The Catalytic Efficiency of Au^{3+} metal ions and Au NPs on the Oxidation of Carbonyl Compounds by *in situ* Generated Na_2FeO_4 under Microwave Irradiation for Industrial Point of View

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The catalytic activity of the Au NPs and Au^{3+} metal ions used in the oxidation of carbonyl compounds by *in situ* generated Na_2FeO_4 from an industrial point of view. In the subsequent study used the chemical reduction and green method in favor of the fabrication of 30 to70nm in the size of Au NPs. Carbonyl compounds converted to aromatic and aliphatic acids by the oxidation process. Au NPs give better yield as compared to Au^{3+} ion since in case of bulk metal the size is enlarged and surface area reduce but converted to nanoparticles the surface area increased so catalytic activity augmented.

Introduction

Oxidation processes are one of the crucial steps in the industrial production of diverse compounds, thus much attention was being given either to switch over to the environmentally benign processes of oxidation or to minimize the use of hazardous chemicals.

Oxidation by Fe (III) in the form of its various salts and complexes has established a great deal interest for most probably due its economical accessibility and a smaller amount difficulty involved in the evaluation and its ability to proceed in both H^+ and OH^- medium [**1**]. Reviews presenting very interesting information about ferricyanide oxidations have been presented by many authors [**2-3**]. Waters and Speak man [**4**] ruled out this simple model of the charge transfer process and recommended that in alkaline hexacyanoferrate(III) oxidation of carbonyl compounds and nitroparaffins, not two but a single step was the rate-determining and the oxidation process involved no organic free radical formation. On the other hand, in some organic oxidations colored and stable radicals were detected and a more complex view describing the exchange of cyanide ligand in the oxidation of phenols was described [**5-6**]. The views of Waters and co-workers were recently completely modified and the complex formation mechanism was ruled out [**7**] the oxidation of thiols observed by Wiberg and co-workers [**8**] in which there was no exchange of cyanide ligand and the oxidation habitually occurred via a charge transfer method. From these studies, it was quite obvious that oxidation occurred mainly via direct charge transfer process without changing the coordination number of iron. In current times iodide ion oxidized by $K_3Fe\ (CN)_6$ using the transition metal ions as a catalyst in the basic medium [**9-12**]. Oxidation of sulphanilic acid by $K_3Fe\ (CN)_6$ ion in a basic medium in the attendance of ruthenium as a catalyst [**13**]. Oxidation of triethylamine in alkaline medium [**14**] and Os (VIII) catalyzed the oxidation of cyclic amines have also been reported [**15**].

Nanoparticles used in different research field involving sciences, medicine, and engineering, has vast possibilities for early discovery, accurate diagnosis, and modified treatment. The shape-controlled fabrication of M NPs has been a very dynamic research area in modern years owing to their catalytic, electronic, and enthralling shape-dependent optical properties [**16-20**].

M NPs dispersed onto various supports are extensively used as catalysts into many processes in the chemical industry, such as fine chemical, polymer, petrochemical, and pharmaceutical industries [**21**]. The catalytic activity and selectivity of such materials are robustly affected by the shape and size distribution of the active metal species, nature of the support, and the interaction of active metal species with the carrier material [**22**].

Metal oxides supported Au NPs have proficient catalysts property for significant oxidation procedure, including the selective oxidation of aromatic and aliphatic hydrocarbons and oxidation of different volatile organic compounds such as HCHO, CH_3OH, and CO at reasonably elevated temperatures [**23,24**].

The narrative effort of Haruta *et. al.*, [**25**] exposed Au was the most excellent catalytic oxidation of carbon mono oxide. Haruta *et. al.*, used in gold catalysis in many organic syntheses [**26,27**]. A focal point is now on the utilization of Au NPs for the oxidation of aliphatic and aromatic alcohols [**28**]. Cyclohexane converted to cyclohexanol and cyclohexanone by an oxidation process in the presence of Au catalyst [**29**].

Elevated effectiveness of Au towards the oxidation process has to lead to the excess of attention in Au mediate catalytic reactions [**30**].

The electrode potential of Fe (VI) is +2.2 V to +0.7 V in acidic and basic solutions so Na_2FeO_4 is the strong oxidizing agent which can oxidize alcohols into ketones or aldehydes [**31,32**]. On oxidation, cyclic alcohols converted to aldehydes and aromatic aldehydes converted to acid. In the case of aromatic hydrocarbons converted to corresponding carbonyl compounds by using oxidizing agent Na_2FeO_4 in presence of transition metal ions as a catalyst [**33**].

Ferrate dianion FeO_4^{2-} gives the monomeric species in aqueous solution [**34**] in the basic medium the rate of decay of ferrate ions is extremely erratic and depends upon the temperature and pH of the medium [**35**]. In dilute solution, maintain the pH 9.4 and 9.7 [**36**] the rate of reduction of ferrate is decreased. The wet method used for the fabrication and decontamination of potassium ferrate [**37,38**] Na_2FeO_4 has established more interest due to its utility in wastewater treatment and green organic synthesis [**39,40**].

Experimental section

Fabrication of Au NPs

The chemical reduction method was employed for the fabrication of Au NPs by using sodium citrate ($Na_3C_6H_5O_7$) as a reducing and stabilizing agent. 10.0 ml of 0.03 M $Na_3C_6H_5O_7$ mixed with 20 ml of $3.24x10^{-3}$ M warm gold chloride solution. The mixture was reserved heating for about half hours waiting at wine red colored was appear, representing the fabrication of Au NPs.

Oxidation of carbonyl compounds

In the oxidation of 3, 4 dimethoxy benzaldehyde to 3, 4 dimethoxy benzoic acids for occurring the reactions in the liquid phase, $0.48x10^{-3}$ mmol of gold chloride solution as a catalyst with 4.49 mmol sodium ferrate (Fe $(NO_3)_3$ $.9H_2O$) and 44.1 mmol sodium hypo chloride (NaClO) both used as oxidant mixed with 3.4 mmol of CH_3COOH solution containing 1.0 mmol of 3,4 dimethoxy benzaldehyde and the reaction mixture is exposed the under microwave irradiation for the desired time and desired power. After complete reaction, the reaction was monitored by TLC method and cooled contents were extracted by diethyl ether. A similar procedure was repeated by Au NPs. Identification of final products confirmed by IR and ^1H NMR spectra.

Results and discussion

Ultra-Violet spectral study

Ultra-Violet spectroscopy is a valuable technique to illustrate the development of metallic species through the fabrication of Au NPs. As revealed in **Fig. 1**, show the 539nm is the optical absorbance plasmon band that confirms the fabrication of the Au NPs in the colloidal suspension.

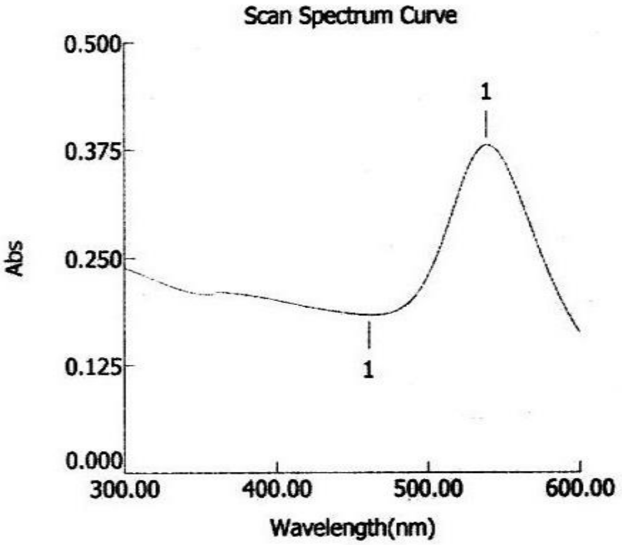


Fig. 1. UV-Vis Spectrum of Au NPs.

Zeta potential and zeta size analysis of Au NPs

Zeta potential value confirmed that the highly stable colloidal mixture formed using trisodium citrate **(-31.8 mV)** and zeta average diameter formed **31.49 (d. nm)** size of Au NPs in **Fig. 2**.

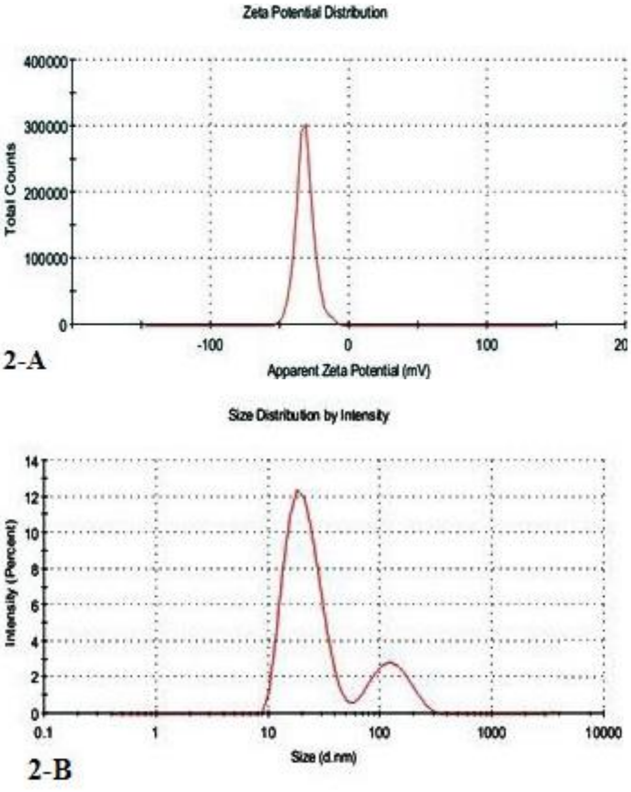


Fig. 2. Zeta potential and zeta size of Au NPs.

XRD analysis of Au NPs

Fig. 3 represents the XRD pattern of fabricated Au NPs in the 2θ range 10° to 60°. The FCC structure of Au NPs is shown by a spectrum of XRD. The sharp peak shows that the crystalline nature of Au NPs. Scherer formula is used to calculate the average size of Au NPs.

$$D = 0.9\lambda / \beta \cos\theta$$

The average particle size of Au NPs was found to be **34.22nm**.

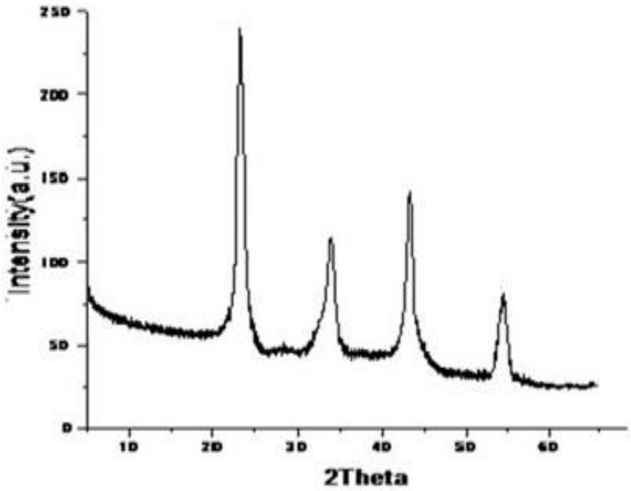


Fig. 3. XRD of Au NPs.

SEM and TEM study of Au NPs

SEM and TEM analysis of fabricated Au NPs is accessible in **Fig. 4**. The picture of SEM clears that the standard diameter of Au NPs was established to be about **50nm**. The picture of TEM clears that large amounts of the Au NPs are the sphere-shaped and dark-colored dot of nanoparticles.

It is established that the standard particle size of individual Au NPs is about **30-70nm** based on SEM, TEM, Zeta size, and XRD analysis.

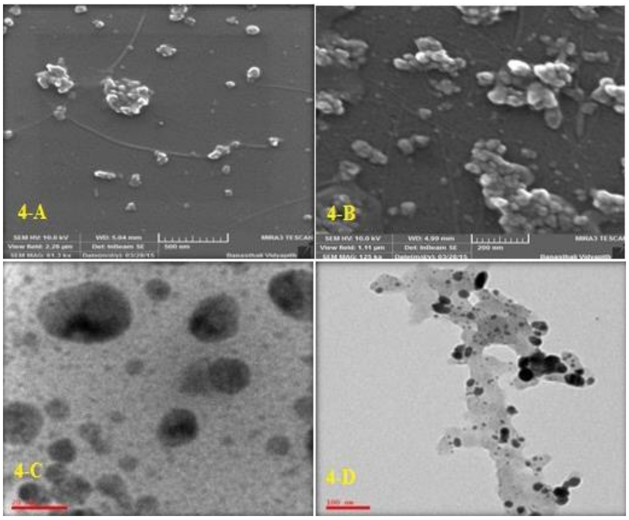


Fig. 4. (a) SEM image and (b) TEM image of Au NPs.

Spectral analysis of organic compounds

3, 4 dimethoxy benzoic acid: IR peaks: ν_{max} = 2928.23 cm^{-1} ($\nu_{O\text{-}H\ strs.}$), ν_{max} = 1587. 08 cm^{-1} ($\nu_{C=C\ strs.}$), ν_{max} = 1420.16 cm^{-1} ($\nu_{O\text{-}H\ bending}$), ν_{max} = 1690.11 cm^{-1} ($\nu_{C=O)}$), ν_{max} = 915.38 cm^{-1} ($\nu_{C\text{-}C\ strs.}$), ν_{max} = 2849.59 cm^{-1}(ν_{OCH3}). NMR Signals: δ 11.090 (1H, s), δ 9.810 (1H, s) δ 7.1268 – 7.4995 (2H, dd), δ 4.4764 (6H, s). **p- methoxy benzoic acid:** IR peaks: ν_{max} = 2929.08 cm^{-1} ($\nu_{O\text{-}H\ strs.}$), ν_{max} = 1596. 88 cm^{-1} ($\nu_{C=C\ strs.}$), ν_{max} = 1419.74 cm^{-1} ($\nu_{O\text{-}H\ bending}$), ν_{max} = 1699.34 cm^{-1} ($\nu_{C=O)}$), ν_{max} = 920.72 cm^{-1} ($\nu_{C\text{-}C\ strs.}$), ν_{max} = 2849.59 cm^{-1}(ν_{OCH3}). NMR Signals: δ 11.096 (1H, s), δ 8.1560-8.1565 (2H, d) δ 6.9960 – 6.9967 (3H, m), δ 2.4740 (1H, s). **Benzoic acid:** IR peaks: ν_{max} = 2811.42 cm^{-1} ($\nu_{O\text{-}H\ strs.}$), ν_{max} = 1568. 26 cm^{-1} ($\nu_{C=C\ strs.}$), ν_{max} = 1413.20 cm^{-1} ($\nu_{O\text{-}H\ bending}$), ν_{max} = 1676.56 cm^{-1} ($\nu_{C=O)}$), ν_{max} = 750.93 ($\nu_{C\text{-}C\ def).}$ NMR Signals: δ 11.1140 (1H, s), δ 7.8931-8.0912 (2H, d) δ 7.5907-7.8862 (3H, m). **Glutaric acid:** IR peaks: ν_{max} = 2940.5 cm^{-1} ($\nu_{O\text{-}H\ strs.}$), ν_{max} = 1393.61 cm^{-1} ($\nu_{O\text{-}H\ bending}$), ν_{max} = 1695. 65cm^{-1} ($\nu_{C=O)}$).NMR Signals: δ 11.1135 (1H, s), δ 2.3447 – 2.3778 (4H, t), δ 1.8034-1.9529 (2H, m).

Adipic acid: IR peaks: ν_{max} = 2940.50 cm^{-1} ($\nu_{O\text{-}H\ strs.}$), ν_{max} = 1449.61 cm^{-1} ($\nu_{O\text{-}H\ bending}$), ν_{max} = 1699.06 cm^{-1} ($\nu_{C=O)}$), ν_{max} = 905.02 cm^{-1} ($\nu_{C\text{-}C\ strs.}$).NMR Signals: δ 11.0695 (1H, s), δ 2.2127-2.2720 (4H, t), δ 1.5115-1.54574 (4H, t).

Table 1. Effect of diverse factors on the yield of 3,4 dimethoxy benzoic acid from 3,4 dimethoxy benzaldehyde (1.0mmol) by Au^{3+}-Sodium ferrate catalytic system in aqueous acetic acid medium in solution phase under microwave irradiation.

S. No.	$Fe(NO_3)_3.9H_2O$ (mmol)	NaClO (mmol)	$Au^{3+}x10^3$ catalyst (mmol)	Time (min)	Temp. (°C)	MW power (W)	% yield with Au^{3+} catalyst
1.	4.49	44.1	0.32	2.0	60	60	64.03
2.	4.49	44.1	0.48	3.0	100	80	76.44
3.	4.49	44.1	0.63	3.0	80	100	62.92
4.	5.61	44.1	0.48	3.0	120	80	54.03
5.	4.49	51.40	0.48	4.0	80	80	57.91

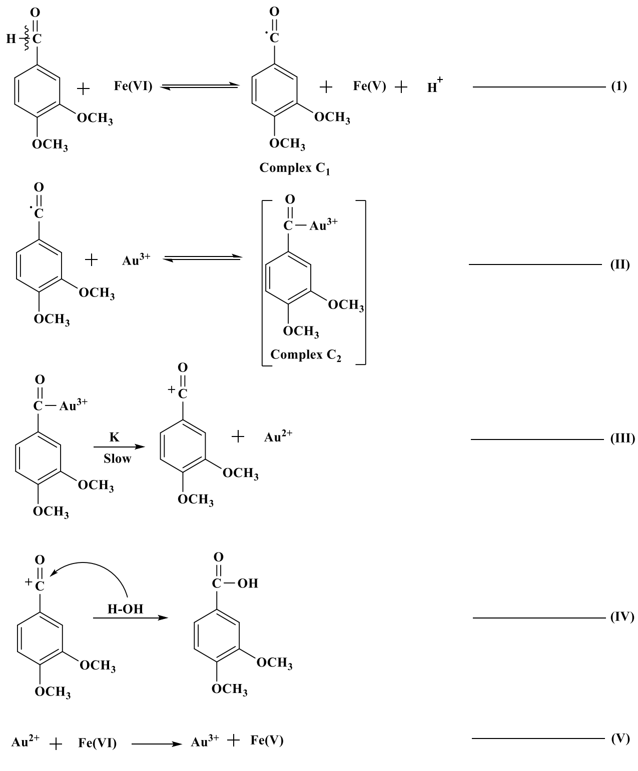
Discussion

The study was performed mostly to conclude the efficiency and selectivity of the novel, simple, and one-pot system. The concentration of Au^{3+} change (entries 01, 02 and 03, **Table 1**) increase the concentration of Au^{3+} to reduce the yield of the 3,4 dimethoxy benzoic acid since at high concentration un-reactive species of Au^{3+} is produced to decrease the rate of reaction and hence the yield of product is reduced. In case of change, the ferric nitrate and sodium hypochlorite concentration (entries 02, 03, and 04, Table 01) yield reaches an utmost and then starts falling with an increase in the concentration of oxidant. Possible causes for this appear to be the breakdown of ferrate ions. In case of temperature (entries 01, 02 and 04, **Table 1**), time (entries 01, 02 and 05, Table 1) and microwave power (entries 01, 02 and 03, Table 1) increased the yield, in the beginning, reached to a maximum and beyond which, further increase in parameter decreases the yield may be due to the evaporation of product due to excess heating under prolonged exposure.

In the present study in which 3, 4-dimethoxy benzaldehyde was more easily oxidized producing a better yield of acid compared to p-methoxy benzaldehyde for which low yield was obtained because methoxy group when attached to benzene ring at o- or p-positions has a negative σ value, but when it was attached at m-position then σ value becomes positive. Thus positive charge developed at carbonyl carbon was diminished due to shifting of electron density towards the benzene ring by resonance effect of a methoxy group (when attached at p-position) due to this the oxidation of p-methoxy benzaldehyde to the corresponding acid is difficult but in 3,4 dimethoxy benzaldehyde when one methoxy groups are is present on m-position, and the other on p-position than m-methoxy abstracted electron from the ring to make the carbonyl carbon more prone towards oxidation.

An analysis of UV-Vis spectra for study the complex formation shifting of the spectral peak of Fe(VI) and that of the mixture of Fe(VI) and 3,4 dimethoxy benzaldehyde from 502nm to 510 nm under the experimental condition supports the formation of a complex between Fe(VI) and 3,4 dimethoxy benzaldehyde (complex-C_1).

As for the mechanism, Fe(VI) oxidize the organic substrate and it gets reduced to Fe(V) under elimination H^+ ions and next step complex C_1 react with Au^{3+} catalyst and form the complex C_2 which in turn in the presence of water produces as 3,4 dimethoxy benzoic acid as the final oxidation product.



Scheme 1

From the **Fig. 5,** the bar diagram illustrates that in the existence of Au NPs give the better yield in comparison to Au^{3+} ion since in case of bulk metal due to enlarge size its surface area is decreased but converted to nanoparticles, the increase in surface area results in an increment of catalytic activity.

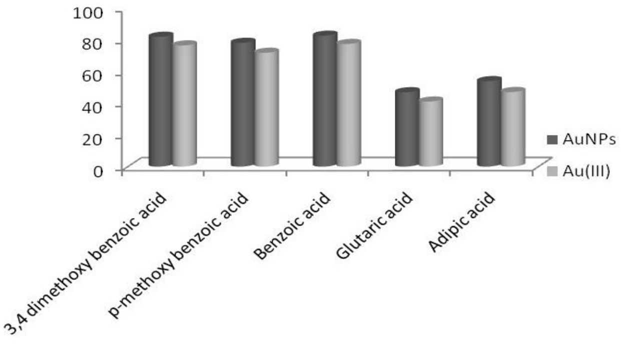


Fig. 5. Comparative studies of Au^{3+} ions and Au NPs on the yield of aromatic and aliphatic acid.

Table 2: Comparative study of Au^{3+} chloride and Au NPs as catalyst in solution phase for oxidation of aromatic aldehydes and cyclic ketones by *in situ* generated sodium ferrate under microwave irradiation

a- In presence of Au^{3+} solution
b- In presence of Au NPs

Organic Substrate	**Product**	**$Fe(NO_3)_3$+ NaClO (mmol)**	**Time (min)**	**Temp (^OC)**	**MP (reported) °C**	**MW Power (W)**	**% Yield With Au^{3+} catalyst^a (mg)**	**% Yield with Au NPs^b (mg)**
3,4 dimethoxy benzaldehyde (A)	3,4 dimethoxy benzoic acid(A’)	4.49+ 44.1^a 4.49+ 44.1^b	3.0^a 3.0^b	100^a 100^b	179 (181)	80^a 80^b	76.44 (140)	81.89 (150)
p-methoxy benzaldehyde (B)	p-methoxy benzoic acid (B’)	5.61+ 51.4^a 5.61+ 51.4^b	3.0^a 3.0^b	100^a 100^b	182 (184)	80^a 80^b	71.78 (110)	78.08 (118)
Benzaldehyde (C)	Benzoic acid (C’)	4.49+ 44.1^a 4.49+ 44.1^b	3.0^a 3.0^b	100^a 100^b	122 (122)	80^a 80^b	77.35 (94)	82.56 (100)
Cyclopentanone (D)	Glutaric acid (D’)	5.61+ 51.4^a 5.61+ 51.4^b	2.5^a 2.5^b	100^a 100^b	172 (174)	100^a 100^b	41.02 (54)	46.89 (62)
Cyclohexanone (E)	Adipic acid (E’)	4.49+ 44.1^a 4.49+ 44.1^b	3.0^a 3.0^b	100^a 100^b	217 (220)	100^a 100^b	47.05 (69)	53.89 (78)

Conclusions

In this research paper, we study the comparative catalytic activity of the Au NPs and Au^{3+} metal ions in the solution phase reaction. We get in the case of Au NPs gives higher yield as compared to metal ions catalyst because in the case of nanocatalyst the size is decreased in nano range and increased the surface area so catalytic activity increased many times. A new catalytic one-pot system is reported which is easy, very capable, and can be utilized to oxidize a variety of other functional groups, for which studies are being performed. The system became attractive from the industrial point of view due to the easy conversion of the carbonyl group to an acidic group and gives a high yield of products. Microwave reactions are also imperative due to less utilization of solvent and nontoxic chemicals in the reaction.

Keywords

Oxidation, carbonyl compounds, Au NPs, Au^{3+} metal ions, *in situ* generated Na_2FeO_4, green, synthesis.

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Abbreviations

NPs – Nanoparticles
M NPs – Metal Nanoparticles
Au NPs – Gold Nanoparticles
IR – Infra-red Radiations
NMR – Nuclear Magnetic Resonance
XRD – X-ray Diffraction
STM – Scanning Tunneling Microscopy
TEM – Transmission Electron Microscopy