Synthesis, characterization and photocatalytic activity of MWCNTs decorated with Cu-doped TiO_2

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INTRODUCTION

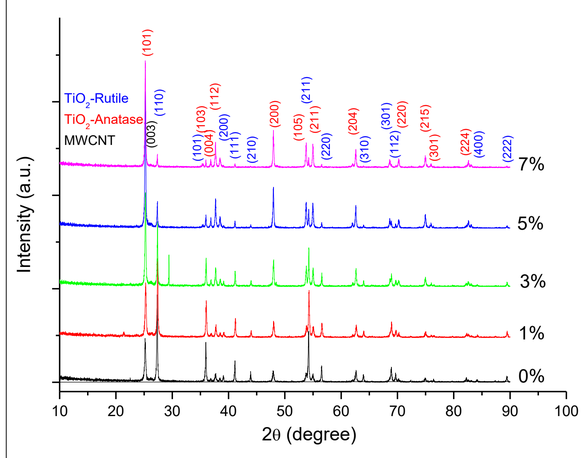
Due to the unique electronic and physical properties of the MWCNTs, the decoration of MWCNTs with TiO_2 can induce interesting charge transfer and enhance the photocatalytic activity of TiO_2. Also recent studies have reported the improvement of the photocatalytic activity of TiO_2 by transition metal doping. At a constant MWCNTs : TiO_2 ratio, the Cu doping concentration influence on the composite properties was studied.

EXPERIMENTAL

- In the first stage MWCNTs were functionalized with –OH and –COOH. TiO_2:Cu nanoparticles were obtained by sol-gel method. The decoration of MWCNTs with TiO_2:Cu nanoparticles was done by a polymer wrapping-technique.
- X-ray diffraction (XRD) measurements were made using a Rigaku - SmartLab automated Multipurpose X-ray Diffractometer .
- SEM images were obtained by using a HITACHI SU-8230 and TEM images were obtained by using a HITACHI HD2700.
- Qualitative and quantitative sample composition was obtained by using X-Ray Photoelectron Spectroscopy (XPS).
- Optical response of samples was studied using UV–Vis absorption spectra recorded from a JASCO V570 UV–Vis–NIR spectrophotometer equipped with absolute reflectivity measurement JASCO ARN-475 accessory.
- The photocatalytic activity of the nanocomposites was evaluated by photodegradation of Rhodamine B (RhB) in a Laboratory-Visible-Reactor system with a 400 W halogen lamp (Osram) which emits in visible range.

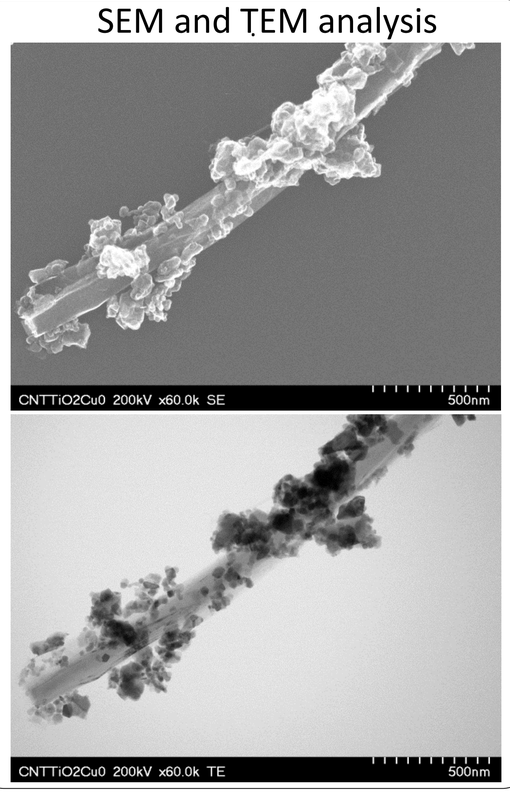
RESULTS

XRD diffraction pattern

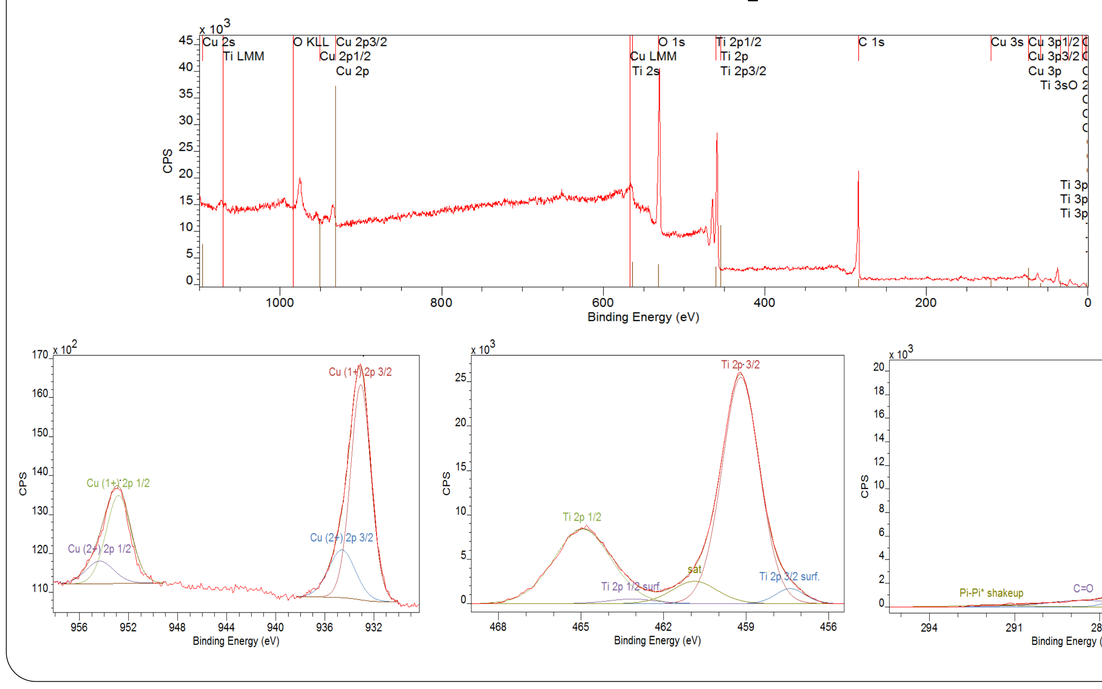


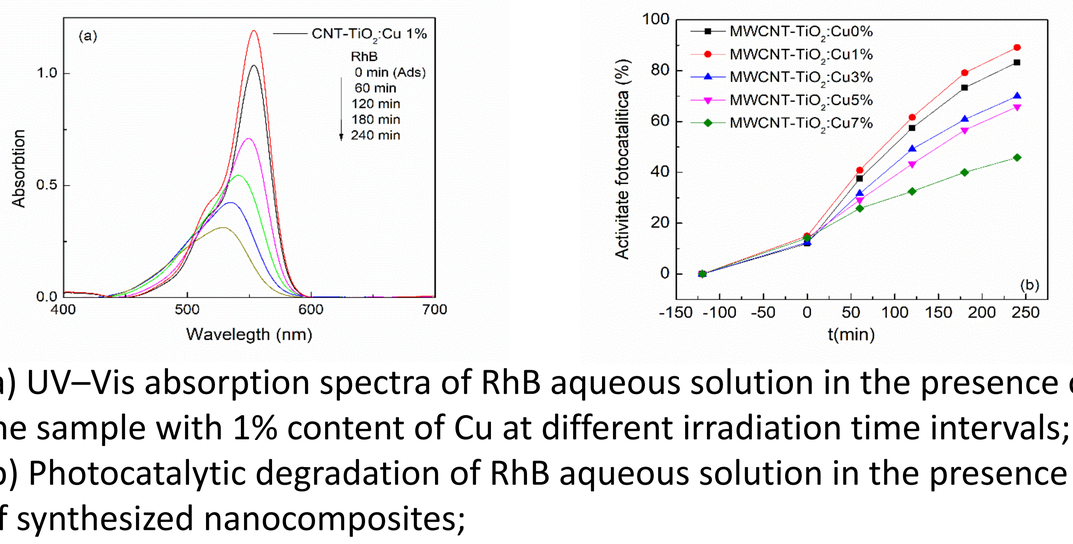
Sample	Anatase <D> (nm)	Rutile <D> (nm)
MWCNTs-TiO_2:Cu0%	27	42
MWCNTs-TiO_2:Cu1%	30	36
MWCNTs-TiO_2:Cu3%	30	36
MWCNTs-TiO_2:Cu5%	36	48
MWCNTs-TiO_2:Cu7%	37	56

SEM and TEM analysis

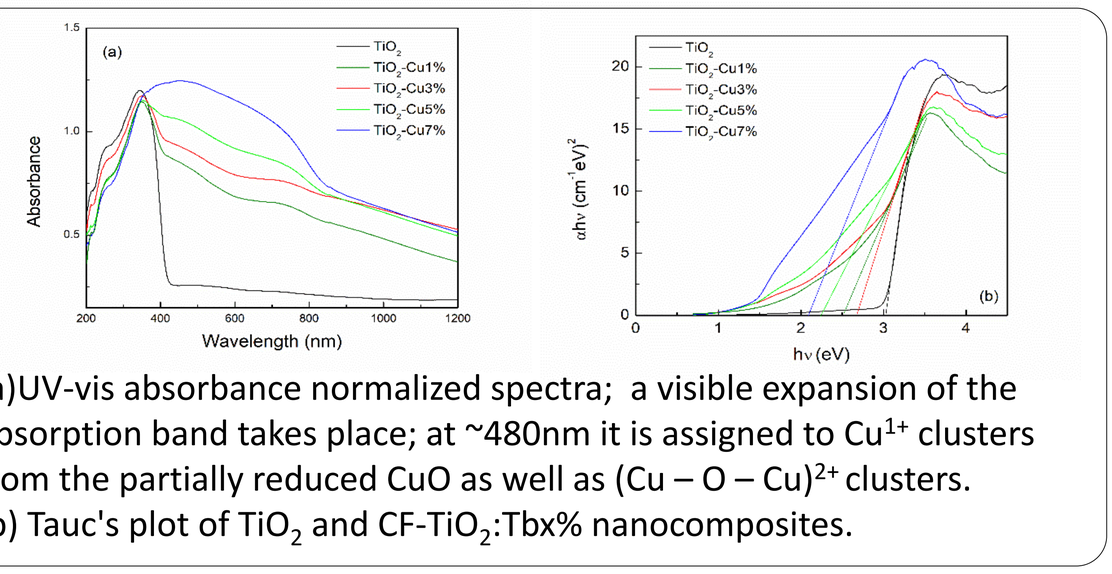


XPS survey spectra and C 1s, Ti 2p, Cu 2p core-level lines corresponding to MWCNT-TiO_2:Cu5% sample





(a) UV–Vis absorption spectra of RhB aqueous solution in the presence of the sample with 1% content of Cu at different irradiation time intervals; (b) Photocatalytic degradation of RhB aqueous solution in the presence of synthesized nanocomposites;



(a)UV-vis absorbance normalized spectra; a visible expansion of the absorption band takes place; at ~480nm it is assigned to Cu^{1+} clusters from the partially reduced CuO as well as $(Cu – O – Cu)^{2+}$ clusters.
(b) Tauc's plot of TiO_2 and CF-TiO_2:Tbx% nanocomposites.

CONCLUSIONS

- XRD results show that by increasing the Cu doping concentration the rutile phase concentration can be lowered to 5%.
- Electron microscopy shows that the MWCNT are decorated with polyhedral nanoparticles.
- XPS spectra deconvolution shows specific lines for CNT with defects, Ti is in 4+ oxidation state and also with surface states, Cu is in 1+ oxidation state with small quantities of 2+ oxidation state as well.
- The band gap is lowered by Cu doping.
- The percentages of RhB degradation varies between 45-89%, whereas the best photocatalytic activity obtained for 1% Cu doping.
- By coupling this semiconductor with MWCNT in the photocatalysis process, two non-radiative excitation channels appear for both electrons and holes.
- The results revealed that by Cu doping one can control the decoration efficiency and photocatalytic activity.

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