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Metal Nanocomposites: Synthesis, Characterization and their Applications

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Outline

Introduction

Nanocomposite (NC) materials have gained much attention and interest of scientists in recent years because of their improved properties than the single metal nanoparticles. Nanocompositeis a combination or matrix, in which different materials combine to develop new properties of the materials ensuring that one of the materials have size in range of 1-100nm [1, 2]. There are hence two parts on NC i.e. continuous phase and discontinuous reinforcing phase. Nanocomposite can be prepared from any combination of materials that can be categorized into three basic building blocks i.e. metals, ceramics and polymers (Figure 12.1a)[1, 3]. The nanocomposite hence can have a combination or have markedly different mechanical, electrochemical, electrical, catalytic, thermal and optical properties from the component materials [1, 4-7]. The nanocomposites have different phases as zero-dimensional (core shell), one-dimensional (nanowires and nanotubes), two-dimensional (lamellar) and three-dimensional (metal matrix composites) [8]. Based on their structural characteristics these nanocomposites are classified as nano-layered composites, nano-filamentary composites and nano-particulate composites (Figure 12.1b). These NC have gained the attention of scientists, researchers and engineers, which had led to the sudden raise in number of publications related to these materials. Further, these NC have emerged as materials of 21st century that offer number of technological and business breakthroughs in all the sectors of life.
The focus of this chapter is on metal oxide nanocomposites (MONC) that fall in all the three categories as shown in Fig. 12.1: these materials have promising properties, which makes them suitable for large number of structural and functional applications in other fields.

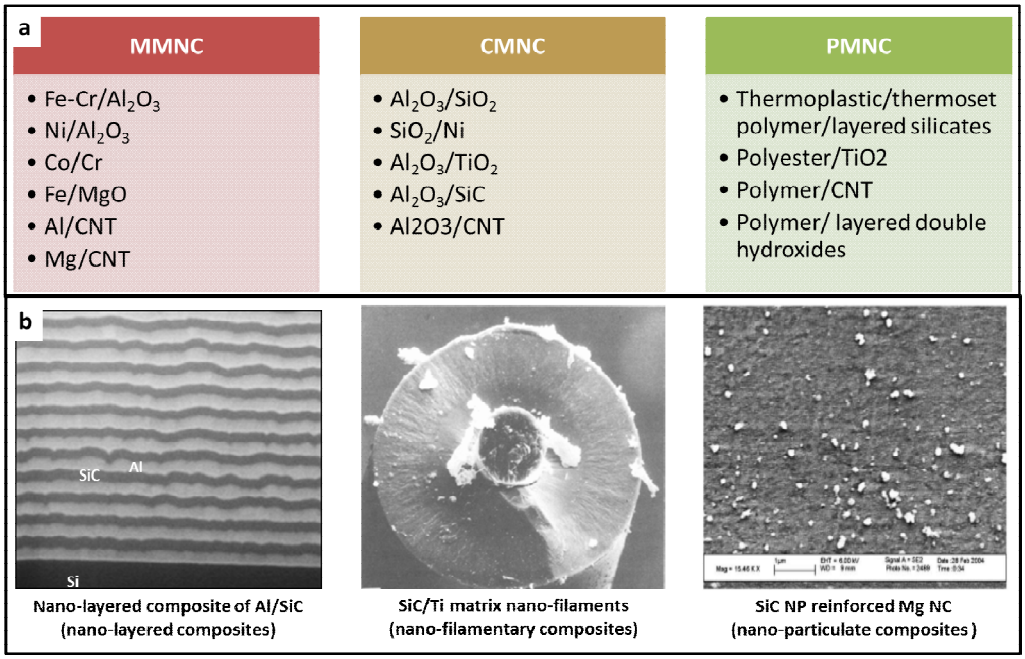

FIGURE 12.1
Examples of (a) three types of Nanocomposites and (b) their three classes [3, 9, 10]

Synthesis of Metal Oxide Nanocomposites (MONC)

The synthesis of uniform sized nanocomposite is very important because their properties include optical, magnetic, electrical and biological properties depending on their size and dimensions [11]. The synthetic methods are frequently classified in to three classes i.e. solution based synthesis, vapor phase synthesis and gas phase synthesis [12]. Another approach is to divide these synthetic approaches into two broad categories (Fig. 12.2) i.e. a) top-down approach which includes physical methods and b) bottom up approach which encompasses wet methods [8, 13]. The choice of synthetic approach depends on the desired characteristics required in the nanoparticles composites e.g. size, morphology, crystal structure etc. [12] but the benefit of physical methods is the production of large amount of nanocomposites but synthesis of equal sized nanocomposite particles is not easily attainable. In comparison, wet chemical methods give uniformity in size of nanocomposites as controlled particle size can be achieved easily. Although by varying conditions of reaction, different shapes (nano-rods, nanowires, nanotubes etc.) of nanocomposites can also be synthesized [14].

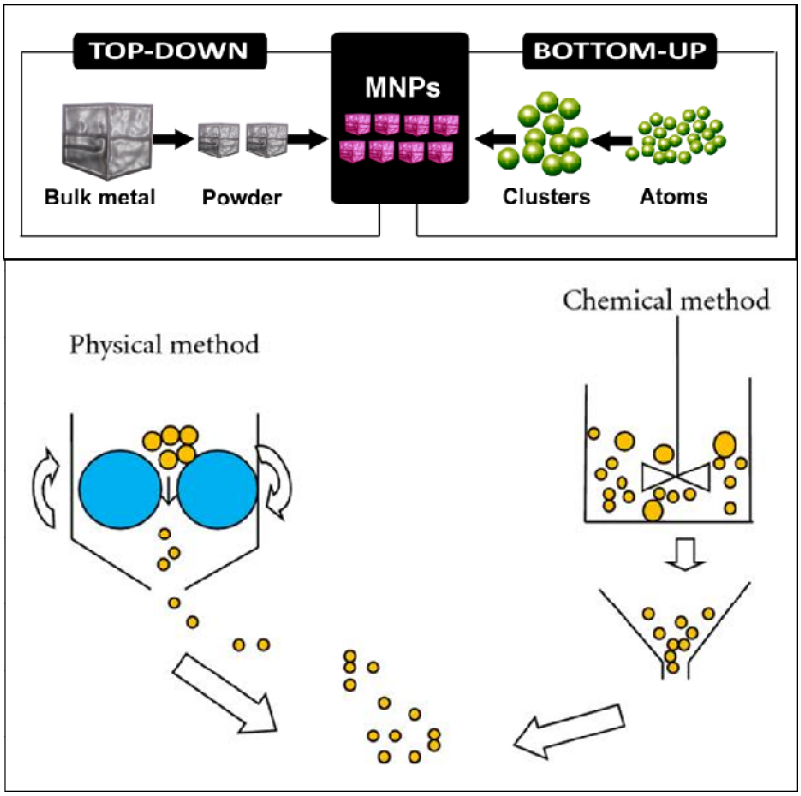

FIGURE 12.2
Schematic representations of top down and bottom up approaches [15]

There are different wet methods for synthesis of metal nanoparticles and nanocomposites but co-precipitation, sol gel and hydrothermal methods are cost effective as compared to other methods so these are discussed in detail.

Co-precipitation Method

The co-precipitation method is used for the synthesis of metal oxides nanoparticles, mixed metal or metal ceramics nano-composites, produces precipitate that are separated from solution. Inorganic salts are used as precursors, dissolved in water and other solvents to obtain homogenous solution of ions, and then these salts start precipitating as hydroxides or oxalates when the critical concentration of species is attained followed by nucleation and growth phases [12]. The size and shape of particles is greatly influenced by solution pH, temperature and concentration of salt [16]. After precipitation, filtration and washing is done followed by calcination to convert hydroxide into oxides with a definite crystalline structure [17].

Different types of metal nanocomposites (metal –metal oxide, oxide-oxide, oxide- matrix) materials synthesized using this approach are listed in Table 12.1. The precipitating medium usually employed includes NaOH, NH_3 or NH_4OH, Na_2CO_3 etc. [18-20]. The use of surfactants is also a common practice to avoid agglomeration which also tampers the particle size of the composites obtained by this technique [18].

The method offers the advantage of being low cost, simple, water based reaction, flexibility, mild reaction conditions and size control [12].

TABLE 12.1
The MONC prepared from different approaches

Synthesis Method	MONC	Precursor	Reaction conditions	Particle size (nm)	characterization	References
Co-precipitation	MgO-Al_2O_3	$MgCl_2$, NaOH	Centrifuged at 100 rpm	4-30	FTIR, HR-SEM, XRD, EDAX, and BET analyses.	[21]
	ZnO-SnO_2	$ZnCl_2$, NaOH	pH 6, 105°C	30	XRD,TGA,SEM	[22]
	ZnO-CuO	$CuCl_2$, $NaBH_4$			XRD,SEM,TEM and DSC	[23]
	MgO-CuO	$Mg(NO_3)_2$, $Cu(NO_3)_2$ and glycine (NH_2CH_2COOH)	120°C	20	XRD,TEM,SAED,AFM, Photoluminescence studies	[24]
	ZnO-Fe_3O_4	Fe_3O_4, NaOH	pH 7 and centrifuged at	40	FT-IR, XRD, SEM-EDX	[25]
	NiO·CeO_2·ZnO	$ZnCl_2$, NaOH	120°C	14-25	FT-IR,XRD,SEM-EDX	[26]
	Ag-Talc	$AgNO_3$, $NaBH_4$	Different molar	7.6-11.3	UV-visible spectroscopy,	[27]

			ratios of silver		FT-IR,XRD,SEM,TEM	
	Ag-MMT	$AgNO_3$, $NaBH_4$	Different molar ratios of Ag, centrifuged at 15,000 rpm	4.19 to 8.53	UVvisible, PXRD, TEM, SEM, EDXRF, FT-IR, and ICP-OES analyzer.	[28]
	Ag-Activated Carbon	soluble starch, NaOH	pH 8, in N_2 Atomsphere	55	XRD,SEM,TEM	[29]
	Zeolite-Y–Fe_3O_4	Zeolite-Y	At different temperatures	Less than 100	XRD,SEM and Magnetic properties	[30]
	ZnO-Activated Carbon	hexamethylenetetramine ($(CH_2)_6N_4$; HMTA)	70°C, pH 8	50-200	XRD,SEM, TEM	[31]
Sol gel method	TiO_2-Al_2O_3	Titanyl sulfate		5-9	XRD, TGA/DTA, BET surface area	[32]
	TiO_2–Fe_2O_3	TiO_2	100-1200°C	4-10	XRD,DCS,TEM	[33]
	Ag-TiO_2	$AgNO_3$, Titanium(IV) isopropoxide	Calcinated at 550°C	13-20	XRF,XRD,EDX, TEM,XPS	[34]
	TiO_2-lanathal	Titanylsulphate	600°C, pH 7	7	XRD,TEM,	[35]
	Al2O3–SiC	aluminium nitrate and hexamethylenetetramine (HMTA)			Creep and Viscosity test, SEM	[36]
	Mullite-SiC	Mullite	Varying concentration of mullite precursor	70	XRD, SEM and TEM	[37]

	WO_3-TiO_2	$Ti(OBu_4)$,ammonium tungstate	pH 10, calcinated at 400°C	60	DTA,XRD,TEM	[38]
	CNTs-TiO_2	titanium isopropoxide, isopropanol	Different carbon loadings, annealed at 500°C,		TEM, XRD, BET and TGA–DSC.	[39]
	TiO_2-MMT	$Ti(OC_4H_9)_4$, ethanol,	60–80 °C and pH 2–4	3.10	TGA, BET, TEM and XRD	[40]
	TiO_2-Clay	$Ti(OC_3H_7)_4$, NaOH	pH 4	1.7-4.5	XRD,SEM-EDX,BET	[41]
Hydrothermal method	Al_2O_3-TiO_2	Al_2Cl_3,NaOH	pH8,500°C	3.25	FT-IR, XRD,SEM and TGA	[42]
	ZnO-kaolinite	$ZnCl_2$, NaOH	Calcinated at 600°C,	14.6-48.2	XRFS,PXRD,FT-IR, SEM,BET,UV-VIS DRS,Photoluminiscencespectroscopy,Evaluation of photodegradation activity and Molecular modeling	[43]
	ZnS-MMT	hexadecyl trimethyl ammonium bromide (HTAB), $Zn(OOCCH_3)_2{\cdot}2H_2O$	170°C	3.77	XRD,SEM,TEM and BET	[44]
	CdS-TiO_2-Montmorillonite	$TiCl_4$,$CdAc_2{\cdot}2H_2O$ and CS $(NH_2)_2$	160°C	4-6	XRD,XPS,BET, UV-visible spectroscopy	[45]
	Co-MgO	Co(NO3)2 ·7H2O,	150°C, centrifugat		XRD,XAS,SEM and TEM	[46]

		Mg(NO3)2·6H2O	ion at 4100 rpm			
	$Al_2(OH)_3(VO_4)$	V_2O_5, $Al(NO_3)_3 \cdot 9H_2O$, and TMAOH			FT-IR,XRD and TGA	[47]
	mixed-phase TiO_2	Titanium chloride,anatase powder			XRD,SEM,EPR	[48]

Sol-gel method

Sol-gel method gained attention as a promising method for the synthesis of nanomaterials owing to their mild reaction conditions and building up the materials from molecular precursors leading to variation in materials and properties[49].The resulting product of sol-gel method is either films [50, 51] or colloidal powder [34, 52, 53]. The sol-gel method has capability of producing micro and nanostructures. The size, shape and structure of final product are greatly influenced by the reaction parameters [54, 55]. The process involves the simple wet chemical reaction based on hydrolysis and condensation leading to formation of sol which through the process of aging results in formation of an integrated network as gel (Figure 12.3).

The sol–gel method is also very attractive for the synthesis of nanostructures containing more than one component, since the slow reaction kinetics allows good structural engineering of the final product. Another advantage is that the reactions are conducted at low temperatures or at room temperature. The sol–gel process involves inorganic precursors that undergo various chemical reactions, resulting in the formation of a three-dimensional molecular network. One of the most common routes is via hydrolysis and condensation of metal alkoxides to form larger metal oxide molecules that polymerize to form the coating. The sol–gel procedure allows coating of substrates with complex shapes on the nanometer to micrometer scale, which some commonly used coating procedures cannot achieve. The substrates include colloidal particles, organic/inorganic crystals, or even fibers and nanotubes [56-58]. The range of materials prepared using this technique is outlined in Table 12.1.

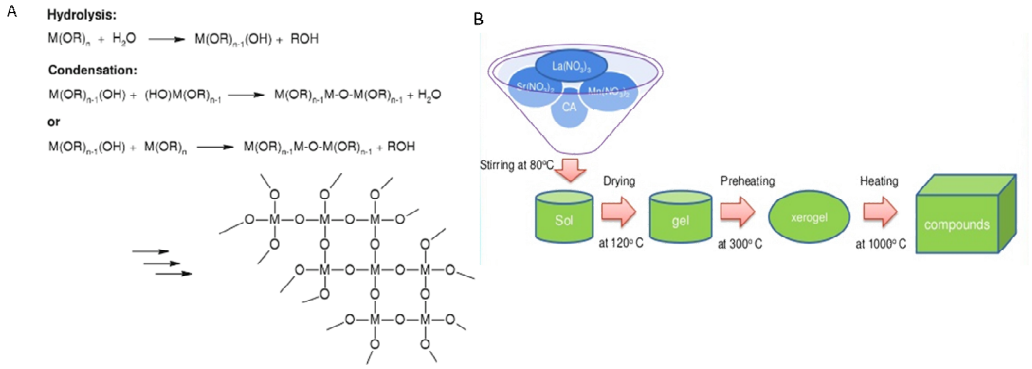

FIGURE 12.3
A) Chemical steps and B) Schematic representation of Sol-gel method [49]

Hydrothermal Method

The hydrothermal method involves the heterogeneous chemical reaction in a solvent (aqueous or non-aqueous) occurring above room temperature and at pressure more than 1atm in a closed system [59]. To modify the size and properties the use of surfactants, capping agents, mineralizers is a common practice [60-63]. The new trend is to use this technique in combination with microwave [64], sol-gel [65] that can not only vary the physiochemical and structural properties of the materials but in addition to that can result in formation of single phased materials with enhanced stability [65]. Further just by altering the temperature, time and pressure of the reaction particle size, phase changes morphology and properties as presented in Figure 12.4 [63, 66].

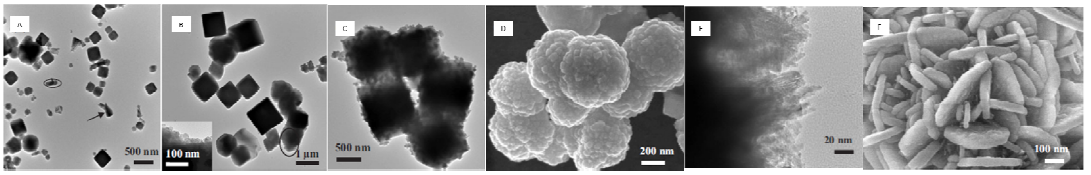

FIGURE 12.4
Effect of time and temperature on size and morphology of ZnO–SnO_2 nanocomposite A) 160°C for 30min B) 160°C for 60min C) 160°C for 4h D) 160°C for 12h E) 180°C for 30min F) 200°C for 12h [63]

Table 12.1 lists down the nanocomposites prepared by hydrothermal approach under varied action conditions.

Characterization of Metal Oxide Nanocomposites (MONC)

The nanocomposites are characterized using different techniques to get insight into the morphology, particle size, phase, composition, thermal stability, optical, magnetic, electrical and thermal properties.

X-ray Diffraction (XRD)

Powder X-ray Diffraction (XRD) is used for phase determination and unit cell information of the nanocomposites under investigation [23]. The technique is also frequently employed to determine particle size using Scherrer's formula (Equation 1) [67-69].

$$D = {K\lambda}/{\beta cos\theta} \quad (1)$$

where D (nm) is the mean size of the crystalline domains, *K* is the dimensionless shape factor which value is close to unity, λ is x-ray wavelength and β is line broadening referring to FWHM and ϑ is Bragg angle. The formula is applicable when nanocomposites have definite crystalline structure while in case of amorphous structure this formula is not applicable for particle size.

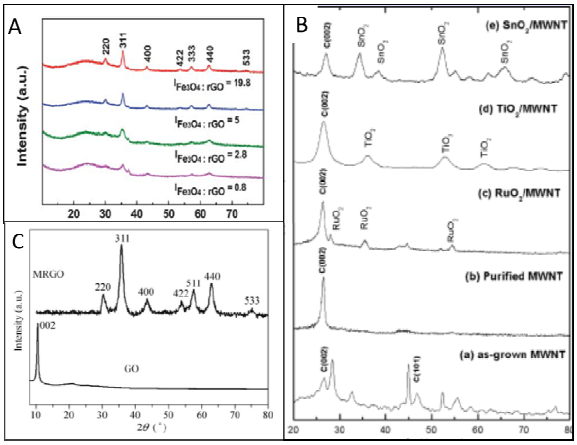

FIGURE 12.5
Powder XRD patterns of A) Fe_3O_4/GO at different ratios, B) MO/MWCNT and C) MnO_2/GO indicating disappearance of GO peak [70, 71]

In majority of cases the phase determination is the usual information obtained from PXRD technique especially when comparing the synthetic approach or effect and present of doping in the matrix structure (Figure 12.5A & B) [72-75]. Kalantari*et.al.* used PXRD as a means to confirm surface binding of Fe^{3+} ions with talc used as matrix in nanocomposite by shifting in d-spacing value of the talc while constant 2θ and FWHM values in matrix and MONC were taken as grantee for talc maintaining its structure [19]. Further the technique is also helpful in determining the nanoscale dispersion in polymer matrix when used in combination with TEM but when used independently the low loading in the matrix structure might lead to negative results as the diffraction peaks are usually not observed [76]. The exfoliation of graphite oxide (GO) by inclusion of metal oxides as indicated by decrease in intensity of GO peak in the nanocomposites was also determined by various researches (Figure 12.5C) [70, 77]. The researchers had also used the technique for determining the presence and absence of impurities from matrix structure by the appearance of peaks in the matrix as shown in Figure 12.5B a and b in which the disappearance of peaks in purified spectra of MWCNT after acid washing confirms the removal of impurities [75].

Microscopic techniques - SEM/AFM/TEM

The microscopic techniques focused in the chapter are scanning electron microscopy (SEM), atomic force microscopy (AFM) and transmission electron microscopy (TEM). SEM is mostly employed for studying the surface morphology of the MONC but that requires the surface to be electrically conductive hence in case of non-conducting samples the thin layer of gold or carbon is coated. The resolution of SEM is around 1-2 nm [49, 78]. The effect of doping of different metal oxide nanoparticles on the matrix [75], agglomeration [73], shape [79] etc. as presented in Figure 12.6.

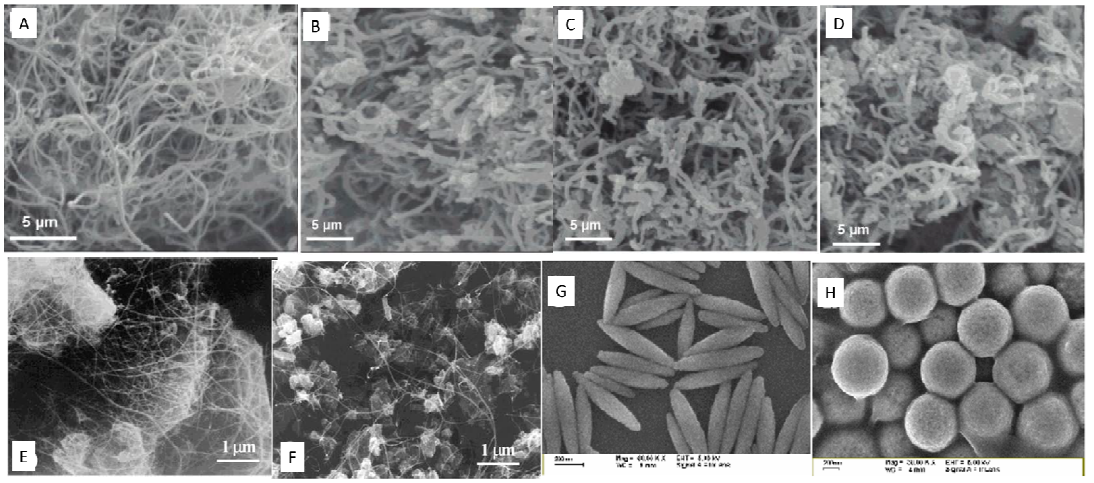

FIGURE 12.6
SEM images showing effect of doping on (A) purified MWCNT matrix with (B) RuO_2, (C) TiO_2 and (D) SnO_2, respectively; (E, F) effect of varying carbon to metal ratio on agglomeration of CNT-Fe-Al_2O_3 i.e. C=4.8% and 5.7% respectively; and (G, H) effect of doping of Fe_3O_4 and CuO on PANi, respectively [73, 75, 79]

TEM technique has gained much attention as compared to SEM because of its better resolution i.e. 0.1-0.2nm and wealth of information that can be extracted from it and especially from high resolution TEM (HRTEM) [49, 78]. The core-shell structure of the nanocomposites [79], doping effects on morphology [75], layering in structure [68], particle size [80], gelling agents impact [81], surface roughness [82], nanoparticle dispersion [83] etc. can be determined. In this regard use of dark field and bright field images can help in getting more information about the structural changes [68, 70]. The main limitation of the technique is in sample preparation which requires low film thickness [49, 78].
AFM enables surface imaging of both conducting and non-conducting materials at atomic resolution level by measuring interactive forces between the atom of sample and AFM tip [49]. It can work under different modes i.e. contact mode, tapping mode and conductive mode [84, 85]. 2D, 3D and line profile data obtained from AFM can give information about the dispersion of the nanoparticles, height of nanoparticles dispersed in matrix and height of matrix itself [86]. The technique also helps in determining the surface roughness of the nanocomposite membrane [87].

Thermal stability

Thermal analysis including thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), dynamic mechanical thermal analysis (DMTA), thermal mechanical analysis (TMA) etc. is a useful tool to determine the stability of the nanocomposite materials and various phenomena occurring because of doping, curing and annealing [88]. The steps leading to thermal decomposition of the nanocomposites, endothermal or exothermic nature of decomposition process, solvent/ moisture loss, weight loss at each step, final decomposed matter etc. are the usual information obtained by the TA [89]. The content of MONP present in the matrix was also assessed by the residue left after complete thermal decomposition of the polymer matrix achieved [20]. Laachachi *et.al.* compared the thermal stability of the PMMA by doping equal amount of TiO_2 and Fe_2O_3 and observed with help of onset degradation temperature that former imparts better

stability than the later. He also used the technique to determine the best wt.% of metal oxide NPs in the polymer matrix that causes decrease in heat release – the property considered good for flame retardants [90]. The change incuring initiating temperature of the resin with introduction of functionalized and non-functionalized nanoparticles and treatments was also tied by changes in TGA spectra [91]. TGA of MnO_2/CNT MONC helped in determining the interlayer water from which nanocomposite formula was derived that further elucidated the oxidation state of Mn in the NC [92].

Applications of Metal Oxide Nanocomposites (MONC)

The applications of metal oxide nanocomposites in different sectors had been widely recognized. The chapter will focus on the four main categories i.e. environment, agriculture/ food and health/ medicine.

Application in Environment

The MONC are frequently used as adsorbents, photocatalysts and sensors to tackle environmental pollution problems. The advantage of being at nanoscale offers the high surface area and high reactivity making them highly effective for water purification and early sensing of pollutants [93]. Metal oxides nanoparticles are used in combination with graphene, silica, other oxides, CNT, polymers for the removal of dyes, heavy metals etc. [93-96].

Application in Agriculture and Food

The MONC are widely used in packaging of foodstuff, not only provides strength as filler material (silicates, clays, TiO2) but also as antimicrobial agent like silver oxide nanocomposites and oxygen scavengers [97, 98]. While in agriculture sector, MONC used as nanosensor for pesticide and pathogen detection in plants and source for delivery of genetic material for improvement of crops [99, 100]. Metal oxide nanoparticles (ZnO, CeO and CuO) and their nanocomposite (with fertilizers and zeolite) used as slow and controlled release of fertilizers provide nutrients to plants for prolonged period and also helps in prevent of soil degradation and improvement of sustainable agriculture [101, 102].

Application in Health and medicine

The MONC have many applications in medicine, for delivery of drugs and imaging, diagnosis and screening of diseases, DNA sequencing, in gene therapy and tissue culturing and in cancer treatment [103-105].

Conclusion

Metal oxide nanocomposites have proven themselves as the materials on 21st century with the range of application in every industry sector. The wet chemicals methods mark the easy route for their fabrication that makes them cost-effective as well. Co-precipitation being the simplest route

enabling the formation of complex matrix based MONC. The materials are characterized using various techniques like powder XRD, electronic microscopy, atomic force microscopy, TGA etc. that give insight into the morphology of the materials, particle size, impurities, roughness, doping level, thermal stability, degradation pattern etc. Because of their simplicity in synthesis and wide range of tailorable properties these MONC are frequently used as adsorbents, photocatalyst, sensors, fuel cells, solar cells, packaging, antimicrobial agents, drug delivery, medical devices, surgical tools etc.

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