Electronic polarization of zinc nitride nanoparticles for interfacial tension reduction in enhanced oil recovery

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Abstract. Even though the application of nanoparticles (NPs) in enhanced oil recovery (EOR) has been reported, but the development of different novel and efficient materials and their potential in EOR still need to explore. In this work, zinc nitride (Zn3N2) were developed and explored for enhanced oil recovery. Zinc nitride (Zn3N2) nanoparticles with triangular shape morphology were synthesized using sol-gel auto combustion method. The prepared NPs were characterized using X-ray diffraction and Field emission scanning electron microscopy for crystal structure, shape and size. The results reveal the formation of Zn3N2 triangular shape particles. Zn3N2 nanoparticle of different concentrations were prepared and their effect on oil-water interfacial tension (IFT) under electromagnetic waves (EM) was investigated. The reduction in IFT was observed by introducing nanoparticles. It was found that Zn3N2 nanoparticle under EM waves can bring an additional reduction in IFT. The value of IFT at 0.1 wt % of Zn3N2 under EM waves of frequency 2.2 MHz was 0.55 mN/m which is 75 % reduction.

1. Introduction
The Zn3N2 powder was first developed by Juza and Hahn [1] in 1940 and remains a comparatively unstudied material. Zinc nitride is a n-type semiconductor and it has a wide direct bandgap and high refractive index (2.2–2.4) [2–4]. Zinc nitride (Zn3N2) is considered a capable new material, because of its favourable electrical and optical properties in view of photovoltaic electronic and optoelectronic applications. Recently the capability of Zn3N2 for reducing interfacial tension under EM in enhanced oil recovery (EOR) was investigated. Electromagnetic (EM) applications depend on the interaction of materials with EM fields. The scheme of active EM materials, therefore, needs regulation over the magnetic and electric magnetic components in these materials, which be able to interact with the time-varying magnetic and electric field components linked with the EM fields [5, 6]. The important EM characteristics of the colloids are deliberated here in terms of the complex dielectric constant (εr) Eq. 1

\[ \varepsilon_r = \varepsilon_1 + i \varepsilon_2 \]  

where \( \varepsilon_1 \) and \( \varepsilon_2 \) are the real and imaginary parts of permittivity, \( \varepsilon_0 \), respectively. The term \( \varepsilon_1 \) related with energy storage and \( \varepsilon_2 \) is linked with energy dissipation loss or within a solid. Dielectric loss can rise from electrical conduction procedures and methods of both dielectric resonance (a recurring procedure related with consistent oscillations of any portion of an arrangement, such as the reaction of individual molecules or atoms) and relaxation [7] linked with the response of electric dipoles, such as dipolar relaxation in water.

In contrast to conductors, dielectric materials consist of materials where bound electrons are predominant. However, displacement of the electric charge can still occur, which leads to a range of
Numerous time associated with this return to equilibrium is original states, driven by interactions with the environment, which results in energy dissipation. The electric dipoles in polarization mechanisms are opposite directions to each other. The displacement of ions leads to an induced dipole moment ions. When such a crystal is effect can occur in ionic crystals (such as NaCl), which are composed of lattices of positive and negative field tends to stretch the bonds between a molecule and lead to the creation of an electric dipole along the electric field and the atom is said to be polarized. A simple schematic representation of the electric dipole is also given in Figure 1. Since polarization arises as a consequence of the electric field, it can be displayed [12] that polarization in dielectric materials is correlated to the electric field by equation 2

\[ P = \varepsilon_o \chi_e E \]  

(2)

where \( \chi_e \) is recognized as the electric susceptibility. This is a dimensionless quantity and is a measure of a material's capability to become polarized, so differs for different dielectric materials. The electric displacement flux density, D, associated with the polarization and applied field is given by

\[ D = \varepsilon_o E + P \]  

(3)

\[ D = \varepsilon_o E + \varepsilon_o \chi_e E \]  

Equation 4 now enables the electric displacement to be defined in terms of the permittivity, \( \varepsilon \) :

\[ D = \varepsilon_o E(1 + \chi_e) \]  

(5)

\[ D = \varepsilon_r \varepsilon_o E \]  

(6)

where \( \varepsilon_r \) is the relative permittivity or dielectric constant of the material given by:

\[ \varepsilon_r = 1 + \chi_e \]  

(7)

The propagation of time-harmonic electromagnetic waves and the resulting interaction of electromagnetic energy with macroscopic solids can be described by the Helmholtz wave equation. This can be derived from Maxwell's equations, but is only quoted here:

\[ \nabla^2 E = \mu E \left( \frac{\partial^2 E}{\partial t^2} \right) + \sigma \mu \left( \frac{\partial E}{\partial t} \right) + \nabla \left( \frac{q}{\lambda} \right) \]  

(8)

The Helmholtz equation shows that the observed electric properties of a material are dependent upon the material parameters associated with the permittivity (\( \varepsilon \)) conductivity (\( \sigma \)) and charge (\( q \)). Dielectric resonance is a periodic procedure related with regular oscillations of any portion of the system at a fixed frequency. Such behaviour can result from the response of individual atoms or molecules, for example, the vibration of intramolecular bonds. These oscillations absorb energy over a narrow range of frequencies, which are generally higher than those of interest in this research. Dielectric relaxation is associated with the response of electric dipoles to an applied electromagnetic field. Many different types of dipoles can be present within dielectric materials [8], which can lead to a range of polarization effects. Ionic or molecular polarization [9] can arise where permanent dipoles moments are present, where the field tends to stretch the bonds between a molecule and leads to a change in the dipole moment. A similar effect can occur in ionic crystals (such as NaCl), which are composed of lattices of positive and negative ions. When such a crystal is exposed to an electric field, the positive and negative ions are moved in opposite directions to each other. The displacement of ions leads to an induced dipole moment. The polarization mechanisms are time-dependent procedures, which happen as an effect of the movement of electric dipoles in reaction to an applied field. Upon removal of the field, the dipoles 'relax' to their original states, driven by interactions with the environment, which results in energy dissipation. The time associated with this return to equilibrium is known as the relaxation time. Numerous production techniques were utilized, containing direct chemical synthesis, chemical vapour deposition, laser deposition, electrochemical deposition and reactive sputtering [10-14]. It is well
accepted that the synthesis routes mostly influences the properties of Zn$_3$N$_2$ [10, 15]. In this work, sol-gel auto combustion method (SGAC) was employed to synthesize Zn$_3$N$_2$ nanoparticles as this technique is low cost, rapid and requires low processing temperatures. It is well recognized that 60-70% of oil stays in place as an irregular phase in the form of oil drops stuck by capillary force after primary and secondary recovery. From the starting of the progress of tertiary recovery techniques oil industries still now exploring for new technology which can enhance oil recovery procedures. Since energy demands rises the oil industries are forced to discover a new solution to recover the entrapped oil after secondary recovery. Various laboratory investigations reveal that nanoparticles are capable to recover trapped oil from reservoir efficiently [16-21]. Application of nanoparticles can reduce the oil-water IFT, change the wettability of the rock surface and lower the chemical adsorption onto the rock surface.

To date, many researchers have used metal oxide nanoparticles in EOR applications [22-24] but no one investigated metal nitrides for oil recovery yet. Therefore a comprehensive analysis is necessary to explore the efficiency of metal nitrides towards oil-water IFT reduction. In this work, we report for the first time, the preparation of Zn$_3$N$_2$ nanoparticles by sol-gel auto combustion method using N$_2$ environment in tube furnace during the annealing process. We also report the structural properties Zn$_3$N$_2$ nanoparticles determined by XRD and EM behavior for application in EOR.

![Figure 1](image)

**Figure 1.** Electric polarization: (a) Electrically neutral atom (zero electric field) (b) Polarized atom in electric field (c) Schematic representation of an electric dipole created by two charges, where d is the vector displacement of +Q from -Q.

2. **Experimental Methodology**

Synthesis of Zn$_3$N$_2$ nanoparticles has been done using SGAC method. An aqueous solution of zinc nitrate was prepared in distilled water. Citric acid was used as fuel. Precursors were mixed and heated on a hot plate at 90°C. After the gel formation magnetic stirrer was removed. The gel heated at 250°C for self-combustion. The combusted porous powder was crushed using pestle and mortar. The powder was heated in tube furnace in N$_2$ environment to get zinc nitride nanocrystals. The microstructure and crystallinity of the sample were examined using x-ray diffraction (XRD) using an Xpert 3 (PANalytical) powder diffractometer find the crystal structure of the synthesized sample. Variable pressure Field emission scanning electron microscope (FESEM) was used to investigate the morphology.

Rame-Hart Goniometer (Model 260) was used to investigate the oil-water IFT after introducing Zn$_3$N$_2$ nanoparticles. The contact angle after surface treatment with Zn$_3$N$_2$ nanofluid was also measured to explore the capability of changing wettability. The pendant drop experiment was performed to find the oil-water IFT and contact angle. The experimental setup consists of light source, CCD camera, cuvette, micro-syringe and drop image software.
3. Results and discussion

The phase behaviour of the synthesized NPs depend on the N₂ concentration in a tube furnace. Figure 2 displays XRD pattern of the synthesized nanoparticles in the N₂ environment. Powder Diffraction File compiled by the Joint Committee on Powder Diffraction, Card No. 35-0762. M. Futsuhara et al. Thin Solid Films 322 (1998) 274–281 observed [13]. At 100% N₂, the diffraction arrangement is identical to the Zn₃N₂ diffraction pattern as reported in previous work. The peaks located at 2θ value 31.82°, 34.47° 36.30° correspond to 222, 321 and 400 reflection planes of Zn₃N₂ nanoparticles and reported in the literature. [25-27]. The intense peaks reveal the formation of crystalline structure. The XRD reflection planes and d-spacing are tabulated in Table 1.

![XRD pattern of synthesized Zn₃N₂ nanotriangles](image)

Figure 2. XRD pattern of synthesized Zn₃N₂ nanotriangles

| No. | Position [°] | FWHM Left [°2Th.] | hkl | d-spacing [Å] |
|-----|-------------|-------------------|-----|--------------|
| 1   | 31.8207     | 0.3129            | 222 | 2.81228      |
| 2   | 34.4729     | 0.3129            | 321 | 2.60174      |
| 3   | 36.3033     | 0.2608            | 400 | 2.47486      |
| 4   | 47.5764     | 0.3651            | 332 | 1.9113       |

3.1. FESEM Analysis

The surface morphology analysis of the Zn₃N₂ nanoparticles was carried out using FESEM. Figure 3 displays the FESEM images of the synthesized NPs. From Figure 3 it is clearly seen that the synthesized sample has triangular morphology. The uniform size particles are well dispersed. The stability of the particles is related to agglomeration. In the present sample, no agglomeration is observed which shows more stability. The average size of the synthesized particles is 35 nm.
3.2. Interfacial Tension

Interfacial tension (IFT) reduction in EOR is a key subject. The ultimate aim of EOR by nano flooding is to rise the capillary number by decreasing IFT of oil-water schemes. The oil-water IFT was measured to find the performance of Zn$_3$N$_2$. Firstly the IFT between oil-water without nanoparticles was investigated. The initial value was 2.24 mN/m which is due to the purified light crude oil. Three concentrations of Zn$_3$N$_2$ were used and 0.1 wt% is found to the optimum value at maximum reduction was observed as shown in Figure 4. After introducing Zn$_3$N$_2$ nanofluid under EM waves a decrease in IFT from 2.24 to 0.55 mN/m was observed at 0.1 wt% as displayed in Figure 5. This reduction in IFT could be due to the polarization behaviour at oil-water interface of dielectric material under EM waves. The oscillating E-field of EM waves interact with nanoparticles and results in continuous polarization and charge oscillation. This charge oscillation produces disturbance due to dielectric loss. The interface absorbs this energy and molecules gain energy which disturbs the interface.
Figure 4. Interfacial tension at various concentrations of Zn$_3$N$_2$

Figure 5. Oil-water IFT using Zn$_3$N$_2$ nanofluid under EM

Miao et al., [28] explained the effect of nanoparticle polarization under electric field on relative permittivity of transformer oil based nanofluids. Figure 6 shows the nanoparticle inner polarization and transformer oil molecules under electric. The continuous polarization of nanoparticles and oil molecules under oscillating electric field results in weak interaction with water. The interfacial tension of oil-water under EM can be explained by considering the polarization of oil molecules and accumulation around nanoparticle as demonstrated in Figure 6. This polarization of nanoparticles helps to remove stick oil at rock surface.
4. Conclusion
The synthesis of Zn$_3$N$_2$ nanoparticles has been done using the sol-gel auto-combustion method in the N$_2$ environment. The FESEM results demonstrate the formation of well dispersed Zn$_3$N$_2$ nanotriangles. The average size is around 35 nm. The reduction in IFT under EM waves of frequency 2.2 MHz show the capability of Zn$_3$N$_2$ in EOR application. It was found that Zn$_3$N$_2$ can reduce the IFT from 2.2 mN/m to 0.55 mN/m. The 0.1 wt% found to be optimum concentration for IFT reduction under EM waves. The results display the electromagnetic response and electric polarization of Zn$_3$N$_2$ under EM waves responsible for dielectric loss and IFT reduction. Thus Zn$_3$N$_2$ can be used for industrial applications in EOR.

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