Effect of the Mn amount on the photocatalytic activity of Mn doped TiO_2-MWCNT nanocomposites

INCDTIM

PIM 2021 International Conference Processes in Isotopes and Molecules

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INTRODUCTION

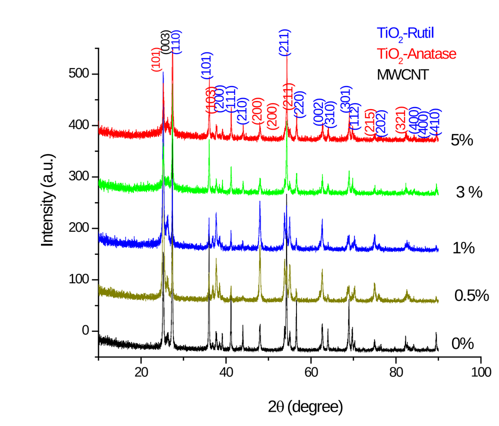
Dye pollution represents one of the greatest global challenges for the environment due to the daily operations of the industry. Synthetic dyes are generally used in numerous manufacturing industries such as paper printing, textile dyeing, cosmetics and pharmaceuticals. During the dyeing processes, about 15–20% of the total world production of dyes is lost. One of the popular dyes used in industrial applications is Rhodamine B (RhB) which is capable to cause irritation to the skin and eyes, gastrointestinal and respiratory tract. Consequently, the treatment of effluents containing dyes such as Rhodamine B represents an important research subject. Concerning the environment, the pollution with dyes is most easily recognized because it can be detected by the human eye at low parts per million levels. In addition, the presence of color reduces light penetration into the water which negatively impacts on the photosynthesis process responsible for supporting the biotic environment. *A cheap and efficient future solution of wastewater remediation is expected to be photocatalysis, achieved by using semiconductor-based nanocomposites.* In this work, Mn doped TiO2-MWCNT photocatalysts were synthesized by a facile chemical route using Mn doped TiO2 nanoparticles and MWCNTs in the presence of poly(allylamine) hydrochloride (PAH). The photocatalytic degradation of RhB was investigated under UV light irradiation. The mechanism of photocatalytic activity was elucidated based on the reactive oxygen species involved in this process.

EXPERIMENTAL

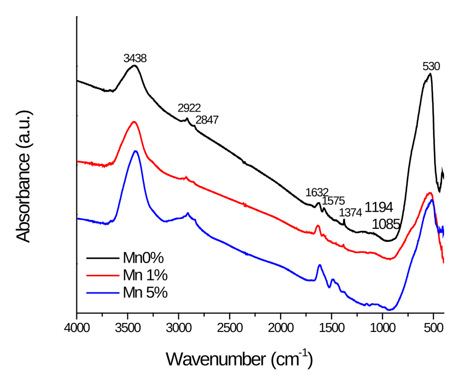
- The functionalization of MWCNT was carried out using acid treatment. The MWCNT were sonicated in a mixture of H2O2 (30%) : HNO3 (65%) was (1:3 vol ratio) for 3 h. Then, the content was centrifuged, and washed with distilled water several times to maintain its neutralization. The decoration of MWCNT with preformed Mn doped TiO2 nanoparticles in mass ratio of 1:1 was carried out using polymer wrapping—technique with poly(allylamine hydrochloride)-PAH . Undoped and Mn doped TiO2 nanoparticles were synthesized by sol-gel process starting from hydrolysis of tetraisopropyl ortotitanate (TIPO) and different concentrations of Mn(NO3)3x2H2O(x=0, 0.5, 1, 3%).
- X-ray diffraction (XRD) measurements were made using a Rigaku - SmartLab automated Multipurpose X-ray Diffractometer equipped with a high-accuracy θ-θ goniometer.
- FT-IR spectra were obtained in the 400–4000 cm−1 spectral range with a JASCO 6100 Fourier transform-infrared (FT-IR) spectrometer by using the KBr pellet technique. The spectral resolution used for the recording of the IR spectra was 2 cm−1.
- EPR measurements of powder samples were carried out on a Bruker E-500 ELEXSYS X-band (9.52 GHz) spectrometer at room temperature under identical conditions: microwave frequency of 9.5248 GHz, microwave power 2 mW, modulation frequency of 100 kHz and modulation amplitude 10 G.
- SEM Scanning Electron Microscopy was done using a HITACHI SU-8230 equipped with a cold field emission electron beam accelerated at 30 kV.
- Optical response of the samples was studied by using UV–Vis absorption spectra recorded from a JASCO V570 UV–Vis-NIR Spectrophotometer equipped with absolute reflectivity measurement accessory.
- The photodegradation of Rhodamine B (RhB) was carried out at room temperature under UV light illumination for 4 h. The UV-irradiation was provided by two 15W UV lamps with a peak wavelength of 365 nm. One piece of membrane (20x20 mm) was suspended in aqueous solution of RhB1.0×10^{-5} mol L^{-1}, 10mL.
- To monitor reactive oxygen species (ROS) production it was used the ESR coupled with the spin trapping probe technique. ESR measurements were carried out on a Bruker E-500 ELEXSYS X-band (9.52 GHz) spectrometer. As spin trapping reagent was used 5,5-dimethyl-1-pyrroline N-oxide (DMPO, Sigma-Aldrich). MWCNT-ZnO (10 mg) were dispersed in DMSO (1 ml) and homogenized in an ultra-sound bath (30 s) before use. DMPO of 0.2 mol/l concentration was added to the suspension. The samples were prepared immediately before measurements and transferred into the quartz flat cell optimized for liquids measurements.

RESULTS AND DISCUSSIONS

XRD diffraction pattern of MWCNT-TiO_2:Mn

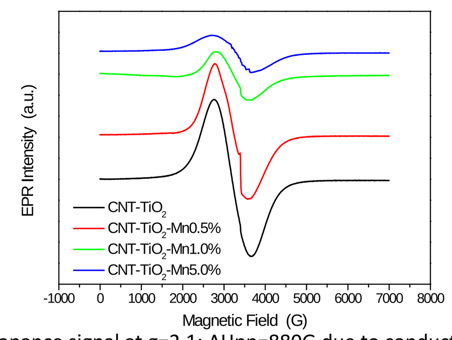


FT-IR spectra and band assignments of MWCNT-TiO_2:Mn



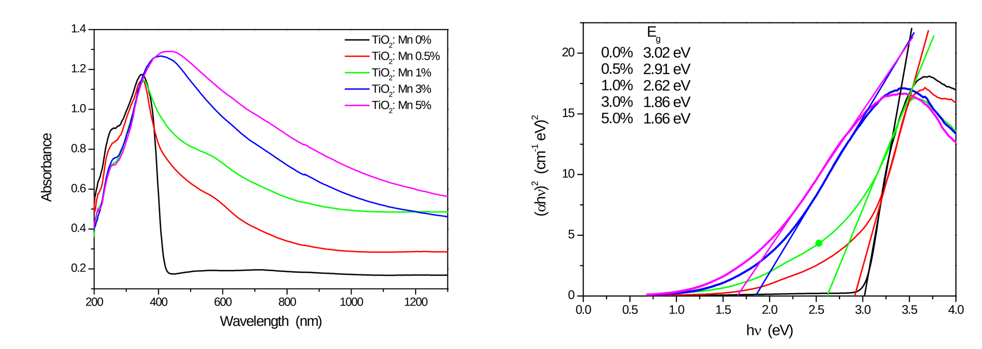
Peaks position (cm^{-1})	Assignments
530	O-Ti-O bending vibration
1085	C–O stretching vibration
1194	C–O stretching vibration
1374	C=C stretching vibration
1632	C=C stretching vibration
2847	C–H stretching vibrations
2922	C–H stretching vibrations
3438	Hydroxyl group OH
3575	C=C stretching vibration

EPR spectra of MWCNT-TiO_2:Mn



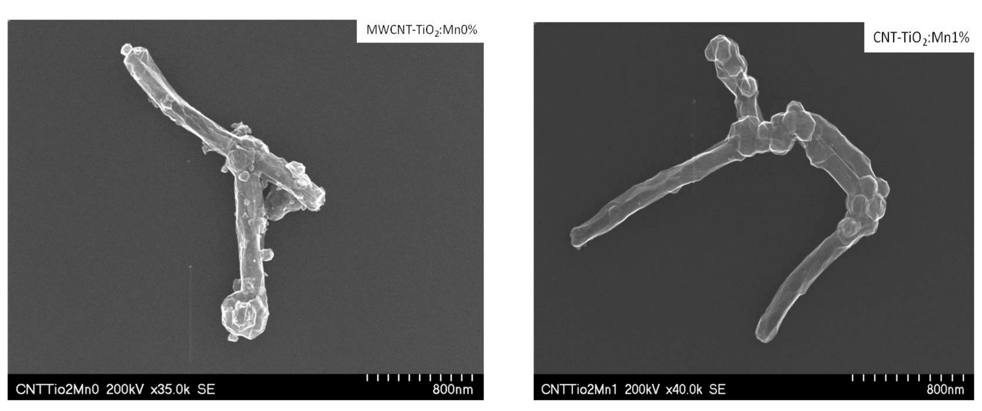
- resonance signal at g=2,1; ΔHpp=880G due to conduction electrons of MWCNT
- resonance signal at g=2,0002; ΔHpp=10G due to impurities or paramagnetic defects associated with amorphous graphite
- hyperfine signal at g = 2,02; A=90G due to Mn2+ ions

UV-Vis spectra and Tauc's plot of TiO_2:Mn

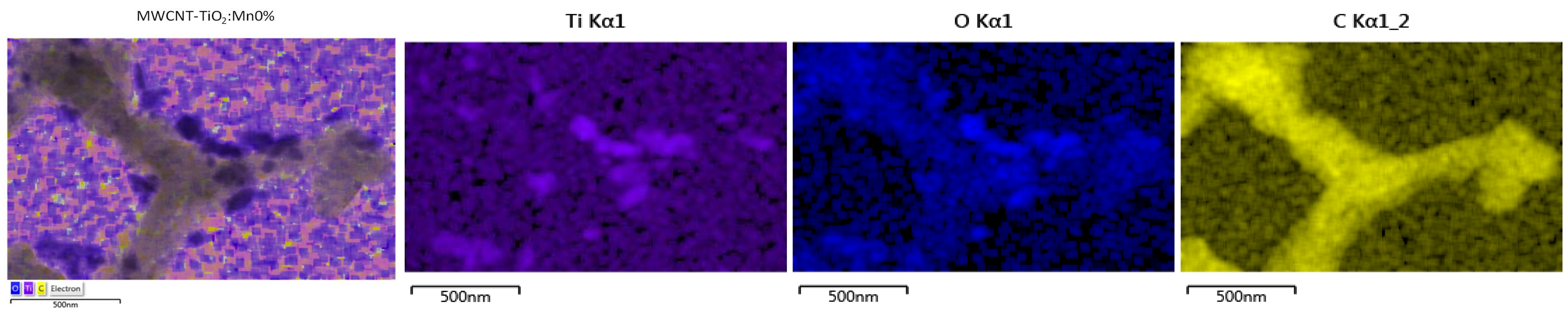


- Band gap energy is decreasing with increase of manganese concentration due to additional levels induced by dopant ions in the band gap of TiO2.

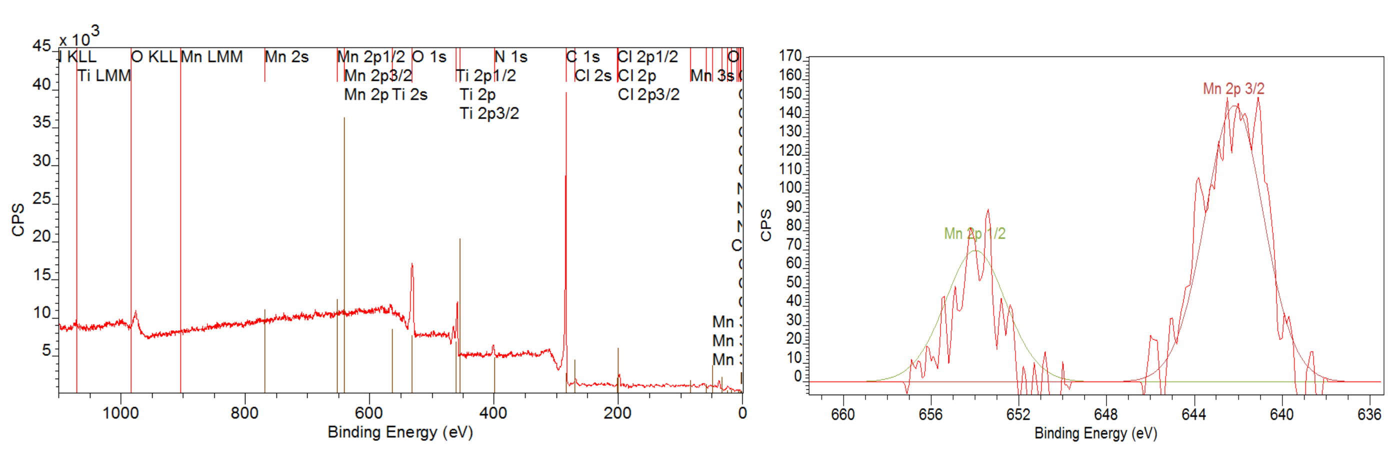
SEM image of MWCNT-TiO_2-Mnx%



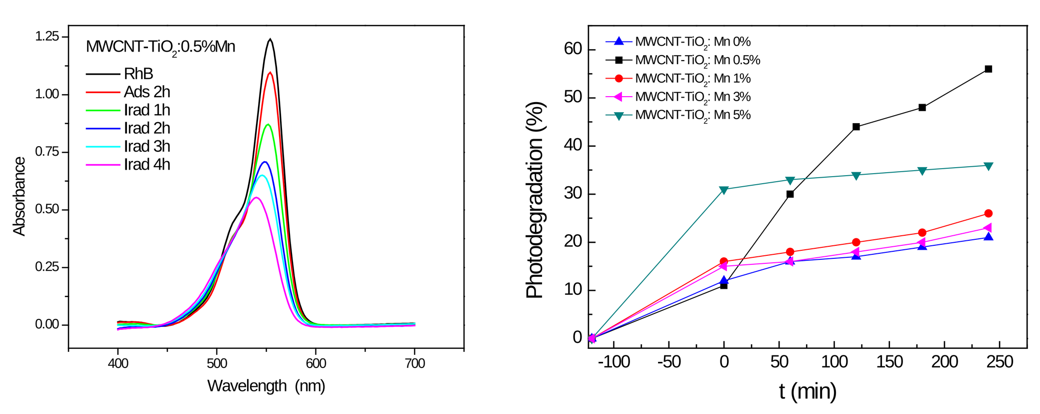
EDS maps of MWCNT-TiO_2



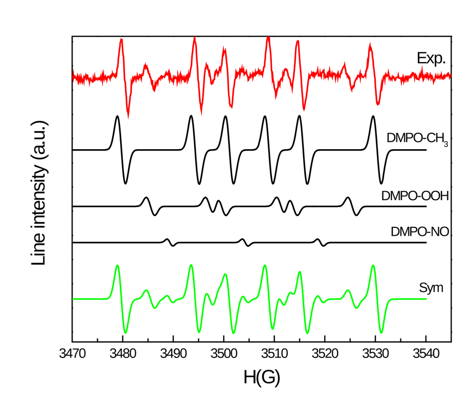
XPS survey spectra of MWCNT-TiO_2:Mn1%. Deconvolution of Mn 2p spectum.



Photodegradation of RhB in the presence of MWCNT-TiO_2-Mnx%



DMPO adducts generated by MWCNT-TiO_2Mn:05% after 25 min of irradiation



CONCLUSIONS

- MWCNT-TiO2:xMn nanocomposites were prepared by decoration of MWCNTs with TiO2:Mn nanoparticles by a polymer wrapping-technique.
- XRD analysis confirm that the synthesized nanocomposites contain mainly C and anatase/rutile crystalline phases of TiO2.
- FT-IR spectra show vibrational bands corresponding to MWCNT and TiO2.
- EPR spectra show three resonance signals at (i) g=2,1; ΔHpp=880G due to conduction electrons of MWCNT; g=2,0002; ΔHpp=10G due to impurities or paramagnetic defects associated with amorphous graphite and a hyperfine one at g = 2,02; A=90G due to Mn2+ ions
- Based on UV-Vis absorption spectra and using Tauc's equation the band gap energy was evaluated. The band gap energy is decreasing with increase of manganese concentration due to additional levels induced by dopant ions in the band gap of TiO2.
- SEM images of MWCNT-TiO2:xMn nanocomposites evidence the decoration of MWCNT with TiO2 nanoparticles
- Compositional analysis was determined by XPS/EDS spectroscopy. From XPS survey spectrum results that MWCNT-TiO2:Mn1% has in composition the following elements: Mn, Ti, O si C. Deconvolution of Mn 2p peak show the presence of Mn2+ ions in sample.
- All the samples show photocatalytic activity against RhB and the best performance was obtained using 0.5% Mn-doped nanocomposites
- Analysis of experimental and simulated spectra of DMPO spin adducts generated by MWCNT-TiO2 Mn:0.5% attested the presence of hydroxyl radical.

ACKNOLEDGEMENTS. This work was supported by the Romanian Ministry of Research, Innovation and Digitization, Core Programme, Project PN19 35 02 03