Effects of Chromium Doping on the Electrical Properties of ZnO Nanoparticles

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Abstract

Nanostructured ZnO has gained a considerable amount of attention due to its unique physical and chemical properties and due to its remarkable performance in the fields of optics, photonics and electronics. The scope of this work is to study the Structural, Optical and Electronic properties of Pure Zinc Oxide (ZnO) and Chromium doped Zinc Oxide nanoparticles. These nanoparticles were synthesized by low-temperature precipitation method at various concentrations in the range ($Zn_{1-x}Cr_xO$; (x = 0, 0.1 & 0.3)). The precursors used were analytical grade Zinc Nitrate Hexahydrate and Chromium Nitrate Nona hydrate. The synthesized nanoparticles were annealed at $400°C$. The Structural property of the synthesized nanoparticles was analysed by XRD (X-Ray diffraction) and was confirmed to exhibit a crystalline hexagonal wurtzite structure with an average crystallite size of 55nm. The functional groups were analysed using FTIR (Fourier Transformed Infra-red spectroscopy). The Morphology was analysed by FESEM (Field Emission Scanning Electron Microscope) and a change in morphology from spherical to spindle like structure was observed. The Optical properties were analysed using UV-Vis spectroscopy, the absorption spectrum for electromagnetic spectrum was observed and the changes in the optical band gap of ZnO nanoparticles with Chromium dopant addition were calculated to be in the range of 3.6 eV. The Electrical property of the synthesised nanoparticles was analysed using Electrochemical Impedance Spectroscopy (EIS) and the conductivity was calculated to be in the range of $1.1e^{-07}$S/m.

1- Introduction

Zinc Oxide nanoparticles have a wide energy band gap of 3.37 eV and high bond energy 60 MeV [1]. It is active in the ultra-violet region at room temperature. It is a multifunctional material with semiconducting [2], magnetic, optical and electronic properties with a wide range of applications in the field of semiconductors like electronics, optoelectronics, laser technology, solar cells, photo catalysis, sensors, etc. [3]. ZnO has gained interest in the recent years due to its oxidation properties, chemical stability, non-toxic nature and cost-effectiveness. One such application is de-toxing water contaminated with dyes used by the textile industries causing serious effects that may lead to diseases like cancer. There are several ways to treat the waste dyes that are being dumped into the water bodies but are ineffective. Photo catalysis is one of the growing areas of treating organic wastes. It is considered one of the best catalysts in de-toxing water [4, 5]. ZnO has maximum optical transparency in visible region of electromagnetic spectrum this property can be altered depending on the dopant added to it. In this work, Zinc Oxide nanoparticles were doped with chromium through low temperature precipitation method. This method was adopted because of its repeatability, homogeneity, control in stoichiometric and cost-effectiveness. The structural, optical and electrical properties of chromium doping in Zinc Oxide nanoparticles synthesized at various concentrations were compared with undoes Zinc Oxide nanoparticles.

2- Experimental Details

2-1- Materials

The materials used in the synthesis of Pure and Chromium doped Zinc oxide (Zn $_{(1-x)}$ Cr$_x$O; x=0, 0.1 and 0.3) nanoparticles are Zinc Nitrate Hex hydrate (Zn (NO$_3$)2.6H$_2$O, 99%), Chromium Nitrate Nona hydrate (Cr (NO$_3$)3.9H$_2$O, 96%) and sodium hydroxide pellets (NaOH, 97%). The precursors were purchased with analytical grade and used without any further Purification. Double distilled water was used for making solutions.

2-2- Synthesis of Pure and Cr Doped ZnO Nanoparticles

Pure and Chromium doped Zinc oxide (Zn $_{(1-x)}$ Cr$_x$O; x=0, 0.1 and 0.3) nanoparticles were synthesized via co-precipitation method. Zinc Nitrate Hexahydrate (Zn (NO$_3$)$_2$.6H$_2$O) was dissolved in 100ml of double distilled water and stirred constantly for 30 minutes. Then, 2M solution of sodium hydroxide (NaOH) is added until the desired pH is attained. The milky white solution is heated to 80ºC for 30 minutes and allowed to age for 18 hours under constant stirring.

The precipitate extracted from the solution by washing and centrifuging at 4000 rpm twice with double distilled water twice with and ethanol, dried at 55 ºC for 36 hrs in the hot air oven. It is then ground well and annealed at 400 ºC for 1hour to obtain pure Zinc Oxide nanoparticles. In the above-mentioned method Chromium Nitrate Nona hydrate (Cr (NO$_3$)3. 9H$_2$O) was added along with the primary precursor at different weight concentrations to obtain chromium doped Zinc Oxide nanoparticles.
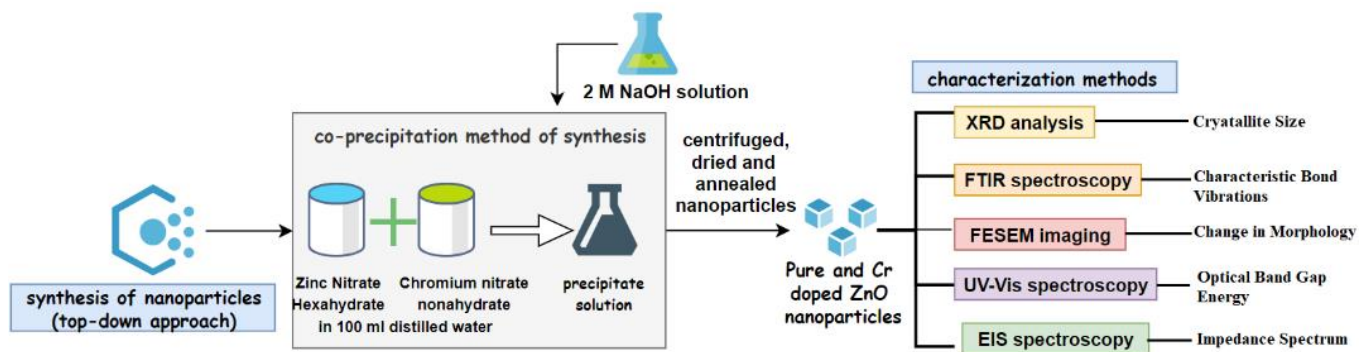

Figure 1. Schematic representation of synthesis of pure and Cr and ZnO nanoparticles.

3- Results and Discussion

3-1- XRD Analysis

X-Ray Diffraction (XRD) studies the structure and phase information of the synthesized nanoparticles using CuKα radiation of wavelength 1.5406 A˚ in the range (2θ) 20˚ to 70˚. Pure and Cr doped ZnO nanoparticles exist in hexagonal wurtzite ZnO structure corresponding to the crystal planes (100), (002), (101), (102), (110), (103), (200), (112) and (201) for pure and (220), (311) and (400) for Cr doped ZnO [6, 7]. The formed peaks are found to increase in intensity with increase in dopant concentration indicating the presence of Chromium atoms in the lattice, the increase in crystallinity and the absence of impurities.

Table 1. Average crystallite size of Zn $_{(1-x)}$ Cr$_x$O (x = 0, 0.1, 0.3) nanoparticles.

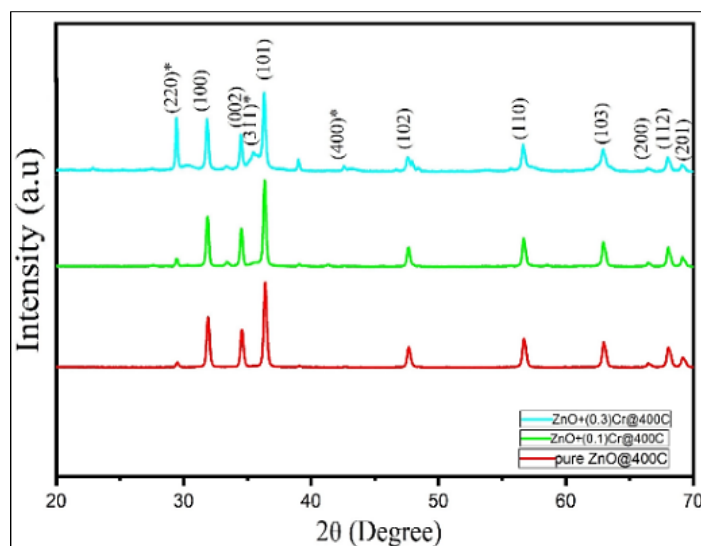| Concentration	Average crystallite size D (nm)
Zn$_{(1-x)}$ Cr$_x$O (x = 0)	50
Zn$_{(1-x)}$ Cr$_x$O (x = 0.1)	57
Zn$_{(1-x)}$ Cr$_x$O (x = 0.3)	62

Figure 2. XRD pattern of Zn $_{(1-x)}$ Cr$_x$O (x = 0, 0.1 and 0.3) nanoparticles.

All the characteristic peaks are in agreement with the JCPDS card no. 36-1451 [8, 9]. The average crystallite size is calculated using FWHM in the Scherrer formula ($D = 0.9 \times \lambda/\beta \cos\theta$) and found to increase with increase in dopant concentration. Table 1 gives the average crystallite of Zn $_{(1-x)}$ Cr$_x$ O (x = 0, 0.1 and 0.3) nanoparticles.

3-2- FTIR Analysis

The FTIR spectroscopy analyses the functional groups present in the synthesized nanoparticles. The absorption spectra of pure and Cr-doped ZnO nanoparticles at various concentrations were studied between the wavelengths 400 cm^{-1} and 4000 cm^{-1}. The characteristic peaks found in the range of 1300 to 1400 cm^{-1}, 700 to 900 cm^{-1} and 550 to 650 cm^{-1} is due to OH- bending vibration [10], Cr-O stretching vibrations and stretching vibration of ZnO respectively. It also shows that there are no impurities present.
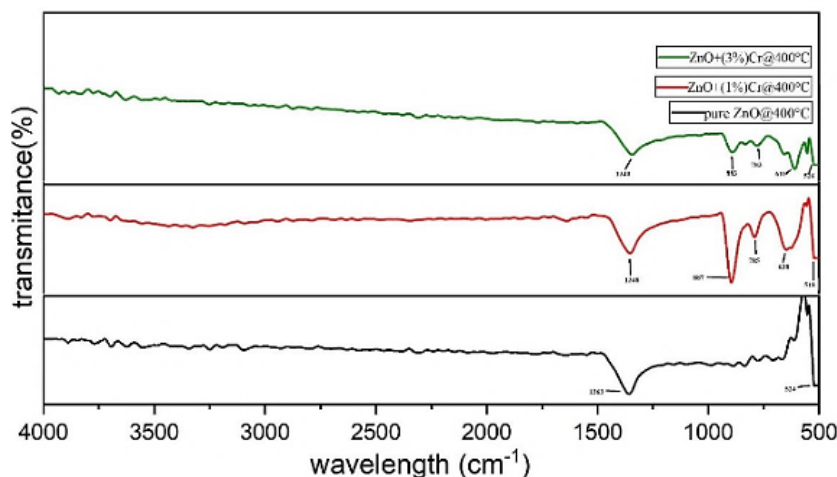

Figure 3. FTIR spectra of Zn $_{(1-x)}$ Cr$_x$O (x = 0, 0.1 and 0.3) nanoparticles.

3-3- UV-VIS Analysis

The UV-Vis absorption spectra for Cr doped ZnO nanoparticles are observed between the wavelengths 200 nm to 800 nm. Strong absorption peaks for pure and Cr doped ZnO is found at 341 nm, 321 nm and 320 nm respectively in the UV region indicating the nanoparticles absorb UV radiation and are transparent to visible radiation of the electromagnetic spectrum [11].

Table 2. Optical band gap energy of Zn $_{(1-x)}$ Cr$_x$O (x = 0, 0.1 and 0.3) nanoparticles.

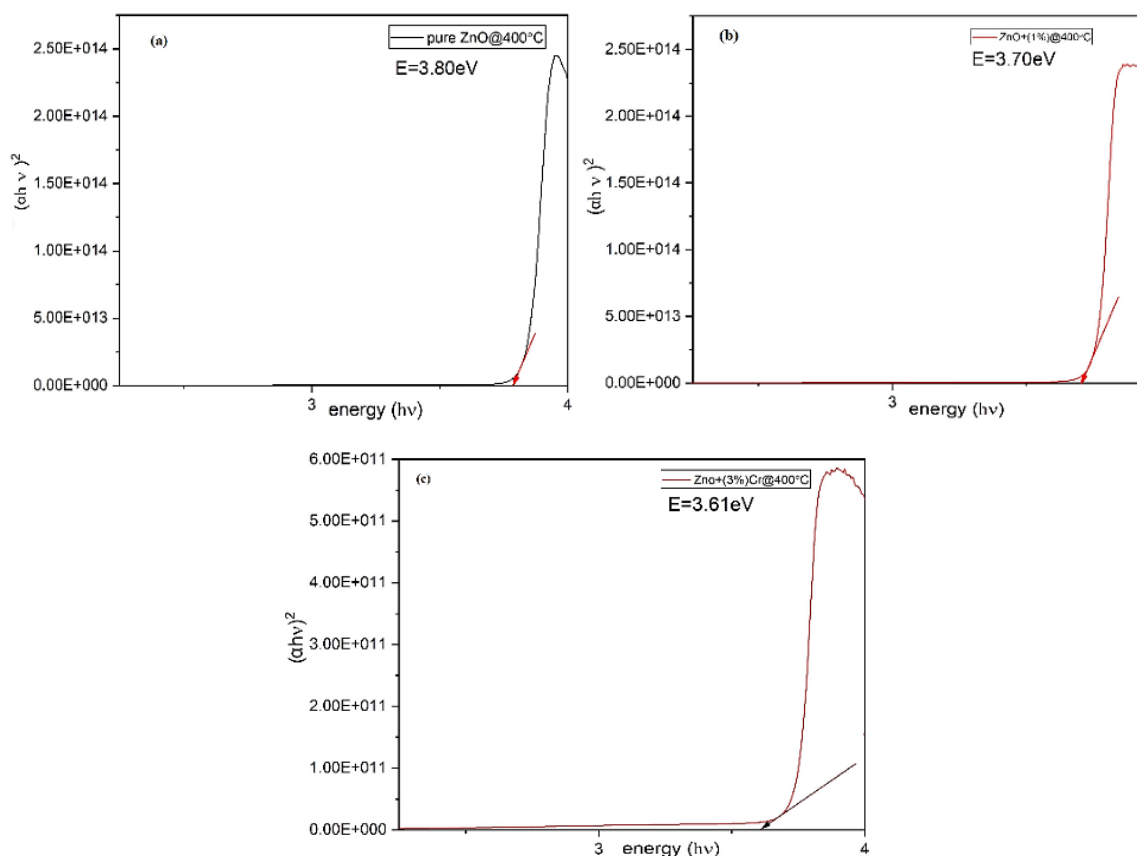| Concentration	Optical band gap energy E (eV)
Zn$_{(1-x)}$ Cr$_x$O (x = 0)	3.80
Zn$_{(1-x)}$ Cr$_x$O (x = 0.1)	3.70
Zn$_{(1-x)}$ Cr$_x$O (x = 0.3)	3.61

Figure 4. (a), (b) and (c) Plot of $(\alpha h\nu)^2$ vs hν $Zn_{(1-x)}$ Cr_xO (x = 0, 0.1 and 0.3) nanoparticles respectively.

This property the nanoparticles aid in applications such as dye degradation [12]. A plot of $(\alpha h\nu)^2$ vs hν was plotted for pure and Cr doped ZnO nanoparticles. The optical band gap energy of the synthesized nanoparticles calculated from the tauc plot is found to be 3.80eV, 3.70eV and 3.61eV [13, 14] for pure and Cr doped nanoparticles respectively and is found to decrease with increase in dopant concentration as in Table 2.

3-4- FESEM Analysis

The FESEM imaging technique is used to visualise the morphology and agglomeration of the synthesized nanoparticles [15] from the images it is seen that the pure Zinc Oxide nanoparticles exhibit spherical morphology. It is also found that as the dopant concentration of chromium increases there is more agglomeration leading to increase in crystallite size and change in morphology from spherical to a spindle like structure.
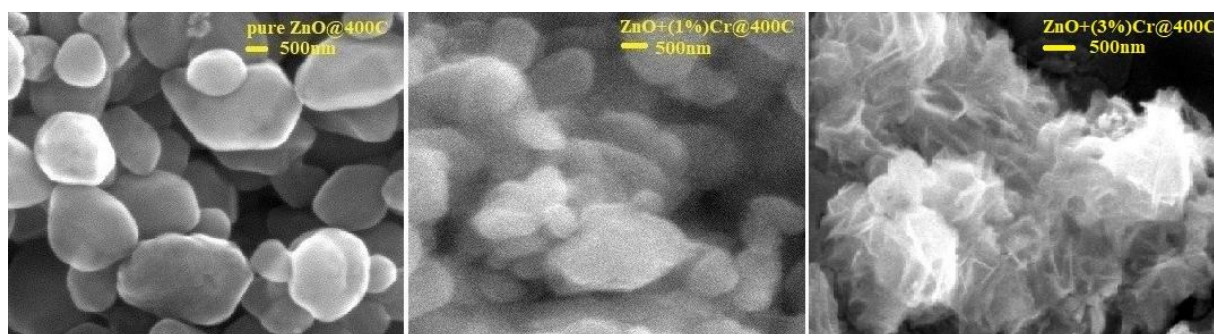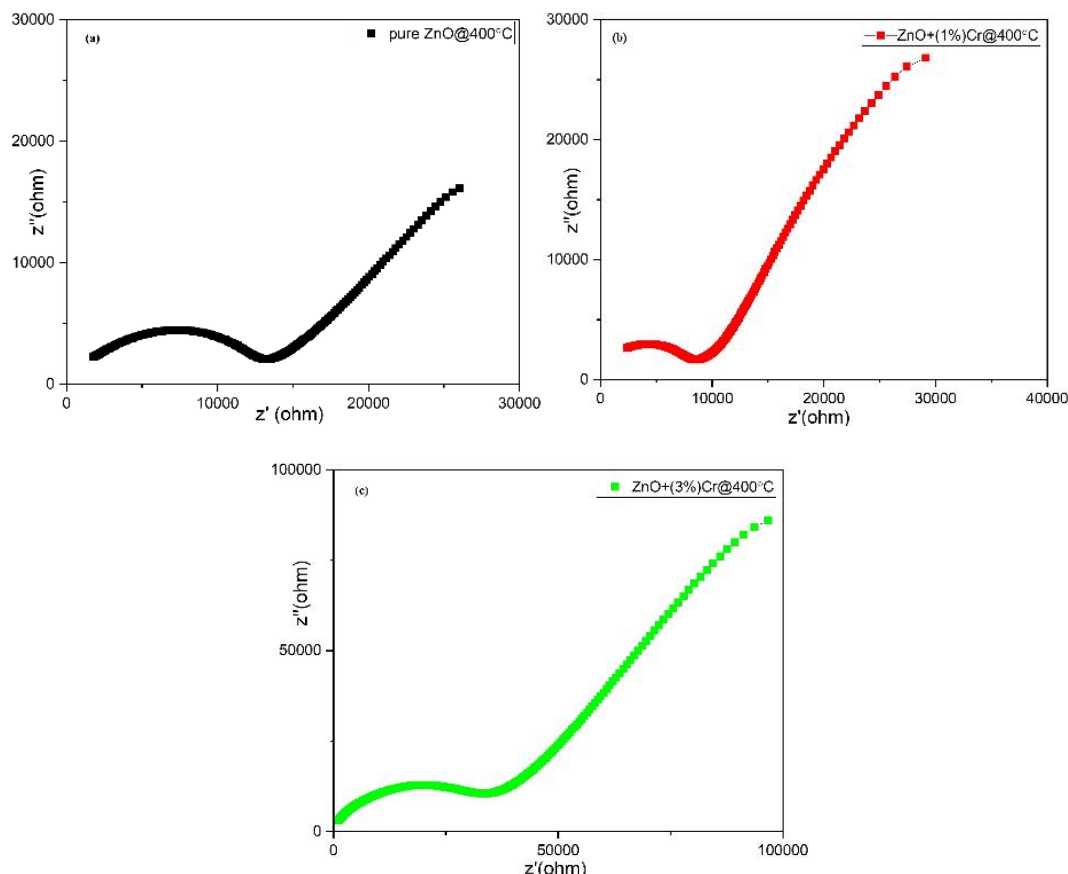

Figure 5. FESEM image of $Zn_{(1-x)}$ Cr_xO (x = 0, 0.1 and 0.3) nanoparticles respectively.

3-5- Electrochemical Impedance Spectroscopy Analysis

A Cole-Cole (Nyquist) plot between Z' and Z'' for pure and chromium doped ZnO $(Zn_{(1-x)}$ Cr_xO; x=0,0.1&0.3) was plotted to study the impedance behavior using an AC impedance spectrometer at room temperature [16, 17] several authors have observed a single arc behavior for different nanoscale metal oxide materials resulting in a very narrow relaxation time distribution.

Table 3. Conductivity of Zn$_{(1-x)}$ Cr$_x$O (x = 0, 0.1 and 0.3) nanoparticles.

Concentration	Conductivity (S/m)
Zn$_{(1-x)}$ Cr$_x$O (x = 0)	1.115E-07
Zn$_{(1-x)}$ Cr$_x$O (x = 0.1)	1.460E-07
Zn$_{(1-x)}$ Cr$_x$O (x = 0.3)	1.148E-07

Figure 6. (a), (b) and (c) Cole-Cole plot of Zn$_{(1-x)}$ Cr$_x$O (x = 0, 0.1and 0.3) nanoparticles respectively.

This discrete single relaxation time τ is due to the above-mentioned behavior which can be calculated from the maximum height of the impedance arc spectrum where, $\tau\omega_{max} = RC\omega_{max} = 1$ ($\omega_{max} = 2\pi f_{max}$) [18]. The impedance spectrum shows two incomplete arc spectra of which the first high-frequency semicircle represents the bulk resistance and the second low-frequency semicircle represents the resistance of the grain boundary. It has an electrical response which is larger compared to the capacitance of the grain core. ZnO nanoparticles that are doped with transitions metals like Chromium shows an increase and a decrease in the resistance with increase in the dopant concentration. This fashion is observed for concentrations greater than 0.1 compared to that of pure ZnO [18]. It might also be due to the increase in agglomeration of Cr^{3+} ions at the grain boundaries as seen in the FESEM images. This condition generates surface acceptors and in turn increases the boundary resistance. The conductivity of the synthesized nanoparticles is found to increase and decrease with the increase in dopant concentration.

4- Conclusion

Pure and Chromium doped ZnO nanoparticles were synthesized with various dopant concentrations Zn$_{(1-x)}$ Cr$_x$O; (x= 0, 0.1 and 0.3) by Co-precipitation method using 2M NaOH solution as reducing agent. The synthesized nanoparticles were annealed at 400°C to remove impurities and the nanoparticles were found to be stable at room temperature. The nanoparticles were characterized using XRD, FTIR Spectroscopy, UV-Visible Spectroscopy, FESEM imaging and EIS Spectroscopy to study the structure, functional groups, optical property, morphology and electrical property respectively. XRD analysis shows that the particles exhibit hexagonal wurtzite structure with an increase in the average crystallite size from 50nm, 57nm to 62nm respectively with increase in dopant concentration. FTIR spectroscopy shows characteristic vibrations between 1400-1300 cm^{-1}, 900-700 cm^{-1} and 650-500 cm^{-1} corresponding to O-H bending vibration, Cr-O stretching vibration and Zn-O stretching vibrations respectively. UV-Vis spectroscopy shows strong absorption peaks in the UV region at 341nm, 321nm and 320nm with increase in

dopant concentration indicating the nanoparticles absorb UV radiation and are transparent to visible radiation. A tauc plot of $(\alpha h \nu)^2$ vs hν was plotted and the optical band gap energy is calculated be 3.80eV, 3.70eVand 3.61eV and found to decrease with increase in dopant concentration. The FESEM imaging shows the morphology of pure and Cr doped ZnO nanoparticles changes from spherical to spindle like structures with increase in dopant concentration.EIS spectroscopy shows the conductivity of the synthesized nanoparticles to be $1.115e^{-07}Sm^{-1}$, $1.460e^{-07}Sm^{-1}$and $1.148e^{-07}$ Sm^{-1}andwas found increase and then decreases as the dopant concentration increases from x=0to 0.3 respectively. This method of synthesis is found to be energy and cost efficient with good repeatability. The increase in optical activity and the decrease in the optical band gap energy of the synthesized nanoparticles enable various applications.

5- Funding and Acknowledgments

6- Conflict of Interest

The author declares that there is no conflict of interests regarding the publication of this manuscript. In addition, the ethical issues, including plagiarism, informed consent, misconduct, data fabrication and/or falsification, double publication and/or submission, and redundancies have been completely observed by the authors.

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