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ARTICLE

Studies on the affect of bio-ionic liquid structures on the spontaneous reduction and dispersion stability of graphene oxide in aqueous media

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Mukesh Sharma,[a] Dibyendu Mondal, [a] Chandrakant Mukesh, [a] and Kamalesh Prasad [a,b] *

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Treatment of graphene oxide (GO) at elevated temperature with four choline based bio-ionic liquids (Bio-ILs) having counter anions with different nucleophilicity namely, choline bicarbonate (chol-HCO_3), choline hydroxide (chol-OH), choline formate (chol-HCOO) and choline caproate (chol-$C_5H_{11}COO$) resulted formation of partially reduced GO (prGO). The prGO formed in the presence of chol-HCOO and chol-$C_5H_{11}COO$ had long term dispersion stability in water (> 1 year). The results showed that ILs having strong nucleophiles were able to reduce GO in higher extent while resulted short term dispersion stability of the prGO, while the ILs with weaker nucleophiles gave formation of prGO with long term dispersion stability in water.

1. Introduction

Graphene (G), the two-dimensional carbon nanostructure is considered suitable for number of applications due to its exceptional physical, chemical, and mechanical properties such as high mechanical strength, high thermal conductivity, high electron mobility and high specific surface area etc.[1] Due to the hydrophobic nature of graphene, water is not a good media for the dispersion of the carbon material. Oxidation of graphite by Hummer's method produces graphene oxide (GO) having good dispersion stability in aqueous media. But certain practical applications need removal of oxygen functionalities of GO to restore π- conjugation and electrical conductivity. Usually this is achieved by the reduction of GO using hydrazine as reducing agent.[2] However, the removal of these groups which are responsible for the hydrophilicity of GO leads to the reduction of the ratio of hydrophilic/hydrophobic domains. The increase in hydrophobic contents result aggregation of chemically reduced GO. Normally this is avoided by adding surfactants in the dispersions or by tuning the pH of the dispersions. The reduced graphene oxide (rGO) is extensively used in various applications including in energy storage devices. [3,4] In order to increase application potentials, attempts are being made to disperse the hydrophobised graphene sheets without any additives to preserve the purity and the films thus obtained are used for various applications. [5]

Being considered as designer solvents and due to high thermal stability, low vapour pressure etc., ionic liquids (ILs) and their analogues are considered as very good solvent systems for the dissolution of various macromolecules e.g., DNA, chitin, tamarind gum etc., and for the preparation of new functional composites.[6-10] Further, ethyl lactate, a green solvent was used for the simultaneous production of a fuel intermediate and rGO.[11] As discussed above GO is conventionally reduced using hydrazine or $NaBH_4$ to yield rGO, which has enhanced hydrophobicity in comparison to pristine GO and is dispersible in water for long time. However the reduction using such chemicals requires lots of care and often there is a fear of contamination of the resultant graphene limiting the targeted applications in the areas where toxicity is not desirable. [12] Hence there are many other reducing agents are being tried to replace hydrazine. Recently, plasma-assisted simultaneous reduction and nitrogen doping of GO nanosheets and preparation reduced GO nanosheets free of paramagnetic metallic impurities were reported.[13,14] Ionic liquids are also being designed to exfoliate graphite in to graphene as well as to reduce GO. [15,16]

Herewith we have prepared choline based bio-ILs with four different anions and studied the affect of the anions on the surface modification and dispersion of GO. It was observed that the nature of the anions attached to choline cation affected the reduction as well as dispersion stability of functionalized GO. The bio-ILs are considered more preferred and suitable alternatives over their synthetic counterparts for various applications due to their non-toxicity, biocompatibility, biodegradability and ease of synthesis. [17]

2. Experimental section:

2.1. Materials

Graphite nano powder (CAS no. 7782-42-5, average particle size : 400 nm) and choline bicarbonate (80% aqueous solution) was purchased from SRL Chemicals, Mumbai, India and Sigma-Aldrich Chemicals, USA respectively. The chemicals used for the oxidation of graphite including sodium nitrate, concentrate sulfuric acid, potassium permanganate ($KMnO_4$) and hydrogen peroxide (H_2O_2, 30 wt%) were all AR grade and were procured from S.D. Fine Chemicals, Mumbai, India and were used without any further purification. Choline hydroxide was procured from TCI Fine chemicals, Tokyo, Japan.

2.2. Synthesis of choline based ionic liquids (choline formate and choline caproate)

The ionic liquids were prepared by following simple metathesis reaction, where formic acid and caproic acid (molar ratio: 1:1) was added drop wise to aqueous choline hydrogencarbonate solution under stirring at ambient temperature and pressure. Water was then removed under reduced pressure using a rotary evaporator (*e.g.* 90◦C, 1h). The ionic liquids were characterised by ^{1}H & ^{13}C (Bruker AVANCE II 500MHz spectrometer) at 25 ^{o}C. Their purity was further confirmed by electrospray ionisation mass spectrometry (ESI-MS) (Waters Q-Tof Micromass instrument equipped with an electro-spray ionization interface, MCP detector, and Waters MassLynx software (version 4.0).

2.3. Preparations of ionic liquid functionalized GO samples:

Graphene oxide (GO) was prepared following Hummers method by oxidation of graphite powder. [2] In a typical reaction, 10 mg GO was treated with 1 ml of different ILs followed by sonication for 30 min and stirring at 100 °C for 12 h. The functionalized GO was isolated by filtration and washed repeatedly several times with milli-Q to remove the excess ILs.

2.4. Characterization

UV-Vis absorbance spectra were recorded on a CARY 500 Varian 8.01 UV-Vis spectrophotometer. Powder X-ray diffraction patterns of different GO samples were recorded at 298 K on a PAN analytical system using Cu anode, K_α radiation (λ = 0.15405 nm) with 2θ range from 5° to 80° at a scan speed of 0.1^o sec^{-1}. Fourier transform infrared (FT-IR) of different GO sample were performed over the wave number range of 4000-400 cm^{-1} on a Perkin-Elmer FT-IR machine (Spectrum GX, USA) using KBr pellets (2 mg sample in 600 mg KBr). Thermo gravimetric analysis (TGA) of different GO sample were carried out on a NETZSCH TG 209F1 Libra TGA209F1D-0105-L machine using a temperature programmer 30-800 °C at a heating rate 5 °C min^{-1} under a nitrogen atmosphere. Transmission electron microscope (HR-TEM) images of rGO were recorded on a JEOL HR-TEM (JEOL JEM 2100, Japan) instrument operated accelerating voltage of 200 kV. Raman spectroscopy measurements were taken using a micro-Raman system (Horiba Jobin-Yvon LabRAM HR800 UV-vis µ-Raman) with argon sourced laser excitation at 514.5 nm employing power 10 mW in the scanning range of 100-4000 cm-1.

3. Results and discussion

GO was synthesized from graphite powder by modified Hummers' method [2] and subsequently functionalized with choline based bio-ILs as shown in Fig.1.

The aqueous dispersion of IL functionalized GO dispersion was blackish in colour in oppose to the brownish colour of GO dispersion indicating modification of the GO structure. Analytically, the functionalization of GO by the ILs was first monitored using UV-Vis spectroscopy. Fig. 2 and Table 1 shows the UV-Vis spectra of GO and GO functionalized with ILs. The much lower absorbance at λ_{max}= 230 nm corresponds to $\pi - \pi$ transitions of aromatic C-C bonds present in GO. After functionalization of GO with chol-HCOO and chol-C_5H_{11}COO, the λ_{max} did not shift but marginal enhancement of absorbance at 295 nm was observed indicating partial reduction of GO by these two ILs. [15] However, unlike above mentioned ILs, chol-OH and chol-HCO_3 functionalized GO showed a distinct λ_{max} at ~295 nm. These red shifted absorption maxima indicated the reduction of GO by these ILs. [15]

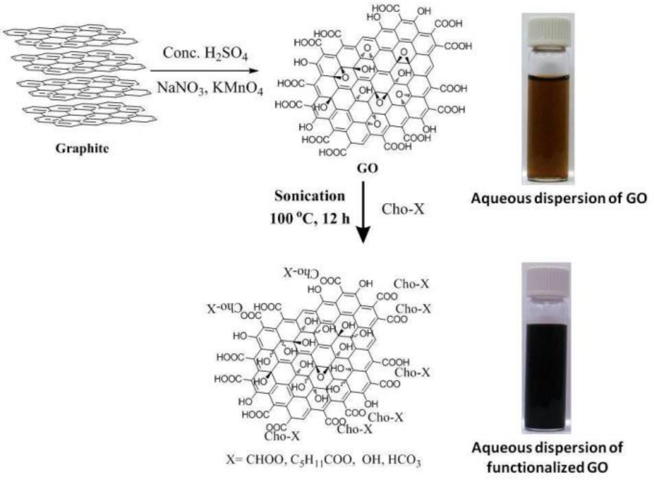


Fig. 1: Preparation of graphene oxide by Hummers method and surface modification using bio-ILs.

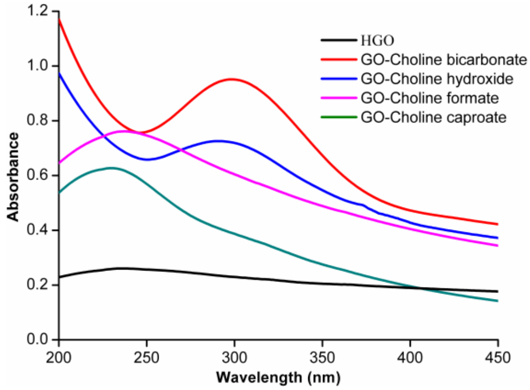


Fig. 2: UV-Vis spectra of pristine GO and IL functionalized GO measured a dilution (50 µg/ml)

The scanning electron microscopic images (SEM) (supporting Fig. S1) and transmission electron microscopic (TEM) images clearly displayed the multi sheet like structure of pristine GO (Fig. 3a) and GO functionalized by the ILs. Few layered graphene structures were visible in the GO functionalized by chol-HCOO (Fig. 3b). The average length of the sheets was 30 nm with average interlayer distance of 0.39 nm.

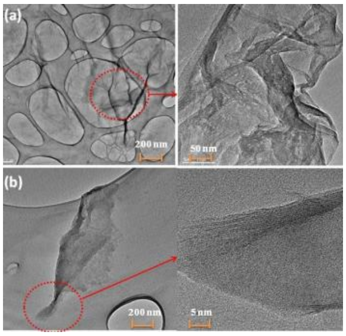


Fig. 3: TEM images of (a) pristine GO and (b) GO functionalized with choline formate.

The FT-IR spectral bands of synthesized GO matches well with the bands reported for GO. [18] Absorption bands at 1205-1315 cm^{-1} is due to C-O-C asymmetric stretching vibration of the epoxides. Sp^2 hybridized C=C in plane stretching vibration are seen between 1500-1675 cm^{-1}. Absorption bands in the range 1695-1790 cm^{-1} is due to C=O stretching vibration of carbonyl of COOH and all C-OH vibration at 3420 cm^{-1} and 1073 cm^{-1} is from COOH and H_2O (supporting Fig. S2). The IL functionalized GO in presence of chol-OH showed reduction of the band due to C=O of COOH and the bands due to epoxides also got affected indicating reduction of GO. Moreover the bands due to C-OH also got little affected indicating surface functionalization of GO (Fig. 4a). GO in presence of chol-HCO_3 showed similar bahaviour but the extent of reduction at COOH and epoxides were lower evident from the presence of relatively enhanced bands due to C=O and epoxy (supporting Fig.S3). No decrement in the band intensity of GO for C=O and epoxide of GO was observed in presence of chol-HCOO (Fig. 4b) and chol-$C_5H_{11}COO$ (Fig. S4), however the bands due to C-OH got substantially affected indicating surface modification of GO.

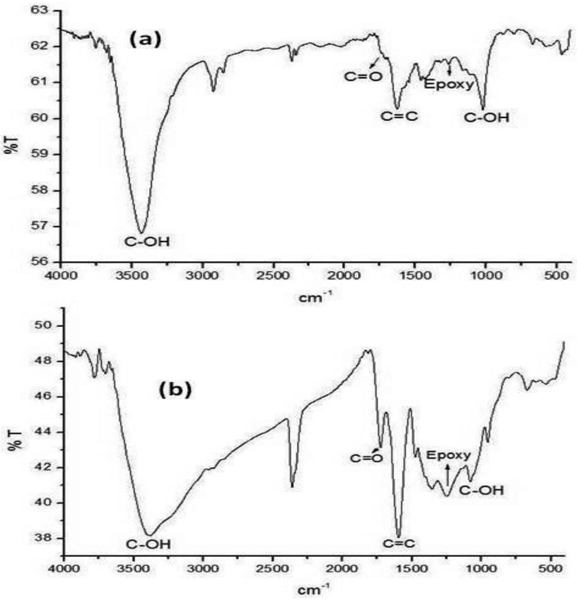


Fig. 4: FT-IR spectra of (a) chol-OH functionalized GO and (b) chol-HCOO functionalized GO

Solid state ^{13}C NMR (SSNMR) spectra of pristine GO and functionalized GO with ILs were recorded and shown in supporting Fig. S5. The peak at 55-60 ppm is assigned due to epoxide carbon present in GO sheet, peak at ~ 70 ppm is due to hydroxylated carbon (C-OH) and peak at ~129 ppm can be assigned due to sp^2 carbon (C=C). [19] The downfield peak position observed above 160 ppm is due to C=O group resulted from lower degree of oxidation of graphite oxide. The peaks due to epoxides and C-OH carbon got affected in presence of all the ILs indicated surface modification. The C=C peaks remained intact indicating non participation of the sp^2 carbons in the functionalization.

To further confirm the reduction of GO, the micro-Raman spectra of the GO samples were recorded. Pristine graphite showed D/G intensity ratio of 0.21 and GO showed the value of 0.89. The chol-HCOO and chol-$C_5H_{11}COO$ functionalized GO showed the value of 0.97 and 0.94 respectively (Fig. 5) indicating formation of more sp^2 domains after the functionalization by the IL and supported the reduction of GO described above. [20] The other two ILs (chol-OH and chol-HCOO) had also showed the values of 1.01 and 0.98 respectively (ESI, Fig. S6).

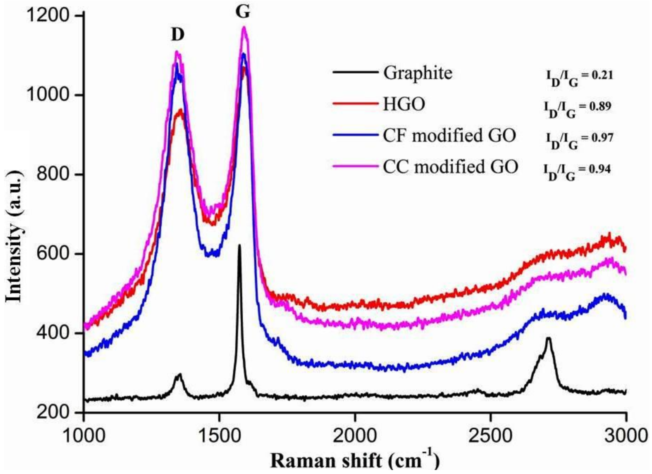
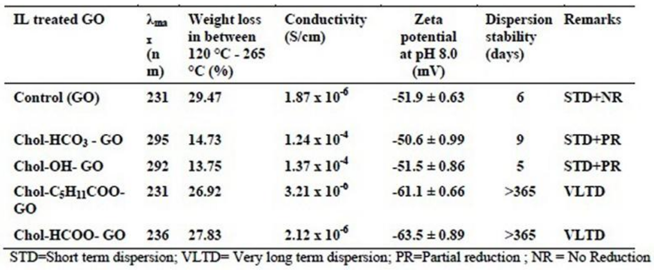


Fig. 5 : Raman spectra of graphite (black), Hummers GO (red); GO functionalized by chol-HCOO (blue) and GO functionalized by chol-$C_5H_{11}COO$ (pink).

Table 1 : Various parameters of GO functionalized with the ILs



IL treated GO	λ_{max} (nm)	Weight loss in between 120 °C - 265 °C (%)	Conductivity (S/cm)	Zeta potential at pH 8.0 (mV)	Dispersion stability (days)	Remarks
Control (GO)	231	29.47	1.87×10^{-6}	-51.9 ± 0.63	6	STD+NR
Chol-HCO_3 - GO	295	14.73	1.24×10^{-4}	-50.6 ± 0.99	9	STD+PR
Chol-OH- GO	292	13.75	1.37×10^{-4}	-51.5 ± 0.86	5	STD+PR
Chol-$C_5H_{11}COO$-GO	231	26.92	3.21×10^{-6}	-61.1 ± 0.66	>365	VLTD
Chol-HCOO- GO	236	27.83	2.12×10^{-6}	-63.5 ± 0.89	>365	VLTD

STD=Short term dispersion; VLTD= Very long term dispersion; PR=Partial reduction ; NR = No Reduction

The increase in conductivity (measured on a KEITHLEY 2635 four probes meter) increased substantially for GO functionalized by –OH and –HCO_3 containing ILs indicating reduction of the moiety, [21] while marginal increase in the conductivity for the GO in presence of –HCOO and –$C_5H_{11}COO$ containing ILs were observed indicating lesser reduction but surface functionalization by these ILs (Table 1). As shown in Table 1, the TGA profile (supporting Fig. S7) showed lower weight loss for the IL functionalized GO samples (18-35%) in comparison to pristine GO (55%) at temperature range around ~ 120 °C to ~ 265 °C. In this temperature range, loss of CO, CO_2 and water molecule took place from carboxylic and hydroxyl functionality present in the GO sheets. Since the % of weight loss in the above mentioned temperature range for the functionalized GO are much lower than GO indicating lower amount of oxygen functionality in the GO surface which is due to partial reduction of GO induced by the ILs. Furthermore the weight loss at less than 800 °C was around 77% for GO, and 50-60% for IL functionalized GO confirmed modification of GO. The X-ray diffraction (XRD) pattern of pristine GO showed a characteristic peak of (001) at $2\theta = 11.58°$ having interlayer spacing of 7.64 Å, confirmed the presence of oxygen functionality after oxidation of graphite. The peak of (002) at $2\theta = 26.53°$ and the peak of (010) at $2\theta = 42.42°$ corresponds to original graphite peaks.[22] The XRD pattern of GO functionalized by the all four ILs exhibited a new peak broadening closer to (002) at $2\theta = 21.7°$, having much lower interlayer spacing of ~ 4.09 Å. This observation confirmed the reduction of GO by the ILs (supporting Fig S8). [23]

GO is oxygenated and consisted of multi sheets having hydrophilic nature. Such material can be easily exfoliated in water to yield a long term stable dispersions consisting mostly of few layer sheets. GO was also found to be dispersible in solvents such as *N*,*N*-dimethylformamide, *N*-methyl-2-pyrrolidone, tetrahydrofuran, and ethylene glycol.[23] After reduction the formation of hydrophobic sheets makes it less dispersible in water. As shown in Table 1, although GO functionalized with chol-HCOO and chol-$C_5H_{11}COO$ was reduced very partially but it showed the long term dispersion stability upto 1 year (upon standing at room temperature in ambient conditions) confirmed by observing Tyndall effect of the diluted dispersions (ESI, Fig. S9), however, chol-HCO_3 and chol-OH functionalized GO, which reduced it substantially displayed short-term dispersion stability and in both the cases *ca*. 75% of GO were precipitated within 6 days of storage at room temperature. This perhaps due to the hydrophobicity developed owing to the excessive reduction of GO. The better water solubility of HCOO group and surface activity of $C_5H_{11}COO$ probably helped the long term dispersion stability of the functionalized GO by the ILs containing these anions (ESI, Fig. S10). Moreover, the GO functionalized with these ILs exhibited long term dispersion stability in water due to the formation of the nano size functionalized graphene oxide. The dispersion of GO and ILs functionalized GO were characterized by AFM (Fig. 6a-c). It was observed that the pristine GO had a sheet like structure with diameter 2.5 µm and height about 20 nm. The GO functionalized by chol-OH and chol-HCO_3 showed the GO with diameter 550 and 302 nm with heights 12 and 7 nm respectively (Fig. 6b and Fig.S11a). On the other hand, the GO functionalized by chol-HCOO and chol-$C_5H_{11}COO$ showed the diameter of 89.9 nm and 120 nm with heights 2.6 and 3.5 nm respectively (Fig. 6c and Fig.S11b). The formation of nanosized GO sheets due to the modification by the later ILs perhaps responsible for the long term dispersion of the functionalized GO in water. The surface modification of GO due to non covalent bond formations with the ionic liquids helped better exfoliation of sheets in water (Fig. S12).

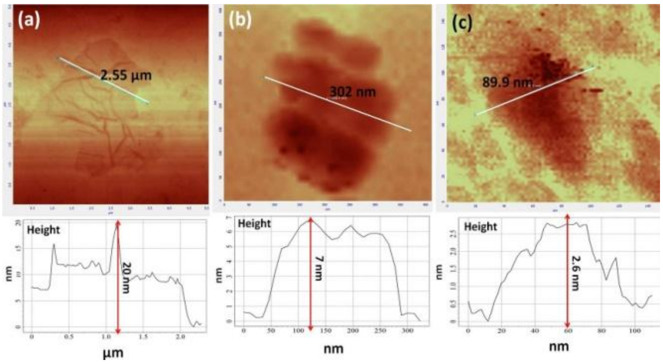


Fig. 6: AFM images of (a) GO and GO functionalized with (b) choline bicarbonate, (c) choline formate

Long term colloidal dispersion stability of GO functionalized with ILs through electrostatic stabilization was further supported by zeta potential (ζ) analysis. As shown in Table 1 & Fig.7, the ζ of the functionalized GO dispersion is pH dependent due to the ionization of carboxylic acid group, which is strongly pH dependent. Although the magnitude of ζ of functionalized GO is lower than that of pristine GO at the same pH, the ζ was below -60 mV when the pH was greater than 6 and reached to -63 mV and -59 mV when the pH approached to 8 and 10 respectively. So the surface charge density of functionalized GO showed that these GO sheets are highly negatively charged when dispersed in water and suitable to make aqueous dispersions with long term stability. [24] It is also evident from the Table 1 that, chol-HCOO and chol- $C_5H_{11}COO$ functionalized GO had higher negative charge in comparison to GO and had higher dispersion stability in comparison to GO functionalized by chol-OH and chol-HCO_3.

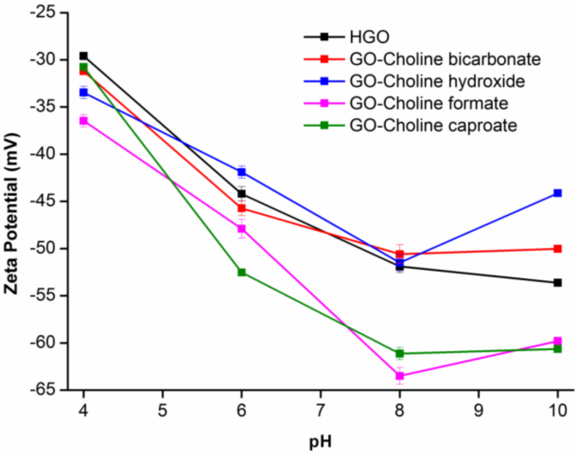


Fig. 7 : Zeta potential for GO reduced by the ionic liquids at different pH values.

4. Conclusions

In conclusion, we have studied the affect of the anions of four different choline based bio-ionic liquids on the spontaneous reduction and dispersion of graphene oxide in water. It was observed that the bio-ILs having –OH, -HCO_3 as counter anions reduced GO substantially while the ILs containing –HCOO and $C_5H_{11}COO$ reduced it in a lower extent but induced very long term dispersion stability in water (>1 year), while the GO functionalized by other two ionic liquids did not disperse for long time. This results infer that strong nucleophiles were able to reduce GO in higher extent while resulted short term dispersion stability of the partially reduced GO, while the ILs with weaker nucleophiles gave formation of partially reduced GO with long term water dispersion stability.

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Notes and references

[a] *Marine Biotechnology and Ecology Discipline, CSIR-Central Salt and Marine Chemicals Research Institute (CSIR-CSMCRI),Council of Scientific & Industrial Research (CSIR),Gijubhai Badheka Marg, Bhavnagar- 364 002, (Gujarat), INDIA , Phone No : +91-278-2567760. Fax No. +91-278-2567562; Email: kamlesh@csmcri.org / drkamaleshp@gmail.com]*

[b] *Academy of Scientific and Innovative Research(AcSIR)-Central Salt and Marine Chemicals Research Institute Gijubhai Badheka Marg, Bhavnagar- 364 002, (Gujarat), INDIA*

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