system with the same MWCNTs loading (2.5 wt %), respectively. Moreover, higher photocatalytic activity was also associated with more effective drug mineralization. The impact of MWCNTs on IMA degradation was examined and the mechanism of IMA decay in UV, solar and visible light was determined, showing slight differences depending on the electromagnetic wavelength. This is due to varying amounts of generating holes, superoxide anion and hydroxyl radicals which are capable of decay of IMA. Because of the above observations, the results indicate that the introduction of MWCNTs actually increases the photocatalytic capacity of the TiO_2 material, and the sol-gel system was recommended for the preparation of the nanocomposites used to purify water from cytostatic drugs.

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