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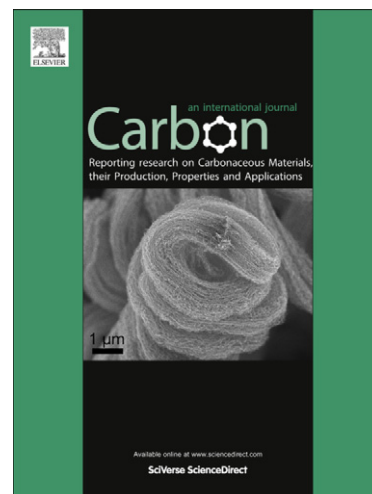
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Preparation and characterization of multiwalled carbon nanotube/ In_2O_3 composites

Péter Berki¹, Zoltán Németh¹, Balázs Réti¹, Ottó Berkesi², Arnaud Magrez³,
Vladimir Aroutiounian⁴, László Forró³, Klara Hernadi^{1*}

¹Department of Applied and Environmental Chemistry, University of Szeged, Rerrich B. tér 1, Szeged, H-6720 Hungary

²Department of Physical Chemistry and Materials Science, University of Szeged, Rerrich B. tér 1, Szeged, H-6720 Hungary

³Laboratory of Physics of Complex Matter, EPFL, Ecublens, CH-1026 Switzerland

⁴Center of Semiconductor Devices and Nanotechnologies, Yerevan State University, 1 Manoukian St. Yerevan 0025, Armenia

Abstract

We have prepared multiwalled carbon nanotube (MWCNT)/ In_2O_3 composites using a simple impregnation method. The precursor compound indium (III) chloride (InCl_3) was used to cover the surface of MWCNTs and distilled water was used as solvent. The applied mass ratio was 4:1 (In_2O_3 :MWCNT), and during the calcination process different temperatures (300°C, 350°C and 400°C) were investigated. The produced materials were characterized by X-ray diffraction, energy-dispersive X-ray spectroscopy, Raman spectroscopy, Fourier transform infrared spectroscopy, transmission and scanning electron microscopy, and a thermogravimetric analysis was executed also. The average thickness of the produced surface layer and the average sizes of the In_2O_3 particles were calculated with the Scherrer formula and the ImageJ-program. The results show that the heat treatment temperature affected the characteristic morphology and the crystal structure of the as-prepared composite. These multiwalled carbon nanotube-based composites are promising candidates as gas sensors and catalyst.

1. Introduction

Iijima's landmark paper on carbon nanotubes (CNTs) in 1991 was a turning point in materials science [1]. They have attracted considerable attention in last few years most notably because of their special features for example very high stability, outstanding tensile strength, good heat transmission ability, unique electronic and special mechanical properties

*Corresponding author. Tel/Fax: +36 62 544 626. E-mail address: hernadi@chem.u-szeged.hu (K. Hernadi)

[2-3]. A single-walled carbon nanotube (SWCNT) can be regarded as a cylinder formed by rolling a graphene layer, and a multi-walled carbon nanotube (MWCNT) is picking up series of concentric SWCNTs with the inter-tube distance of ~ 0.34 nm [4]. Because of the earlier mentioned special chemical, physical and electronic properties, the area of applications were examined very comprehensive by the carbon nanotubes such as composite materials [4-7], field emission materials [8-9] and chemical sensors [10-11].

Multiphase nanocomposites are materials that consist of nanosized particles in a matrix of a standard material. Commonly nanoparticles are dispersed into the matrix material during the synthesis process. The resulting composite exhibits a drastic improvement in properties that can include mechanical properties such as stiffness, strength and toughness, and electrical or thermal conductivity [5,14].

In recent years, many chemical researches were concerned with the combination of carbon nanotubes with polymers or metal-oxide nanoparticles [4,12]. The applications of these composite materials are very extensive, which usually determines the performance of the composites. The carbon nanotubes could be implicated in polymer matrixes, and so can change the mechanical properties of these materials. In certain cases the surface of carbon nanotubes could be covered with an inorganic layer from metal oxides, which layer may consist of separated nanoparticles [13] or can be totally homogenous [14]. These composites are expected to deliver exceptional performance since solar cells, catalyst and nanoelectric devices.

The n-type semiconductive indium oxide (In_2O_3) has potential application in toxic-gas detection, solar cells, biosensors, chemical sensors, and photocatalysis [15-16]. In_2O_3 nanoparticles were successfully prepared in earlier studies at different temperatures and methods [17-18], for example Qurashi et al. produced high-density pyramids from In_2O_3 at 800°C and regular octahedrons at 900°C with hydrothermal synthesis, solvothermal synthesis,

electrochemical desorption etc. [19]. In recent years extensive studies were focused on the synthesis and properties of this material with specific morphologies such as nanowires nanobelts, nanoparticles, nanotowers, nanotubes, nanocables, etc. [19]. Several further studies dealt with the gas sensing properties of In_2O_3 . Based on the electrical conductivity or resistance of this material gas sensor devices can be prepared for detection of many toxic gases such as NH_3 , CO etc. [19].

In this study we are presenting a simple one-step method to prepare MWCNT/ In_2O_3 composites. Since literature data are inconsistent concerning the formation of In_2O_3 crystals, we are trying to clarify the effect of the heat treatment on the morphology. We searched the lowest calcination temperature which is high enough to produce MWCNT/ In_2O_3 composite, because the MWCNT begins to burn at 500°C . We also studied whether these composites can be considered just as mechanical mixtures or some kind of chemical bond was evolved between the MWCNT and In_2O_3 . It is hoped that these new composite materials will have a synergic physical and chemical properties of the two components in further applications.

2. Experimental

2.1. Chemicals

MWCNTs were prepared by catalytic chemical vapour deposition (CCVD) method in a rotary oven at 720°C in nitrogen flow [20-21]. Acetylene was used as carbon source and Fe,Co/ CaCO_3 as catalyst, and the total concentration of the metal was 5 wt% [21]. The support material and the catalyst-particles were removed with stirring the product in 10% hydrochloric acid for 1 h, and then it was washed with diluted HCl and subsequently with distilled water until neutral pH was achieved. The average diameter of the MWCNTs was 20-60 nm, while average lengths were about few hundred nanometers to few micrometers [20-

21]. The main features of MWCNT Raman spectra are the D, G and G' peaks. The purity of the carbon phase can be easily determined by the ratios of these three peaks, and the metal content was previously regarded with a quantitative ICP-MS analysis by the co-authors [22]. This analysis and peak intensity ratios in case of MWCNT indicate good quality and highly graphitic nature.

Indium (III) chloride (98%) was purchased from Sigma-Aldrich Ltd. It was analytical grade and was used as received without further purification.

2.2. Preparation method

The MWCNT/ In_2O_3 composites were prepared by a simple impregnation method. Purified MWCNT was applied as raw material and InCl_3 as precursor. Initially, 100 mg MWCNT was added in 150 cm^3 distilled water and a suspension was prepared via sonication for 45 min. During this time the calculated amount of precursor (638 mg) was dissolved in another portion of distilled water (20 cm^3), and for complete dissolution it was continuously stirred for half an hour using a magnetic stirrer. Finally the solution of the precursor was added drop by drop into the MWCNT-suspension and then the mixture was heated to 90°C to evaporate water on a heated magnetic stirrer. When the solvent was completely removed, a black powder was obtained. This powder was dried further at 110°C for 24 h, and then it was separated to three parts. The portions were annealed in air for 3 h at three different temperatures: 300°C, 350°C, and 400°C. Reference materials (InOCl and In_2O_3) for comparative examinations were prepared exactly in the same way as the composites were synthesized but without MWCNT.

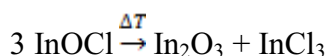
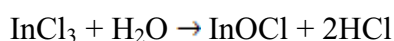
2.3. Characterisation of composite materials

Transmission electron microscopy (TEM), scanning electron microscopy (SEM), X-ray powder diffraction (XRD), Raman spectroscopy, Fourier transform infrared spectroscopy (FT-IR) and energy-dispersive X-ray spectroscopy (EDX) measurements, and a thermogravimetric analysis were used for the characterization of the samples. ►

The formation of inorganic coverage on the surface of MWCNTs was verified both with Philips CM 10 TEM (100 kV) and FEI Tecnai G² 20 X-TWIN HR-TEM. For TEM investigations a small amount of the examined sample was sonicated in 1,25 cm³ of distilled water. A few drops from this suspension were dribbled onto the surface of the grid (CF 200 Cu TEM grid) afterwards. The SEM analysis was carried out on a Hitachi S-4700 Type II FE-SEM scanning electron microscope equipped with a cold field emission gun operating in the range of 5-15 kV. The samples were mounted on a conductive carbon tape. Powder XRD analysis was effectuated on a Rigaku Miniflex-II Diffractometer (angle-range: $\theta = 20-70^\circ$) utilizing characteristic X-ray (CuK α) radiation. The Raman spectroscopy measurement was done on a Thermo Scientific DXR Raman microscope with a 532 nm laser (5 mW). The FT-IR spectra were recorded on a Bio-Rad Digilab Division FTS65A/896 FT-IR spectrometer equipped with a DTGS detector and a Ge/KBr beamsplitter, between 4000 and 400 cm⁻¹, at 4 cm⁻¹ optical resolution. A Harrick's Meridian® SplitPea Single Reflection Diamond ATR accessory was used, so no sample preparation was required. The spectrometer was controlled by Win IR Pro v. 3.3 (Bio-Rad Digilab Division) software, and the spectra were analyzed using GRAMS/AI v. 7.0 (Thermo Galactic) software. The energy-dispersive X-ray spectroscopy measurement was completed with the scanning electron microscope and a R ntec XFlash Detector 3001 SDD device. The thermogravimetric analysis was executed on a NETZSCH STA 409 PC device in air (measurement range: 25-800°C, heating rate: 20°C/min, flow velocity: 40 cm³/min).

3. Results and discussion

In the absence of MWCNT, the following reaction occurs: the precursor InCl_3 reacts with H_2O first to form InOCl as intermediate product, then the InOCl is further decomposed to form In_2O_3 due to the heat treatment. The chemical reactions of the formation of In_2O_3 crystals can be described as follows [17]:



In our synthesis process we investigated the possible effect of the presence of MWCNT on the above mentioned reactions.

3.1. Indium-containing MWCNT composite calcinated at 300°C

Firstly, the produced composite materials were examined by SEM and TEM. Figs. 1a and b show SEM images at various magnification of the sample calcinated at 300°C. These investigations revealed that the surface of carbon nanotubes has drastically changed viz. a covering inorganic layer can be observed. TEM and HR-TEM micrographs in Figs. 1c and d confirm that there is a layer covering on the surface of MWCNTs. From the analysis of the TEM pictures we calculated that the thickness of this layer was 10-11 nm in average. The average crystalline size and the average thickness of inorganic layers can be estimated from X-ray diffractogram by the Scherrer formula [23]:

$$D = (K\lambda) / (\beta \cos \Theta)$$

where D is the diameter of the grain or the layer, K is the shape factor (0,89), λ is the X-ray wavelength of $\text{CuK}\alpha$ (0,154 nm), β is the experimental full-width half maximum of the respective diffraction peak(s), and Θ is the Bragg angle. The Miller indexes of the sample

reflections belong to the InOCl from which the average layer thickness was calculated: 24.44° -(101), 27.53° -(011), 33.63° -(012), 35.40° -(111), 40.04° -(103), 42.05° -(013), 44.71° -(200), 45.98° -(201), 47.90° -(113), 51.75° -(020), 53.10° -(021), 57.03° -(022), 58.02° -(121).

From the TEM and HR-TEM images it can also be seen that the sample consist bigger inorganic and segregated agglomerates too. With the analysis of X-ray diffractograms (Fig. 2, black line) and Raman spectra (Fig. 3, black line) it can be concluded that there is a good correspondence with the reference InOCl. The characteristic D, G, G' peaks of MWCNT also appear in the Raman spectra of the composite. The energy-dispersive X-ray spectrum of this sample (Fig. 4a) shows the presence of carbon, indium, oxygen, and also chlorine in a large amount. The spectrum also contains a little peak from aluminium which comes from the sample-holder. From these results it can be concluded that as a result of calcination at 300°C covering inorganic layer with InOCl chemical composition formed on the surface of MWCNTs. Due to the adhesion of InOCl the surface of the MWCNTs has definitely changed, however, the applied calcination temperature was too low for the formation of crystalline In_2O_3 .

With the thermogravimetric analysis carried out on this sample it was possible to deduce the phase transformations. In Fig. 5 the thermogravimetric curve (TG, red) and the differential thermogravimetric curve (DTG, blue) can be seen. The analysis revealed that over 100°C a little weight-loss was observable which can be explained with the vaporisation of adsorbed water. A more intense weight-loss ($-16,06\text{ \%/min}$) appeared at about 350°C which corresponds with the decomposition process of InOCl when the In_2O_3 starts crystalline and the chloride leaves the system. A third weight-loss can be also observed in Fig. 5 which can be explained with the burning of the carbon nanotubes which starts after 500°C .

3.2. Indium-containing MWCNT composite calcinated at 350°C

The electron microscopy images of the sample calcinated at 350°C showed drastically different morphology than that of heat treated at 300°C. It can be seen on SEM (Figs. 6a and b) and TEM (Fig. 6c) images that the surface layer, what was observed in the previous sample, has significantly changed. Presumably inorganic agglomerates, both nanoparticles (averagely in size of 10-20 nm) and bigger crystal pieces (approximately 300-400 nm) evolved among the carbon nanotubes as a result of heat treatment. The presence of InOCl is still obvious from the XRD and Raman analysis (Figs. 2 and 3, red line), but In₂O₃ also emerged in a little amount in this sample. The appearance of the typical reflections is due to the crystalline oxide form of indium [30.51°-(222), 37.63°-(411), 51.02°-(440), 60.68°-(622), 63.73°-(444)]. The EDX analysis (Fig. 4b) shows that the indium-oxychloride has started to pass into indium-oxide which is in accordance with the decreasing quantity of chlorine in the sample. It was also observed that a slight crystallization process has already begun at 350°C, and irregular In₂O₃ crystals formed around the MWCNTs during the synthesis.

3.3. Indium-containing MWCNT composite calcinated at 400°C

Significantly new results were produced by the sample calcinated at 400°C (the highest we applied). The SEM (Figs. 7a and b) and TEM (Fig. 7c) images show that the crystallization process, which has started at about 350°C, became complete in this sample. The produced composite material consists of regular octahedral In₂O₃ particles of different sizes (200-500 nm in average), and the MWCNTs were built into these crystals. These images show clearly that the carbon nanotubes stick out from the octahedrons and bound the crystals to each other. The suspicion that chemical bond formed between MWCNT and In₂O₃ during the impregnation process was confirmed by FT-IR analysis. Beside the reference In₂O₃ (green line) the IR spectra of the composite samples calcinated at 300°C (black line) and 400°C (red line) are shown in Fig. 8, in the range of 650 and 420 cm⁻¹. This low frequency range features

mainly the metal-oxygen stretching vibrational bands. It is clearly shown that the composite sample calcinated at 300°C has only one band with considerable intensity at 485 cm^{-1} while the composite calcinated at 400°C has additional three bands at 593, 557, and 530 cm^{-1} , while the band at 485 cm^{-1} shifted to 489 cm^{-1} . The spectrum of In_2O_3 prepared at 400°C under same conditions as the composite calcinated at 400°C, indicates that these new bands can be assigned to the characteristic bands of the In_2O_3 itself, although they were somewhat shifted from the original 596, 561, and 535 cm^{-1} respectively. Since it was proved that InOCl was incorporated into the composite sample calcinated at 300°C and In_2O_3 into the sample calcinated at 400°C, it can be assumed that the bands at 485 and 489 cm^{-1} originated from the interaction of the indium ion and the oxygen containing surface functional groups of carbon nanotube. It can be presumed that the InOCl bonded to MWCNTs at the beginning of the synthesis, and then transformed into In_2O_3 due to the calcination. Due to the chemical bond between these materials and the long calcination time during crystallization process the evolving crystals embraced the MWCNTs.

The XRD analysis (Fig. 2, green line) confirmed that we produced successfully In_2O_3 nanoparticles in this sample [typical reflections: 21.33°-(211), 30.51°-(222), 35.42°-(400), 37.63°-(411), 41.87°-(332), 45.76°-(431), 51.02°-(440), 55.93°-(611), 60.68°-(622), 63.73°-(444)]. Raman spectroscopy (Fig. 3, green line) also confirmed this fact, and it can be seen that the peaks belonging to MWCNT appeared also in the spectra. The elemental analysis (Fig. 4c) also supports our opinion, because the chlorine disappeared totally from this sample, just indium, oxygen, and carbon remained in the system.

4. Conclusion

Nanostructured indium-containing coating was successfully developed on the surface of MWCNT via impregnation using InCl_3 as precursor. Raman and XRD investigations

confirmed the presence of InOCl or In₂O₃ and MWCNT in the samples. The FT-IR analysis proved that chemical bond formed between these materials. Using various electron microscopy techniques it was verified that different layer construction and morphology can be obtained using the impregnation method only by varying the temperature of the heat treatment. As it was concluded from XRD and Raman investigations, calcination temperatures 300°C and 350°C were not high enough to form regular crystalline In₂O₃. Applying 400°C during calcination process the resulted composite contains uniform octahedral In₂O₃ particles around MWCNT. Based on these results it is verifiable, that 400°C is the lowest temperature at which manufacturing a crystalline In₂O₃ substance through an InOCl intermediate product is possible. However, this temperature is significantly lower than it was expected for required calcination temperature from thermogravimetry measurement, the kinetics of crystallization of In₂O₃ octahedral explains the difference in temperature. It is planned that these new composite materials will be tested in various applications in the near future. Due to the intense linking between MWCNT and covering indium compound, it is hoped that the selectivity and the sensitivity of gas sensors based on these composite materials will be more effective than other devices based on only In₂O₃ because of the proved synergic combination of the materials.

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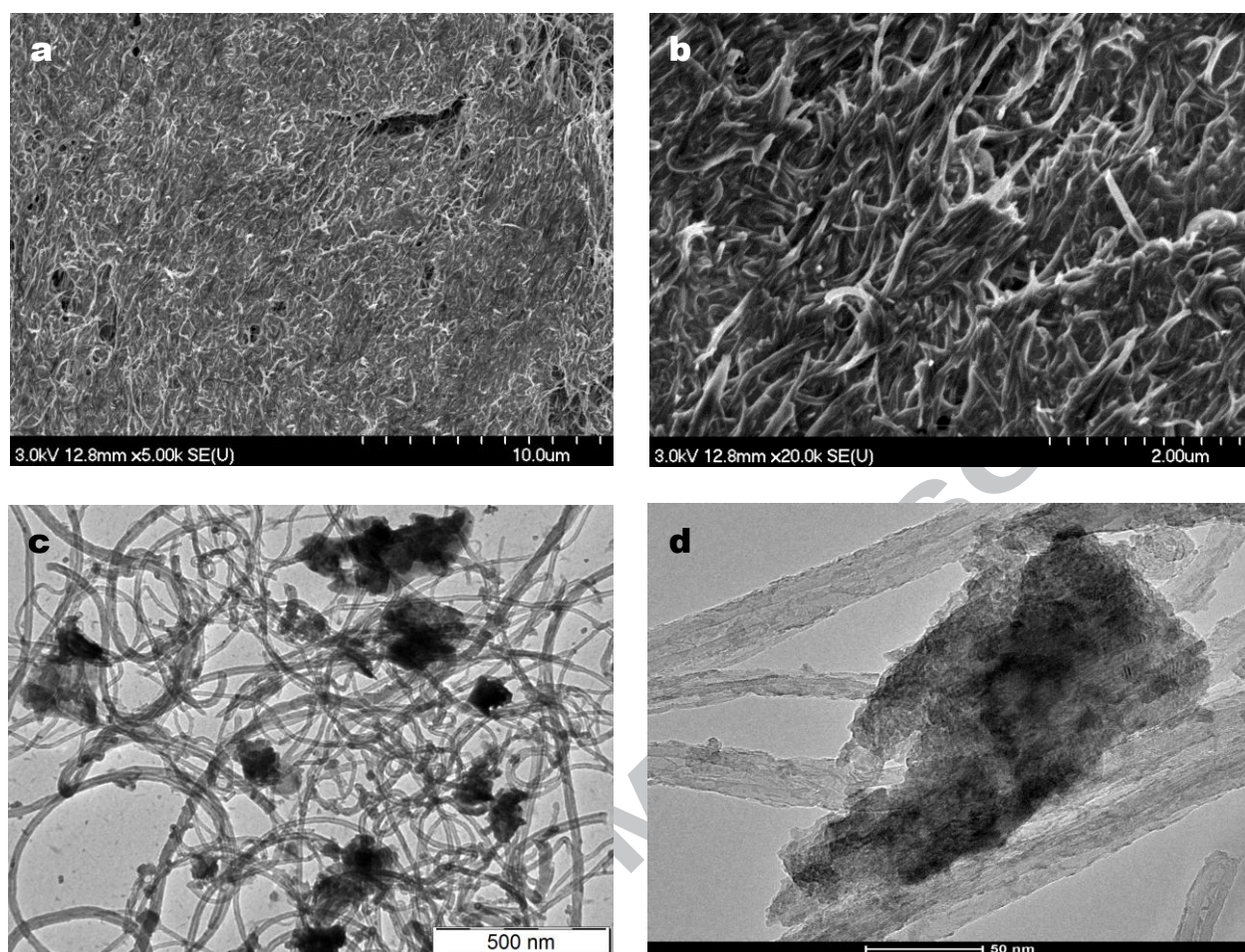


Figure 1: SEM (a and b) images at various magnification and TEM (c) and HR-TEM (d) images of sample that was calcinated at 300°C.

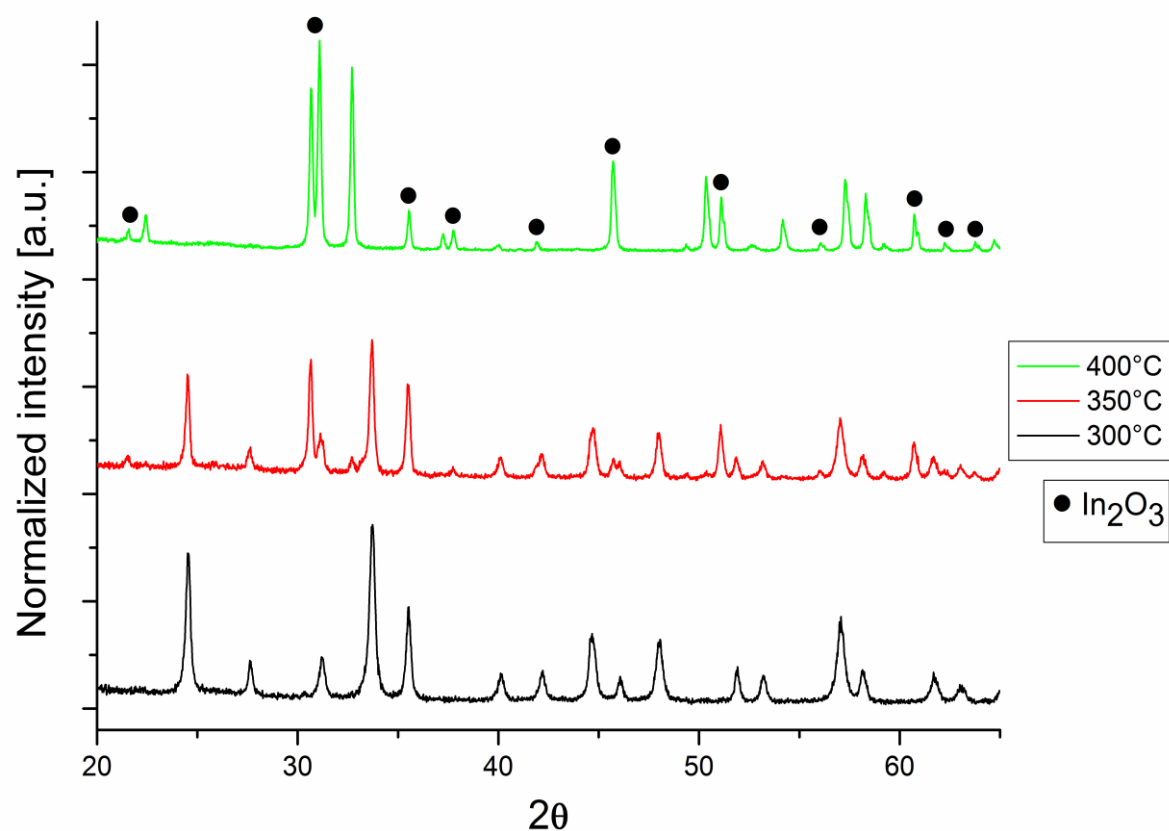
XRD analysis of 1:4 MWCNT - In_2O_3 composite samples

Figure 2: Comparative X-ray diffractograms of composite samples calcinated at 300°C, 350°C and 400°C

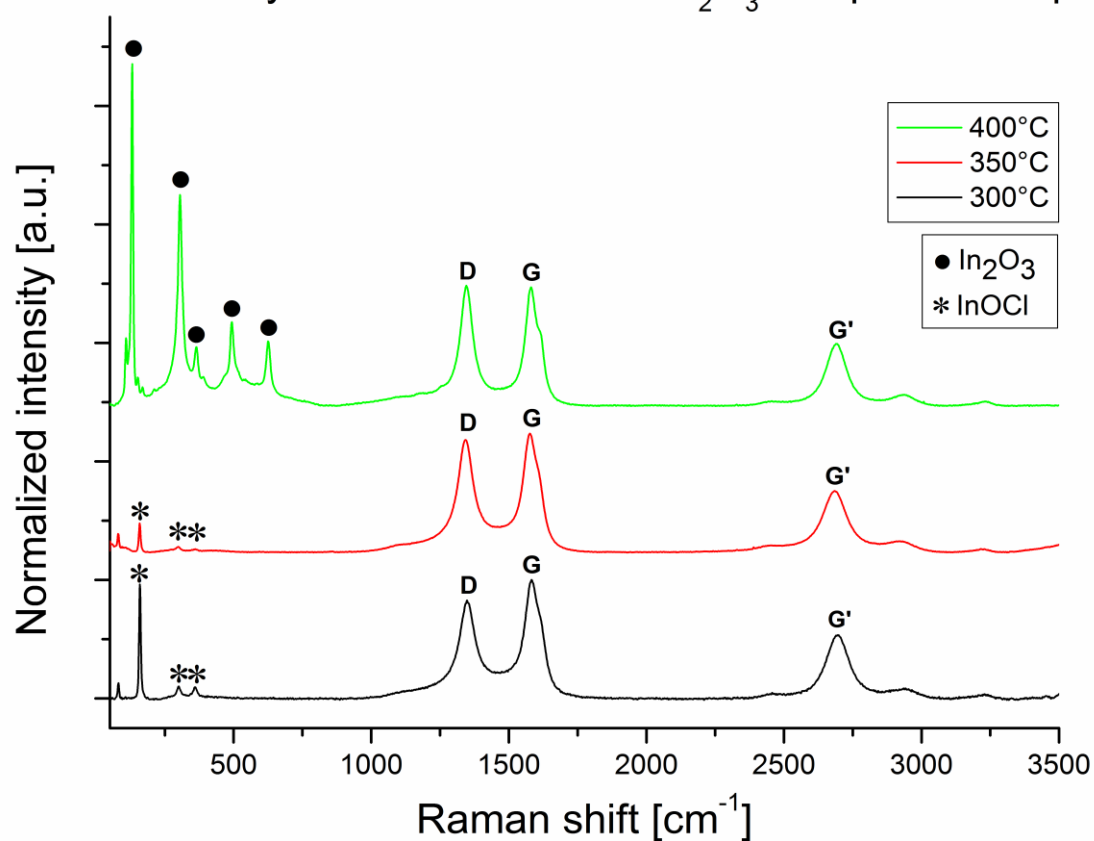
Raman analysis of 1:4 MWCNT - In_2O_3 composite samples

Figure 3: Comparative Raman spectra of composite samples calcinated at 300°C, 350°C and 400°C

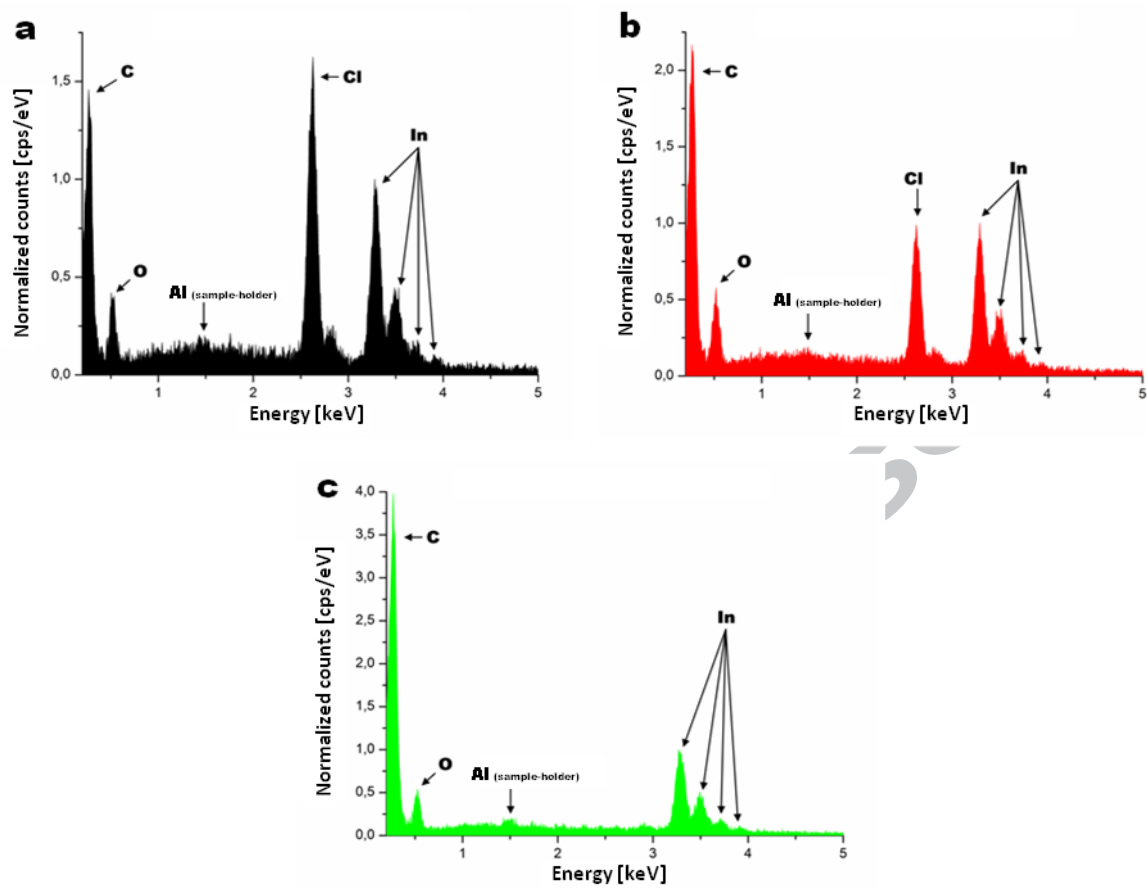


Figure 4: EDX analysis of composite materials, which were produced at 300°C (a), 350°C (b) and 400°C (c).

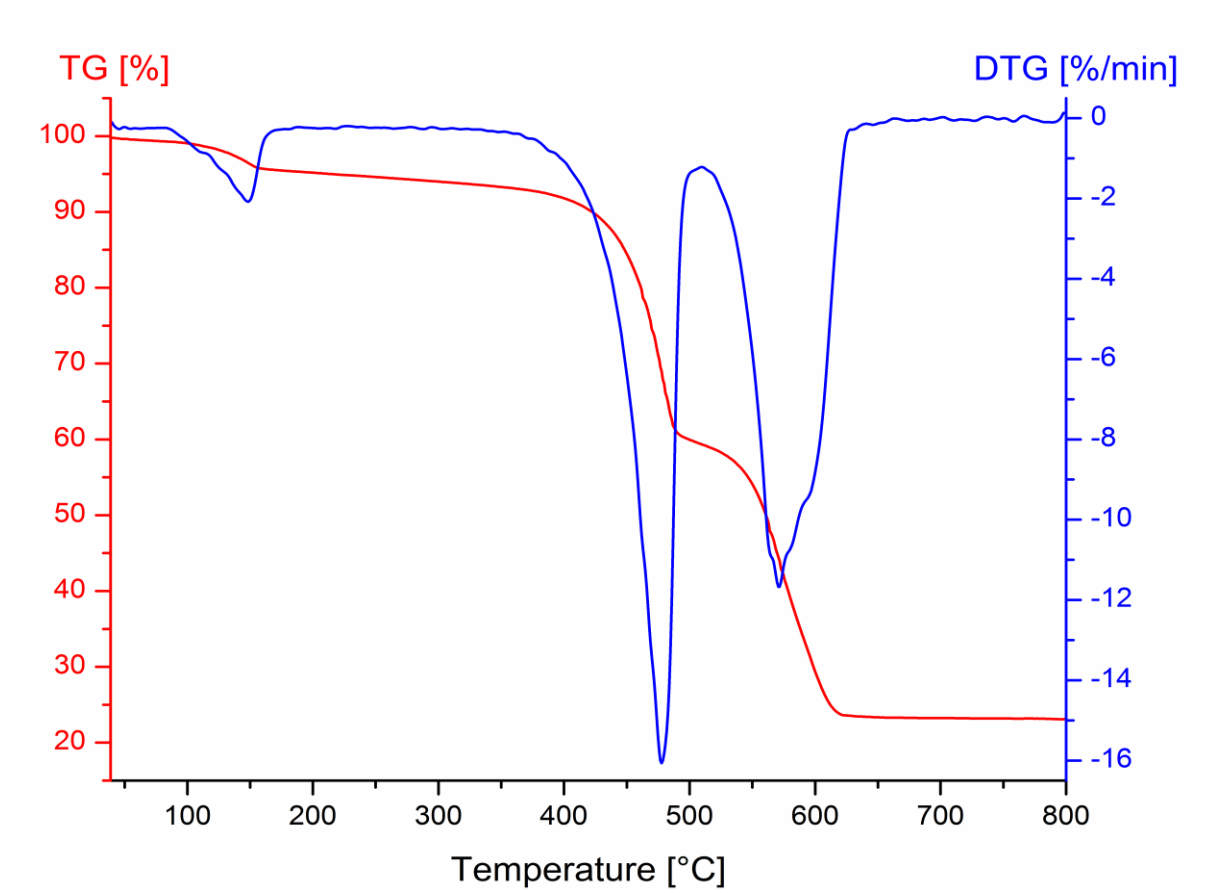


Figure 5: The thermogravimetric analysis of the sample calcinated at 300°C.

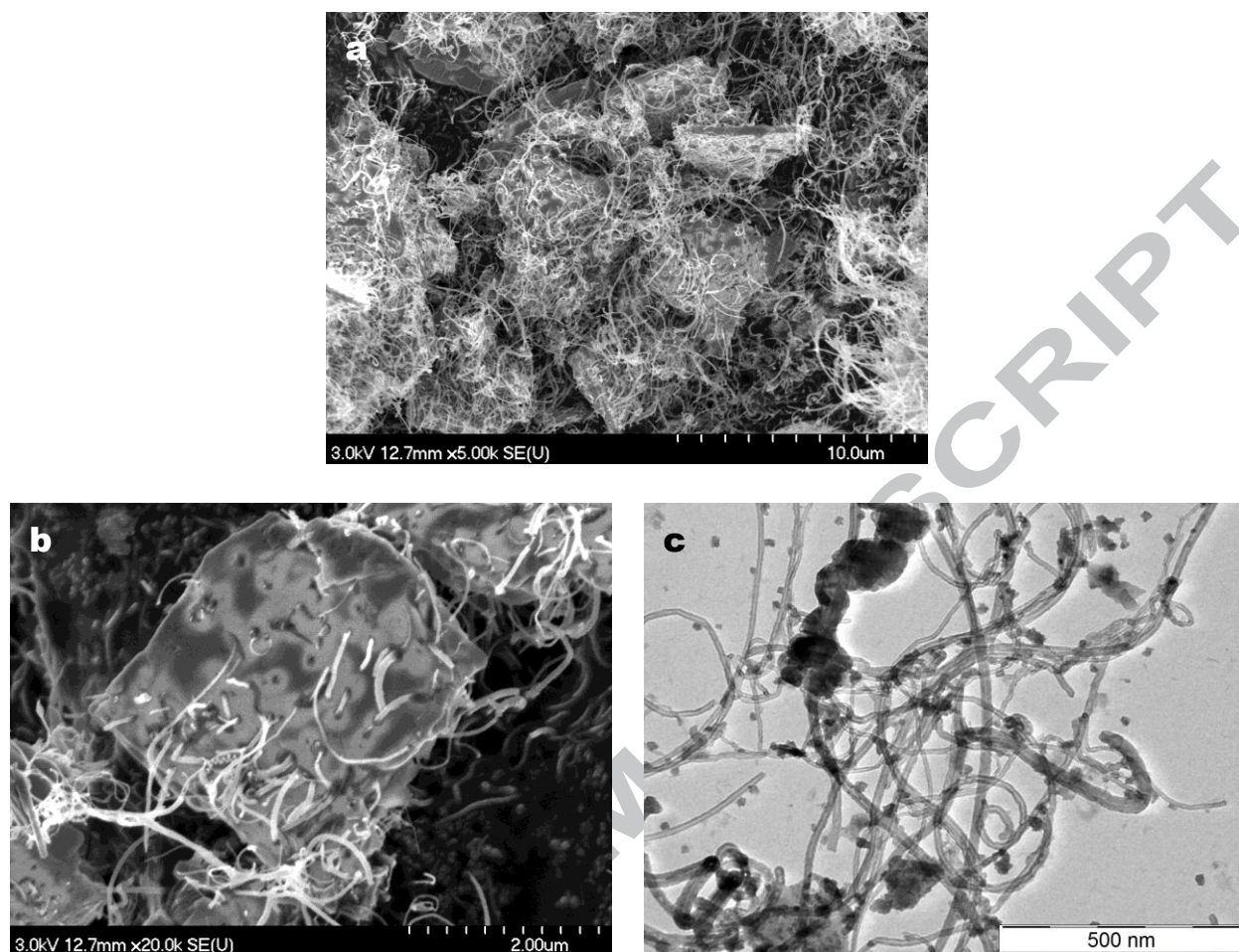


Figure 6: Electron microscopy images (SEM – a and b, TEM – c) of the sample heat treated at 350°C.

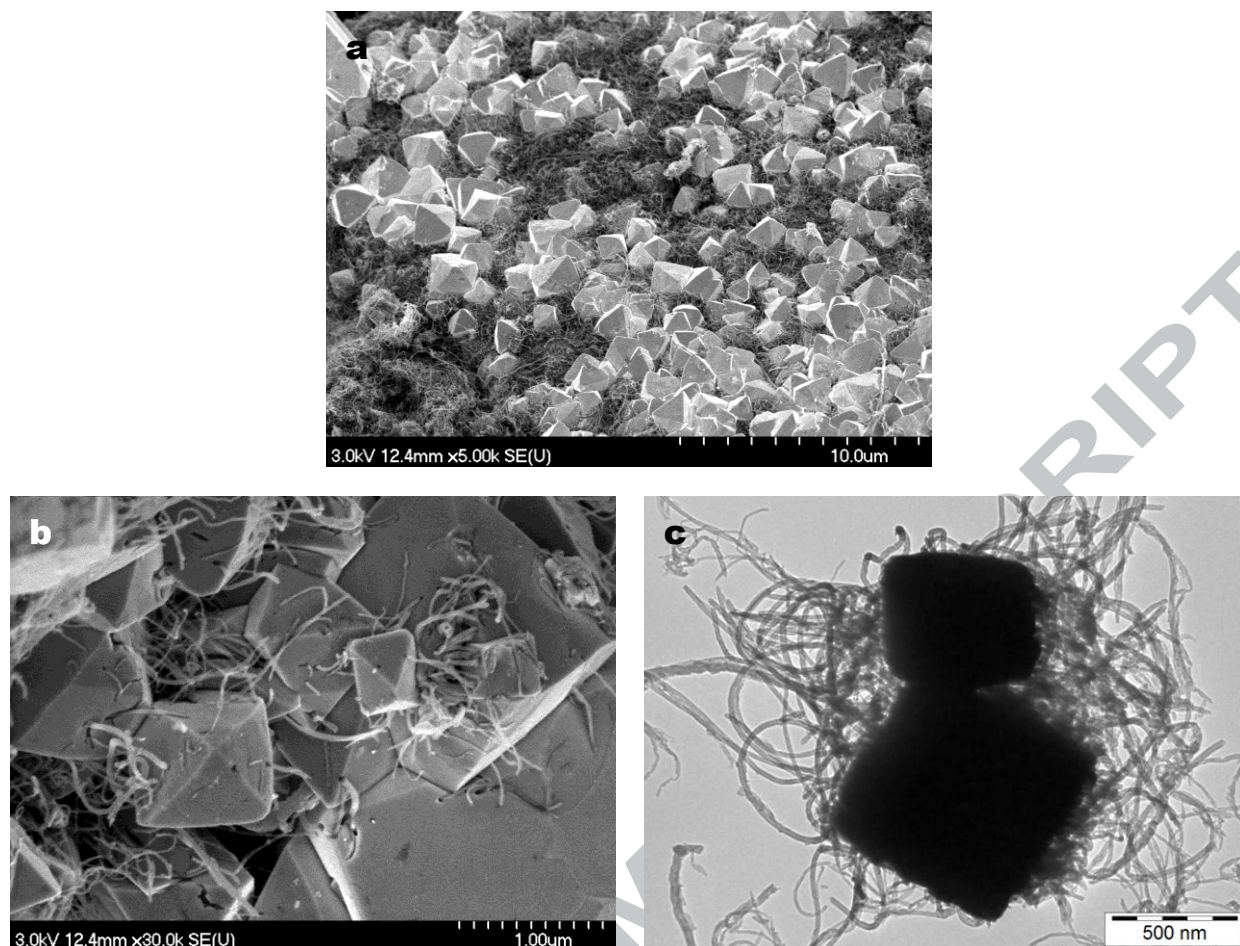


Figure 7: SEM (a and b) and TEM (c) pictures of MWCNT/In₂O₃ composite prepared by impregnation and calcinated at 400°C.

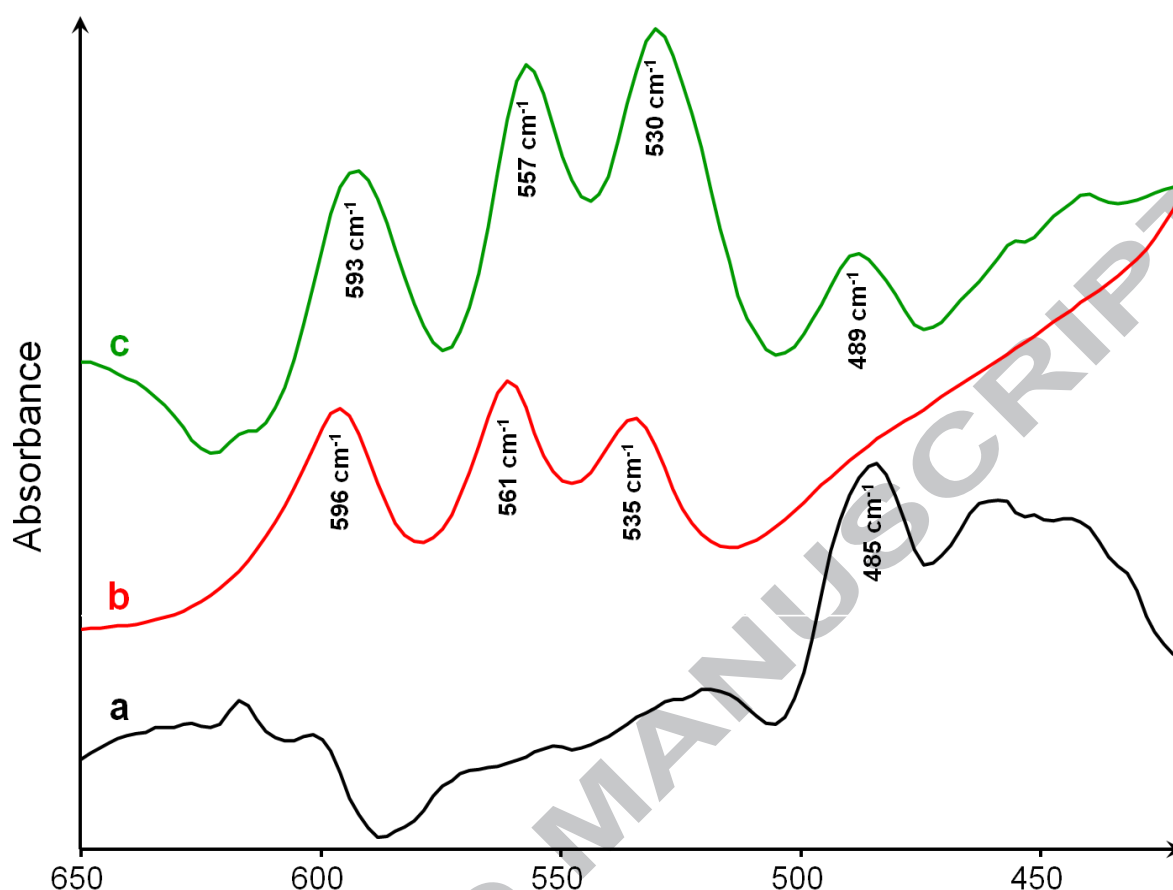


Figure 8: FT-IR spectra of the MWCNT/ In_2O_3 composite materials calcinated at 300°C (a) and 400°C (c), and the reference In_2O_3 (b). The three strong band between 600 and 500 cm^{-1} in spectrum (c) indicates the presence of In_2O_3 , while the band at 485 cm^{-1} in spectrum (a) and at 489 cm^{-1} in spectrum (c) is assigned to the metal-oxygen stretching band due to the presence of interaction between the MWCNT and the indium containing species, since there are no characteristic bands of the MWCNT in this region. Spectra were offsetted for clarity.