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Research Article

FABRICATION OF TRIMETAL NANOPARTICLES FOR EFFICIENT PHOTOCATALYTIC DEGRADATION OF METHYLENE BLUE DYE

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ABSTRACT

Photocatalysis is an important method for degradation of dyes and organic pollutants in waste water. In this studynovel trimetal nanoparticles La/Bi/Cu were synthesized by a simple chemical reduction method using sodium borohydride as a reducing agent. The synthesized trimetal nanoparticles were characterized by XRD, SEM, EDAX, FTIR and UV-VIS spectra to study the crystalline size, morphology, elemental composition and surface properties of nanoparticles. The size of the nanoparticles was determined by using XRD and found to be in the range of 10.86nm-61.46nm.The photocatalytic activity of synthesized La/Bi/Cutrimetal nanoparticles was assessed by photocatalytic decomposition of Methylene Blue dye under solar light irradiation.

Keywords: Photo catalyst, Trimetal, Methylene Blue

1. INTRODUCTION

Nanoscience and nanotechnology are the study and application of extremely small things that can be used across all the other science fields, such as chemistry, biology, physics, material science, and engineering. Nanotechnology plays a very important role in modern research.It is the most capable technology that can be applied to almost all fields such as pharmaceutical, electronics, optoelectronics [1], health care, food and feed, biomedical science, drug and gene delivery, chemical industry, energy science, cosmetics, environmental health, mechanics and space industry. It has also been utilized for the treatments of infection [2], cancer [3], allergy [4], diabetes [5] and inflammation [6].

Nanoparticles exhibit new or enhanced size-dependent properties compared with larger particles of same material [7]. Synthesis of metal nanoparticles, their characterization and application to different fields have become an important trend in the modem investigation. Nanoparticles have unique chemical, electronic, magnetic and optical properties due to their small size and high surface area. Alloying of metals is a way of developing new materials that have better technological usefulness than their starting substances. Alloy nanoparticles show different structural and physical properties than bulk samples [8, 9]. Bimetallic nanoparticles (BMNP) have excelled monometallic nanocrystals owing to their improved electronic, optical and catalytic performances [10, 11].

Trimetal nanoparticles are an advanced class of nanomaterials gaining much more attention in recent times because of their enhanced catalytic properties.Due to their diverse applications, a variety of fabrication routes have been reported for the trimetal nanoparticles.Trimetal nanoparticles have an extra degree of catalytic activity compared to the bimetallic and monometallic nanoparticles. The trimetal nanoparticles were found to be efficient catalyst for various applications [12-14]. The chemical reduction of salts is the easiest, simplest and the most commonly used synthetic method for metal nanoparticles.

In the present work nanosized Trimetal particles are synthesized from an aqueous solution of corresponding metal precursors, using sodium borohydride as a reducing agent for the preparation of lanthanum, bismuth, coppertrimetal nanoparticles and starch as a stabilizing agent.

2. MATERIAL AND METHODS

2.1. Material

All the reagents used in this experiment were obtained from Sigma Aldrich chemicals India. Double distilled water was utilized for all processes. Filtration was done using Whatman no.1 filter papers. Glasswares used for the reactions were washed well, rinsed with double distilled water and dried in hot air oven.

2.2. Synthesis of La/Bi/Cu Trimetal nanoparticles

In this study, lanthanum nitrate, bismuth nitrate and copper nitrate were used as a starting material while sodium borohydride and starch as a reducing and stabilizing agent, respectively.About10ml of 0.01M lanthanum nitrate, bismuth nitrate and copper nitrate were taken in a 100mL beaker and stirred in a magnetic stirrer. After 15mins5mL of 0.01M $NaBH_4$ was added dropwise to the solution with constant stirring.2mL of 1% starch solution was then added to the solution. The solution in the beaker was stirred in a magnetic stirrer for about 6 hours. The formation of La/Bi/Cu trimetalnanoparticles was indicated by colour change from light colour to dark colour.

2.3. Characterization

UV-Vis spectral analysis was performed on a JASCO, V-600 spectrophotometer at V.O.C. College, Thoothukudi. SEM was recorded in MIRA3 TESCAN instrument, EDX was recorded in EDAX APEX (Element C-2B) instrument at Avinashilingam Higher Secondary and Higher Education for Women, Coimbatore. XRD was recorded in Brucker-D8 by using monochromatic Cu Kα radiation with a wavelength of 1.54Å at Manon-manium Sundaranar University, Tirunelveli. Electro-catalytic activity was studied in the electrochemical analyzer, CH Instruments, Electrochemical workstation model 660C at V.O.C.College, Thoothukudi.

2.4. Photocatalytic measurement

The photocatalytic activity of La/Bi/Cu Trimetal nanoparticles was examined by degradation of methylene blue dye under sunlight using UV-Visible spectrophotometer. For a typical photocatalytic experiment, 0.2g of the prepared sample was added to dye solution. The aqueous suspension was put under constant stirring in dark for 1hr, for the adsorption of dye on the surface of metal nanoparticles. Then the solution was exposed to the sunlight. About 10 ml of suspension was taken out after every 5 min for measuring absorbance. The photocatalytic degradation of dyes mixed with synthesized La/Bi/Cu Trimetal nanoparticles was examined using UV-Visible spectrophotometer.

3. RESULTS AND DISCUSSION

3.1. Visual observation

The colour of the La/Bi/Cu trimetal nanoparticles prepared with sodium borohydride was initially light blue and turns to dark colour due to reduction.The nanoparticles show visible colour change from light blue to dark. This variation in the final colour of the reaction medium may be due to the variation in the size of the nanoparticles.

3.2. UV- Vis spectra of synthesized La/Bi/Cu trimetalnanoparticle

Formation of La/Bi/Cu trimetal nanoparticles using sodium borohydrideby magnetic stirring method was confirmed by UV-Vis spectral analysis. UV-Vis spectra of synthesized La/Bi/Cu trimetal nanoparticles are shown in Fig.1.

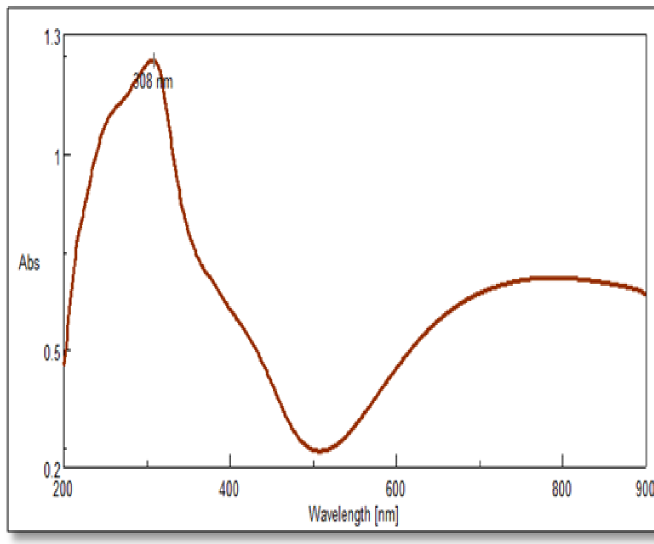

Fig.1: UV- Vis spectra of La/Bi/Cu trimetal nanoparticles

It was observed that the absorbance peak appears at 308 nm show La/Bi/Cu trimetal nanoparticles formed in the reaction media. The broad peak at around 600 nm is contributed by the clusters of trimetal nanoparticles [15].

3.3. Scanning Electron Microscopy

The surface morphologyof the nanoparticles was studied by Scanning Electron Microscopy (SEM) analysis.

The Fig.2 shows the SEM image La/Bi/Cu trimetal nanoparticles. It shows a grain like shape. Some nanoparticles were found to be bigger in size; it may be due to the aggregation of the smaller ones.

3.4. Energy Dispersive X-Ray analysis (EDX)

Energy dispersive X-Ray analysis was carried out to find out the elemental composition of the synthesized La/Bi/Cu trimetal nanoparticles. The EDX shown in Fig. 3 along with data in table 1 shows presence of the three metals.

The pie graph of La/Bi/Cu Trimetal nanoparticles indicates the percentage of elemental composition of trimetal nanoparticles[16].The sodiumand oxygen signals were most likely due to the reducing and stabilizing agents on the surface of the prepared nanoparticles.The other elements Cl, Si may be due to the presence of impurities.

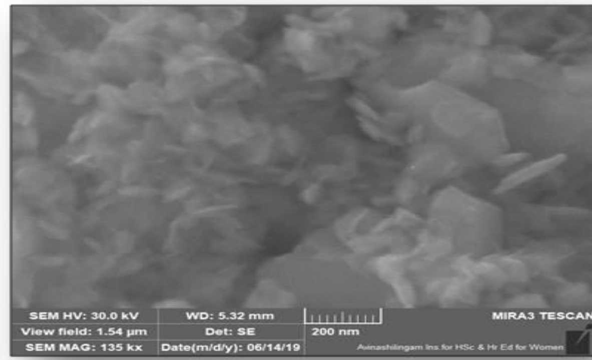

Fig.2: SEM image of La/Bi/Cu trimetal nano-particles

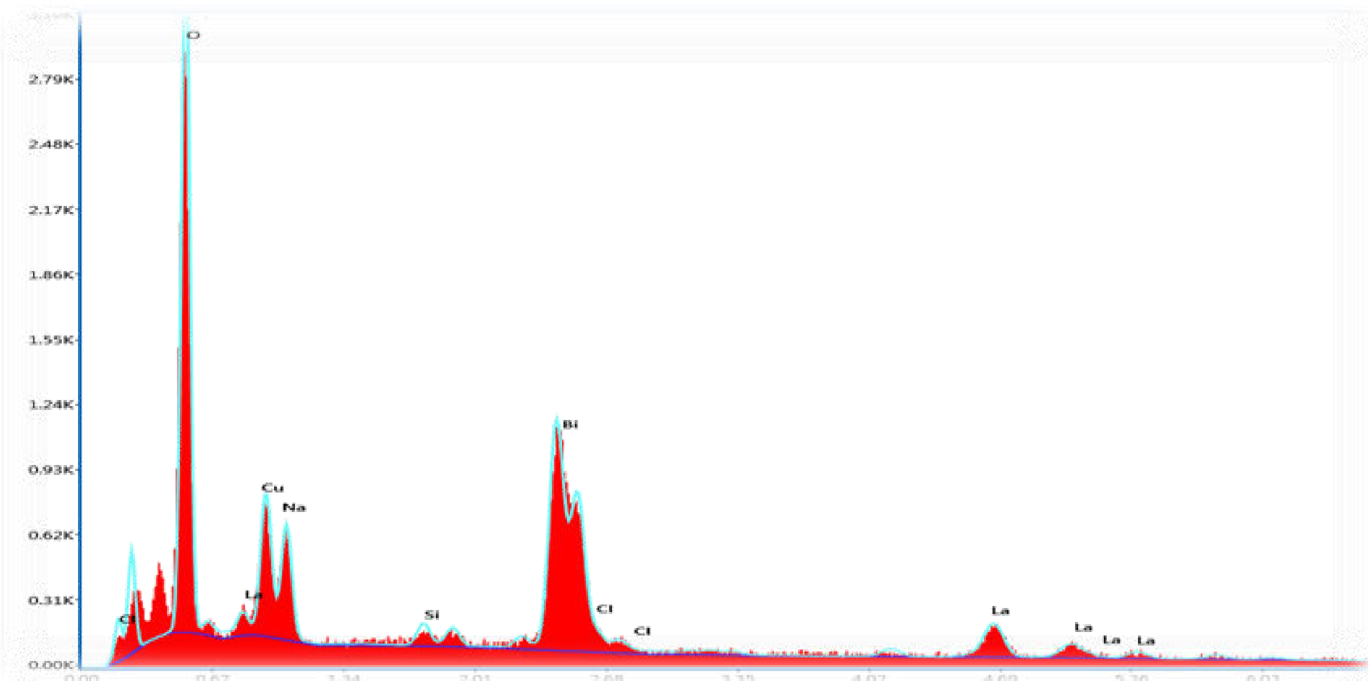

Fig.3: EDX graph of La/Bi/Cu trimetal nanoparticles

Table1: EDX data of La/Bi/Cu Trimetal nano-particles

Element	Weight%	Atomic%	Error%
O K	11.35	38.33	7.52
Na K	4.19	9.85	10.69
Si K	0.59	1.13	14.65
Bi M	22.94	5.93	5.34
Cl K	0.89	1.35	19.35
La L	16.64	6.48	16.10
Cu K	43.41	36.93	31.99

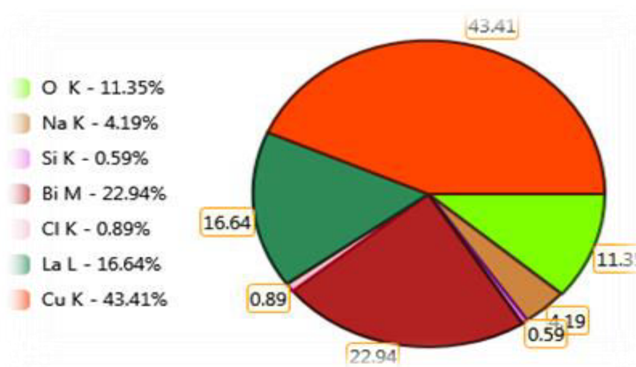

Fig. 4: Pie graph ofLa/Bi/Cu Trimetal nano-particles

3.5. X- Ray Diffraction Analysis (XRD)

X-ray diffraction (XRD) measurements were carried out to confirm the crystalline nature, phase composition and preferential orientation of formed La/Cu/Bitrimetal nanoparticles. The XRD pattern for sample is shown in Fig.5.

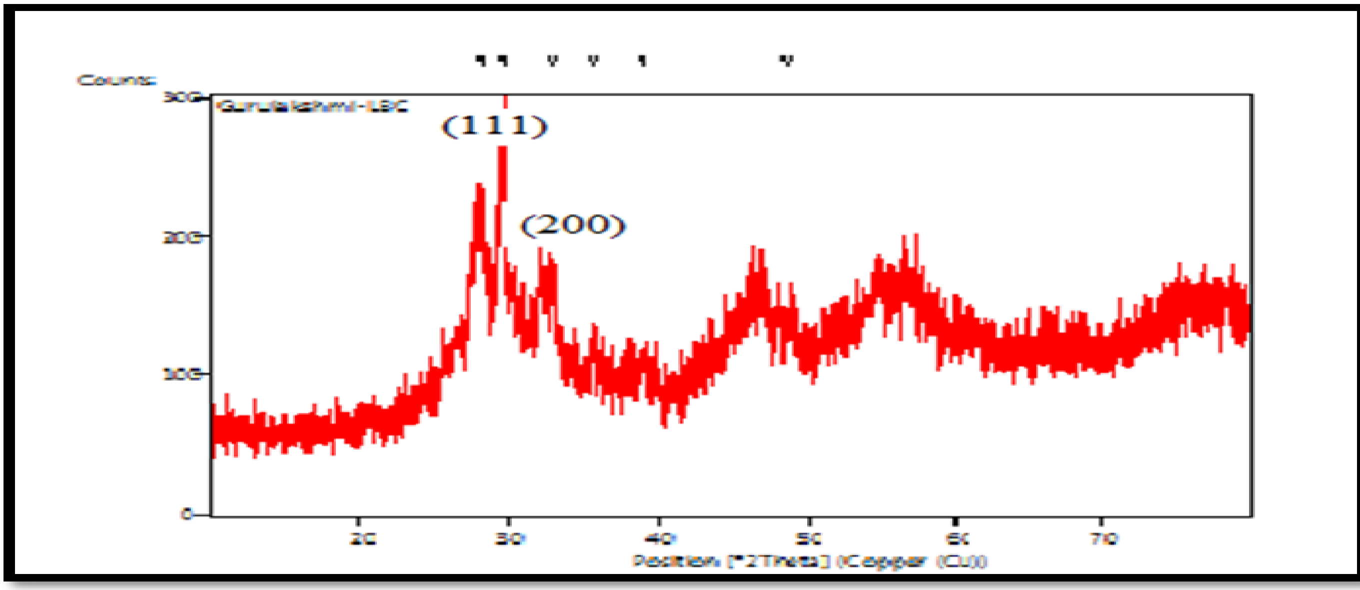

Fig. 5: XRD pattern of synthesized Trimetal La/ Cu/Bi nanoparticles

The XRD pattern of synthesized La/Bi/ Cu Trimetal-nanoparticles shows peaks at 2θvalues of 28.1670^0, 29.6049^0, 32.9392^0, 35.6260^0, 38.9967^0 and 48.6397^0. The peak indices at (111) and (200) plane indicates the crystalline nature of synthesized Trimetal La/Cu/Bi nanoparticles.

The size of the Trimetal La/Cu/Bi nanoparti-clescalculated by using Debye- Scherer's formula

$$d = \frac{K\lambda}{\beta cos\theta}$$

Where d is the mean crystalline size, K is the constant (Shape factor). K= 0.94, λ is the Wavelength of X- ray (λ = 0.154 nm), β is the FWHM of the diffraction peak, and θ is the Bragg diffraction angle

Table-2 shows XRD data and the size of synthesized nanoparticles was found to be in the range of 10.86nm-61.46nm.

Table 2: XRD data of La/Cu/Bi trimetalnano-particles

2θ	θ	Cosθ	FWHMβ	FWHMβ(rad)	D(nm)
28.1670	14.0835	0.9699	0.5353	0.009335	15.30
29.1670	14.8024	0.9668	0.1338	0.002333	61.46
32.9392	16.4696	0.9589	0.4015	0.007002	20.64
35.6260	17.813	0.9521	0.4015	0.007002	20.79
38.9967	19.4983	0.9426	0.4015	0.007002	21.00
48.6397	24.3198	0.9113	0.8029	0.01400	10.86

3.6. Cyclic voltammetry

The cyclic voltammogram recored in pH 1 solution is shown in fig.6. The cyclic voltammogram cycled between -0.7 and 1.2V at the scan rate 50 mVs^{-1} for the electrochemical redox reaction of on Glassy Carbon Electrode shows an anodic peak at 0.15 V and 0.20 V indicating there is oxidation and cathodic peak at -0.20V which shows there is reduction and the reaction was found to be reversible. The cathodic and anodic peak suggests that the La/Bi/Cutrimetal nanoparticles can be used as a redox catalyst.

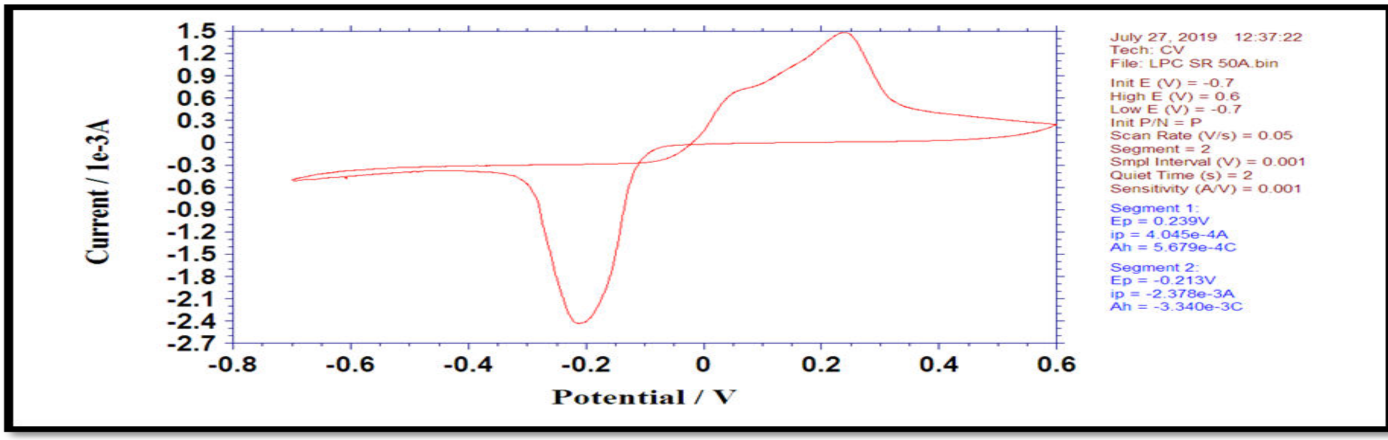

Fig. 6: Cyclic Voltammogram of synthesized La/Bi/Cutrimetal nanoparticles

3.7. Photocatalytic Activity

The photocatalytic activity of trimetal nanoparticles was examined by studying the degradation of dye solution using UV-Visible spectrophotometer.

The Photocatalytic activity of La/Bi/Cu trimetalNPs was inferred by using methylene blue dye as a test compound. The progression of the photocatalytic degradation of MB dye in presence of sunlight can easily be examined by decrease in absorbance around 620 nm, as shown in fig.8.The absorbance of methylene blue (100mM) in the absence of NPs shows only a small increase of reductive degradation with time under the exposure of sunlight. However, the photocatalytic (in presence of sunlight) degradation observed after addition of La/Bi/Cu trimetalNPs catalyst in the same sample solutions show a larger decrease in absorbance of MB dye as shown in fig.9. It was also observed that the reaction rate of MB dye degradation with La/Bi/Cu trimetalNPs in presence of sunlight enhanced the degradation efficiency when compared with the results of the control test. This indicates the La/Bi/Cu trimetal NPs act as good photocatayst [17].

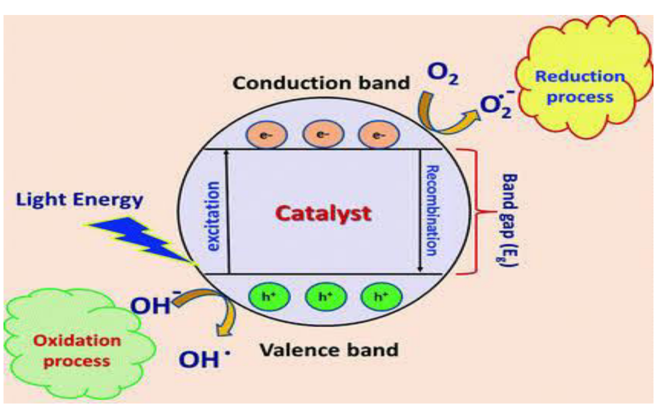

Fig. 7: Mechanism of Photocatalytic Activity

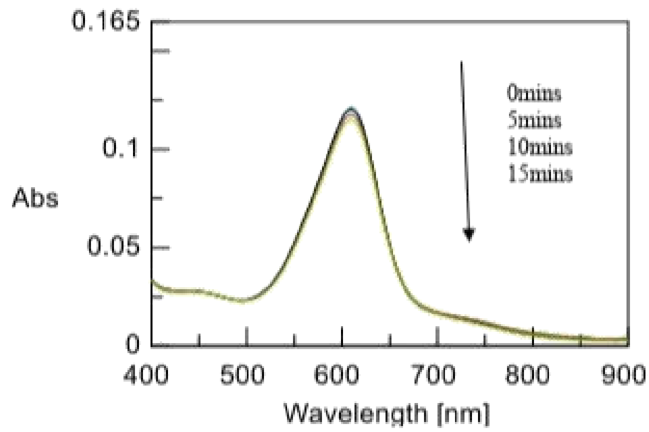

Fig. 8: UV-Vis spectra of MB as a function of time in exposure to sunlight in the absence of nanocatalysts

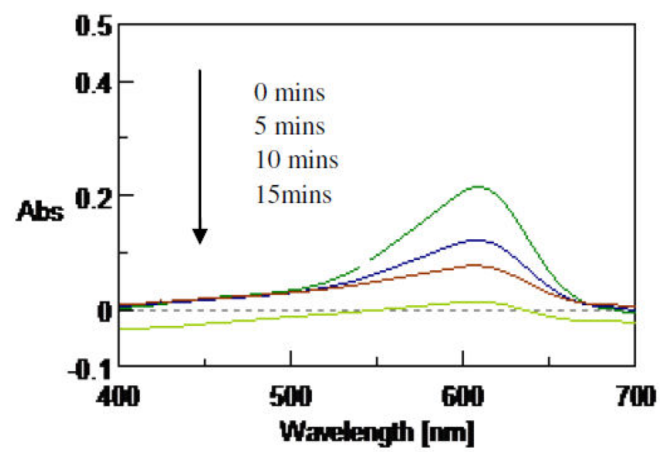

Fig. 9: UV-Vis spectra of MB as a function of time in exposure to sunlight in the presence of nanocatalysts

4. CONCLUSION

The La/Bi/Cu trimetal nanoparticles were successfully synthesized by using sodium borohydride which provides easy and proficient method for synthesis. The Trimetal nanoparticles were analyzed using UV-spectropho-tometer, SEM and EDAX,XRD.In future, this can be utilized for removal of organic pollutants.

5. REFERENCES

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