Chapter III

SYNTHESES AND CHARACTERIZATION OF PANI-RuO₂ COMPOSITE THIN FILMS BY CBD METHOD AND THEIR SUPERCAPACITOR AND GAS SENSOR PERFORMANCE
## Chapter III

**SYNTHESIS AND CHARACTERIZATION OF PANI-RuO$_2$ COMPOSITE THIN FILMS BY CBD METHOD AND THEIR SUPERCAPACITOR AND GAS SENSOR PERFORMANCE**

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Chapter III: Synthesis and Characterization of PANI-RuO$_2$ Composite Thin Films by CBD Method and Their Super capacitor and Gas Sensor Performance

Section A

Synthesis and Characterization of PANI-RuO$_2$ Composite Thin Films by CBD Method

3.1.1 Introduction

Nanocomposites are a special class of materials having unique physical properties and wide potential application in various areas [1]. This is achieved by the successful combination of the characteristics of parent constituents into a single material. A number of different metal and metal oxide particles have so far been encapsulated into the shell of conducting polymers giving rise to a host of nanocomposites [2]. These materials differ from both the pure polymers and the inorganic nanoparticles in some of the physical and chemical properties.

The literature survey on Ruthenium oxide (RuO$_2$) shows that both hydrous and anhydrous forms of RuO$_2$ have been reported to be promising electrode materials for supercapacitor due to their intrinsically high pseudocapacitance. Commonly, an anhydrous ruthenium oxide with a crystalline structure (rutile) is fabricated by thermal decomposition from its metal chloride and its specific capacitance was found to be much lower. Consequently, hydrous ruthenium oxide (denoted as RuOx.nH$_2$O) with amorphous structure is considered to be a potential material for supercapacitors [3]. Hydrous ruthenium oxide can be prepared by a sol-gel process from its chloride precursor in alkaline media or by electrochemical methods via polarizing the pure bulk metal to positive potentials [4-6]. On the other hand, sol-gel process steps are very complicated and not easily controlled. Also in electrodeposition, there is a necessity of source for the generation of electricity to deposit thin films. Thus, it is more desirable to develop new methods to replace the sol-gel and electrodeposition process for preparing of thin films for application in supercapacitors. The high production cost of the supercapacitor requires a search in order to look for cheaper methods.

The CBD is a simple and cost effective method for preparation of thin films. In the CBD method, the deposition medium for the material consists of one or more metal salts, a source of oxygen with/without complexing agent. The deposit is a metal hydroxide or hydrated oxide which can be formed by reaction of the
metal ions with slowly generated hydroxyl ions. In addition, the homogeneity and stoichiometry of the product are maintained by the solubility product of the material. Therefore, PANI-RuO$_2$ composite thin films were synthesized by low-cost and feasible CBD method on the stainless steel and glass substrates [7].

In this chapter, section A gives the synthesis and characterization of PANI-RuO$_2$ composite thin film. The section B represents the supercapacitive and section C gives gas sensor performance of the PANI-RuO$_2$ composite thin films. In order to study the supercapacitor and gas sensor application of PANI-RuO$_2$ composite thin films, the PANI-RuO$_2$ composite thin films have been deposited on the both the substrates conducting stainless steel and non conducting glass substrate.

### 3.A.2 Experimental Details

#### 3.A.2.1 Substrate Cleaning

Substrate cleaning plays an important role in the deposition of thin films. Extreme cleanliness of the substrate is mandatory for the deposition as the unhygienic substrate surface offer nucleation sites facilitating growth resulting into non-uniform films. Glass microslides and stainless steel were used as substrates.

(a) The microslides supplied by the "Blue star" of the dimensions 75 mm X 25 mm X 1.35 mm have been used as substrates. The following procedure has been adopted for cleaning of glass substrate.

1. The micro slides are washed with double distilled water,
2. Then washed with 0.5 M chromic acid for 1 h and kept in it for 24 h,
3. The substrates were again washed with double distilled water,
4. The substrates were ultrasonically cleaned for 10 min. and
5. Finally, the substrates were air dried, degreased in AR grade acetone and were used for deposition.

(b) Electrically conducting substrate is required to investigate supercapacitive performance of thin film. Stainless steel was used as a conducting substrate. Stainless steel substrates were cleaned according to following procedure.

1. The substrates were polished using zero grade polish paper.
2. The substrates were washed with detergent and double distilled water,
3. Then, the substrates were ultrasonically cleaned for 15 min, and
4. Finally, the substrate were dried by air and used for the deposition.

3.A.2.2 Experimental Setup for Deposition of PANI-RuO$_2$ Composite Thin Films

Preparation of PANI-RuO$_2$ composite thin film by CBD method is based on the simultaneous polymerization of aniline monomer and precipitation of ruthenium (III) oxide. The separate solutions were prepared using 0.2 M aniline monomer in 1 M H$_2$SO$_4$, and 0.01 M RuCl$_3$·xH$_2$O precursors. The separately prepared precursors were taken in another beaker with volume ratio 1:1 (i.e 30 ml: 30 ml). Then the 0.1 M ammonium persulphate ((NH)$_4$S$_2$O$_8$) (APS) was added to it for the formation of PANI-RuO$_2$ composite thin films. The substrates were immersed in the bath; the bath was kept at room temperature (300 K) for 30 min. Initially, color of the prepared bath was blackish. After the addition of APS, it was turned into greenish. The change in color and the precipitation PANI-RuO$_2$ was started in the bath. During the precipitation, heterogeneous reaction occurred and a thin layer of PANI-RuO$_2$ composite took place on the substrate. The substrates coated with thin layer of PANI-RuO$_2$ composite were removed after 30 min. The PANI-RuO$_2$ composite thin films were washed with double distilled water and air dried. The maximum thickness obtained was 0.033 and 0.018 mg.cm$^{-2}$ on the stainless steel and glass substrate, respectively. In order to increase the film thickness, this process was repeated for four times. It was observed that the thickness increases up to third deposition. Furthermore, slight decrease in film thickness was observed which may be attributed to the formation of outer porous layer and/or the film which may develop stress to cause delamination, resulting in peeling off the film after the film reaches at maximum thickness [8]. The optimized preparative parameters for the PANI-RuO$_2$ composite thin films are shown in the Table 3.1.
3.A.2.3 Characterization Techniques

The thickness of PANI-RuO₂ composite thin films was measured by weight difference method using a sensitive microbalance. The X-ray diffraction (XRD) patterns were obtained with Philips (PW-3710) diffractometer using CrKα radiation (\(\lambda = 2.29361 \text{ Å}\)). Surface morphology was studied with the help of scanning electron microscope (JEOL –JSM 6360). For this, the films were coated with a 10 nm platinum layer using a polaron scanning electron microscopy (SEM) sputter coating unit E-2500 before taking the image. The surface wettability of the thin film is evaluated by means of water contact angle measurement using Rame-hart USA equipment with CCD camera. Fourier transform infrared spectroscopy (FT-IR) was recorded between 4000 and 400 cm\(^{-1}\) at a spectral resolution of 2 cm\(^{-1}\) on a PerkinElmer 1710 spectrophotometer using KBr pellets at room temperature. The FT-Raman spectroscopy was used as a complement to characterize the composition of the synthesized PANI-RuO₂ composite material. Raman studies were conducted using Bruker make FT-Raman spectrophotometer. Samples, in the powder form, were excited with a 514.5 nm Argon laser (0.5 mW), using a Perkin-Elmer, model 783, USA. All Raman data acquisitions were obtained at room temperature (300 K). The Shimadzu UV-1800 spectrophotometer was used to obtain UV-VIS absorption spectra of thin films with glass as a reference substrate. The supercapacitor study was carried out using the 263A EG & G Princeton Applied Research Potentiostat forming an electrochemical cell consisting of PANI-RuO₂ composite electrode as working electrode, platinum as a

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counter electrode and saturated calomel electrode (SCE) as a reference electrode. The WonATech Automatic Battery Cycler, WBCS3000 system interfaced to a computer was used to study the charge-discharge of PANI-RuO$_2$ composite electrode. The electrochemical impedance measurements were conducted with WonATech made electrochemical workstation (ZIVE SP5).

The ammonia (NH$_3$) gas sensing properties of PANI-RuO$_2$ composite thin films were studied in the gas sensor assembly consisting of cylindrical stainless steel chamber (volume 250 cc). The two-probe d. c. measurement technique was used to measure the electrical resistance in presence of NH$_3$ gas and air atmosphere.

### 3.A.3 Results and Discussion

#### 3.A.3.1 PANI-RuO$_2$ Composite Thin Film Formation and Reaction Mechanism

The CBD is based on the formation of solid phase from a solution, which involves two steps as nucleation and particle growth. In the nucleation, the clusters of molecules formed undergo rapid decomposition and particles combine to grow up to a certain thickness of the film by heterogeneous reactions at the substrate surface. Generally, metal ions are complexed in such a way that reaction takes place between slowly released metal ions to form product in thin film. The formation mechanism of PANI-RuO$_2$ composite thin film can be expressed as follows,

The ammonium persulphate plays the role of oxidizing agent in case of aniline monomer and provides the OH$^-$ ions for the metal oxide.

$$(\text{NH}_4)_2\text{S}_2\text{O}_8 \rightarrow 2\text{NH}_3 + 2\text{H}^+ + \text{S}_2\text{O}_8^-$$  \hspace{1cm} 3.1

In aqueous solution, ammonia slowly releases the OH$^-$ ions as,

$$\text{NH}_3 + \text{H}_2\text{O} \leftrightarrow \text{NH}_4^+ + \text{OH}^-$$  \hspace{1cm} 3.2

PANI is composed of aniline repeat units connected to form a backbone. The existence of a nitrogen atom lying between phenyl rings allows the formation of different oxidation states. The oxidative blending involves the oxidation of monomers to form a radical cations followed by coupling to form di-cations and the repetition leads to the polymer formation. The reaction mechanism for the PANI formation is explained in the following reaction [9-11],
For the deposition of RuO$_2$ film, RuCl$_3$ is used as a source of ruthenium ions (Ru$^{3+}$). The Ru$^{3+}$ ions react with OH$^-$ ions in the solution to form ruthenium hydroxide (Ru(OH)$_3$) which then react with excess OH$^-$ ions to form RuO$_2$. The following reaction gives the formation of RuO$_2$,

$$2\text{Ru(III)Cl}_3 \rightarrow 2\text{Ru}^{3+} + 6\text{Cl}^-$$

$$\text{Ru}^{3+} + 3\text{OH}^- \rightarrow \text{Ru(OH)}_3$$

$$\text{Ru(OH)}_3 + \text{OH}^- \rightarrow \text{RuO}_2 + 2\text{H}_2\text{O}$$

This describes the PANI-RuO$_2$ composite thin film formation mechanism by CBD.

### 3.3.3.2 Thickness Measurement

Thickness of PANI-RuO$_2$ composite thin film was measured by the gravimetric weight difference method using equation 2.11. The density of the deposited material is assumed to be the same as that of the bulk material. The density of the film material is expressed as [12],

$$\rho = \frac{1}{2} (\rho_1 + \rho_2)$$

Where, ‘$\rho_1$’ and ‘$\rho_2$’ are bulk densities of the film material for PANI (1.30 g.cm$^{-3}$) and RuO$_2$ (6.97 g.cm$^{-3}$), respectively.

Variation of the thickness of PANI-RuO$_2$ composite thin films deposited on the substrates with the no. of deposition is shown in Fig. 3.1. The thickness in terms of weight of PANI-RuO$_2$ composite film deposited depends on number of deposition, since the thickness obtained in single deposition is less. The terminal thickness, at which the highest amounts of PANI-RuO$_2$ composite material deposited on the stainless steel and glass substrates were 0.12 and 0.095 mg.cm$^{-2}$
respectively after 3rd depositions. The time of each deposition was 30 min. as after 30 min., film thickness remained constant as the reaction was complete. The initial nucleation growth rate on the crystalline substrates is higher than the amorphous substrates, as the crystalline substrate promote nucleation very speedily as compared to the amorphous substrate. Therefore, different growth kinetics of PANI-RuO$_2$ composite material was observed onto the different kinds of substrates and hence the PANI-RuO$_2$ composite thin film has the more thickness on the stainless steel substrate [13, 14].

Fig. 3.2 shows the photographs of the (a) RuO$_2$, (b) PANI-RuO$_2$ composite and (c) PANI thin films on the stainless steel substrate having the area > 10 cm$^2$ (both sides of the substrate). The films are well adherent to the substrate. The PANI-RuO$_2$ composite films are slightly black greenish in color, different from PANI green and RuO$_2$ black color. Therefore, CBD method can be considered as a feasible method for the deposition of PANI-RuO$_2$ composite thin films.

![Graph](image-url)

**Fig. 3.1:** Variation of PANI-RuO$_2$ composite film thickness with no. of depositions on the (a) stainless steel and (b) glass substrates.
Fig. 3.2: Photographs of the (a) RuO₂, (b) PANI-RuO₂ composite, and (c) PANI thin films deposited on the stainless steel substrate.

3.A.3.3 X-ray Diffraction Study

Film crystallinity was analyzed using X-ray diffraction pattern. Fig 3.3 shows the XRD patterns of (a) RuO₂, (b) PANI-RuO₂ composite, and (c) PANI thin films onto the stainless steel substrate. The XRD pattern of PANI-RuO₂ composite (Fig. 3.4. b) thin films consists of no well-defined diffraction peaks other than stainless steel substrate, indicating that PANI-RuO₂ composite thin film is amorphous. The amorphous phase obtained for each material is feasible for supercapacitor application [15]. Also the Fig. 3.4 (a) and (c) indicates the amorphous nature of RuO₂ and PANI thin films on the stainless steel substrate.
**Fig. 3.3:** X-ray diffractograms of (a) RuO$_2$, (b) PANI-RuO$_2$ composite, and (c) PANI thin films on stainless steel substrate.

### 3.A.3.4 Surface Morphological Study

In order to check the supercapacitor and gas sensor performance, one has to deposit the material on conducting and non-conducting substrates. Fig. 3.4 shows the SEM images of (a) RuO$_2$, (b) PANI-RuO$_2$ composite, and (c) PANI thin films on stainless steel substrate, at 10,000 X magnification. Fig. 3.4 also shows the SEM images of (d) RuO$_2$, (e) PANI-RuO$_2$ composite, and (f) PANI thin films on glass substrates at 10,000 X magnification.

Fig. 3.4 (a) shows the SEM image of RuO$_2$ thin film. The compact morphology with ordinary shaped nanograins spread over the substrate surface with small cracks on the surface was observed from the SEM image. Also the agglomerated and stacked globular structure spread over the entire substrate surface was observed for PANI thin film (Fig. 3.4 c).

Globular structure of PANI-RuO$_2$ composite thin film is observed on the stainless steel substrate (Fig. 3.4 b). The substrate is covered with densely agglomerated spherical particles of PANI-RuO$_2$ composite material.

SEM morphology of all the films on the glass substrate shows the smooth and compact nature except some cracks on the PANI thin film. However, one can
observe some overgrowth of wire like structure on the surface of RuO₂, spherical particles on the surface of PANI-RuO₂ composite and irregularly shaped particles on the surface of PANI thin films. The observed morphology on the stainless steel substrate is different from the morphology on glass substrate.

Fig. 3.4: SEM micrographs of (a) RuO₂, (b) PANI-RuO₂ composite, and (c) PANI thin film on stainless steel and (d) RuO₂ (e) PANI-RuO₂ composite, and (f) PANI thin film on glass substrates at 10,000 X magnification.

3.A.3.5 Wettability Study

The wetting of solid with water, where air is the surrounding medium, is dependent on the relation between the interfacial tensions (water/air,
water/solid and solid/air). The ratio between these tensions determines the contact angle ($\theta$) between a water droplet on a given surface. Both super-hydrophilic and super-hydrophobic surfaces are important for practical applications such as supercapacitor and gas sensor. Fig. 3.5 shows the water contact angles of (a) RuO$_2$, (b) PANI-RuO$_2$ composite and (c) PANI thin films on the stainless steel substrate. It is observed that the water laid with contact angle of 95° on (a) RuO$_2$, 37° on (b) PANI-RuO$_2$ composite, and 29° on (c) PANI thin films, respectively. The SEM study of the RuO$_2$ supports (compact morphology) to its hydrophobic nature, as the contact angle is > 90°. The PANI-RuO$_2$ composite and PANI thin film shows the hydrophilic nature due to porous the morphology revealed from SEM study. This specific property is attributed to amorphous or nanocrystalline nature that is expected to possess very high surface energy, which increases with reduction in particle size [16]. It is reported that nanocrystalline thin films show high surface energy due to the presence of uniform and non-uniform strains [17, 18]. Neumann’s equation of state was used to estimate the surface energy of various thin films [19]. From the measurements of water contact angles, the surface energies were found to be 23.73, 60.54 and 64.21 mJ.m$^{-2}$ for the (a) RuO$_2$, (b) PANI-RuO$_2$ and (c) PANI thin films on the stainless steel substrate, respectively.
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Fig. 3.5: Water contact angle measurements of (a) RuO$_2$, (b) PANI-RuO$_2$ composite, and (c) PANI thin films on the stainless steel substrate.

3.A.3.6 Fourier Transform Infrared (IR) Spectroscopy Study

FT-IR spectroscopy was employed in order to identify the presence of bonding or stretching vibrations in the synthesized RuO$_2$, PANI-RuO$_2$ composite and PANI thin films and hence to confirm material formation. Fig. 3.6 shows the FT-IR absorption spectra of (a) RuO$_2$, (b) PANI-RuO$_2$ composite, and (c) PANI thin films in the range of 4000–400 cm$^{-1}$. Fig. 3.6 (a) shows the FT-IR spectrum of pure RuO$_2$ with the small peak at 466 cm$^{-1}$, which may be influenced by hydrous RuO$_2$ [20]. The broad band at 669 cm$^{-1}$ is associated with characteristic vibrational mode of rutile RuO$_2$ [21]. The absorption peak at 1019 cm$^{-1}$ is assigned to characteristic stretching vibration of peroxo groups [22]. The absorption band around at 1648 cm$^{-1}$ is due to the bending vibration of hydroxyl groups of molecular water [23]. The broad absorption band at 3408 cm$^{-1}$ is attributed to the stretching vibrations of O-H group [24]. The FT-IR spectrum of PANI-RuO$_2$ composite material is shown in Fig. 3.6 (b). It is observed that all the characteristic bands of RuO$_2$ are present in the PANI-RuO$_2$ composite. The relative intensity and shifting of some bands of RuO$_2$ are observed due to the interaction between RuO$_2$
particles and PANI chain. The small peak at 608 cm\(^{-1}\) is associated with the characteristic vibrational mode of rutile RuO\(_2\) [21]. The peaks at 1108 and 802 cm\(^{-1}\) are attributed to the in-plane and an out-of-plane C-H bending mode, respectively. The peak at 1301 cm\(^{-1}\) corresponds to N-H bending [25]. The peaks at 1582 and 1477 cm\(^{-1}\) are assigned to C-C ring stretching vibrations. The peak at 2931 cm\(^{-1}\) is assigned to the free N-H stretching vibrations of secondary amines and vibration associated with the NH\(^{2+}\) part in the –C\(_6\)H\(_4\)NH\(^{2+}\)C\(_6\)H\(_4\) group [26] The characteristic peak N-H stretching of PANI (Fig. 3.7 (c)) and the broad band stretching vibration of O-H group in RuO\(_2\) disappeared in the PANI-RuO\(_2\) composite thin films. This may be due to the strong interaction of ruthenium particles and N-H stretching group in the PANI. This result indicates the formation of PANI-RuO\(_2\) composite thin film [27].

![FT-IR spectra](image)

**Fig. 3.6:** FT-IR spectra of (a) RuO\(_2\), (b) PANI-RuO\(_2\) composite, and (c) PANI thin films.

### 3.A.3.7 FT-Raman Study

In order to get insight about the bending and stretching vibrations, the films were characterized for their FT-Raman spectra. Fig. 3.7 shows the FT-Raman spectra of (a) pure RuO\(_2\), (b) PANI-RuO\(_2\) composite, and (c) PANI thin films. In the Raman spectrum of RuO\(_2\), three peaks are observed. Fig. 3.7 (a). The peaks at 523,
670 cm\(^{-1}\) and 440 cm\(^{-1}\) correspond to the crystalline ruthenium oxide in the rutile form [28, 29].

Fig. 3.7 (b) shows FT-Raman spectrum of PANI-RuO\(_2\) composite. The bands at 1505 and 1175 cm\(^{-1}\) are assigned mainly to the benzenoid C-C ring stretching vibrations and a band at 1591 cm\(^{-1}\) is attributed to the quinoid C=C stretching mode of the polymer chain [30]. The characteristic band 1367 cm\(^{-1}\) corresponds to C=N stretching of quinoid units [31]. The characteristics peak at 523 cm\(^{-1}\) shifted to 521 cm\(^{-1}\), and the peak at 670 cm\(^{-1}\) is shifted to 720 cm\(^{-1}\). Also some characteristics peaks of PANI have been shifted in PANI-RuO\(_2\) spectrum. The shifting of the peaks in PANI-RuO\(_2\) spectrum may be due to the interaction of PANI chain and RuO\(_2\) particles. Thus the FT-Raman indicates the formation of PANI-RuO\(_2\) composite material. In Fig. 3.8 (c), the peaks at 1172, 1373, 1508 cm\(^{-1}\) and 1594 cm\(^{-1}\) corresponds to the amorphous PANI [32].

Fig. 3.7: FT-Raman spectra of (a) RuO\(_2\) (b) PANI-RuO\(_2\) composite, and (c) PANI thin films.
3.A.3.8 Optical Study

The optical absorption study of (a) RuO$_2$, (b) PANI-RuO$_2$ composite, and (c) PANI thin films on glass substrate was carried in the wavelength range of 350–750 nm and is shown in Fig. 3.8. The spectrum of (Fig 3.8 (b)) PANI-RuO$_2$ composite film revealed broad range of low absorbance in the middle of visible wavelength region. The high absorbance around 730 nm in the present work might be due to intermediate species, possibly a mixture containing major amount of conducting emeraldine salt and a little amount of its base [33]. Fig. 3.8 (a) shows the optical absorption of RuO$_2$ thin film. It has high absorbance in the low wavelength range and decreases towards the higher visible wavelength range. Fig. 3.8 (c) shows the optical absorption of PANI thin film. The pure PANI thin film has relatively lower absorbance in the visible range. The peak at 430 nm is due the polaron –π* transition of the benzenoid ring [34]. This peak disappears in the PANI-RuO$_2$ composite and has the slightly sharp band edge at 478 nm. This shows that there is a interaction of metal oxide particles and polymer chain comprising the composite thin film [35].

![Absorption spectra](image-url)

**Fig. 3.8:** Absorption spectra of (a) RuO$_2$, (b) PANI-RuO$_2$ composite, and (c) PANI thin films.
3.4.3.9 Conclusions

In conclusion, the PANI-RuO$_2$ composite thin films have been successfully synthesized at low temperature on stainless steel and glass substrates using simple and cost effective CBD method. The XRD study revealed that the all films are amorphous. The FT-IR and FT-Raman studies showed the formation of PANI-RuO$_2$ composite material. Both the studies showed that there is a strong interaction between metal particle and polymer chain, since the shifting of bands and decrease in relative intensity of bands was observed. This also confirms the formation of composite material. The composite of PANI-RuO$_2$ shows the hydrophilic nature. The optical studies showed that PANI-RuO$_2$ composite thin films have low absorbance in visible region compared to RuO$_2$. 
Section B

Supercapacitive Performance of PANI–RuO₂ Composite Thin Films

3.B.1 Introduction

In the present section, the supercapacitive properties of PANI-RuO₂ composite electrode have been carried out using the cyclic voltammetry, galvanostatic charge-discharge and electrochemical impedance analysis. The PANI-RuO₂ composite electrode stability studied over the 5000\textsuperscript{th} cycles. Also the comparative study of supercapacitive parameters of RuO₂, PANI-RuO₂ and PANI-RuO₂ composite has been reported.

3.B.2 Experimental Details

3.B.2.1 Cyclic Voltammetry

Fig. 3.9 (a) shows the schematic of experimental set up and (b) shows the actual experimental set up for the supercapacitor study. The electrochemical measurements for supercapacitor were carried out in a three electrode electrochemical cell, in which the PANI-RuO₂ composite thin film electrode was used as the working electrode, platinum as the counter, and saturated calomel electrode (SCE) as the reference electrode.

The cyclic voltammetry (CV) experiments were performed to determine the specific capacitance of the PANI-RuO₂ composite thin film electrode in 1 M H₂SO₄ electrolyte. The capacitance 'C' of film was calculated from the relation

\[
C = \frac{I}{(dV/dt)} \quad \text{3.8}
\]

Where, 'I' is the average current in amperes and (dV/dt) is the scan rate in mV.s\textsuperscript{-1}. Similarly the interfacial capacitance (Cᵢ) is obtained by dividing the capacitance by respective electrode area in the electrolyte.

\[
Cᵢ = \frac{C}{A} \quad \text{3.9}
\]

Where 'A' is the area (1 cm\textsuperscript{2} in this study) of electrode dipped in the electrolyte. The specific capacitance (Cₛ) of the electrode is obtained by dividing the capacitance by the weight of PANI-RuO₂ composite thin film electrode dipped in the electrolyte.
**CHAPTER III: SYNTHESIS AND CHARACTERIZATION OF PANI-RuO$_2$ COMPOSITE THIN FILMS BY CBD METHOD AND THEIR SUPERCAPACITOR AND GAS SENSOR PERFORMANCE**

$C_s = C/W$

Where ‘$W$’ is the weight of the PANI-RuO$_2$ composite thin film electrode dipped in the electrolyte.

**Fig. 3.9 (a):** Schematic of experimental set up for the supercapacitor study.

**Fig. 3.9 (b):** Experimental set up for the supercapacitor study. Arrow shows the area (1cm$^2$) of PANI-RuO$_2$ composite thin film electrode dipped in 1 M H$_2$SO$_4$ electrolyte.
3.B.2.2 Charge-Discharge Study

Fig. 3.9 (c) shows the actual experimental set up for the charge-discharge study. The different parameters of supercapacitors, such as specific power, specific energy and coulombic efficiency are evaluated from the constant current density charging curves of the PANI-RuO$_2$ composite thin electrode. The specific power (SP) and specific energy (SE) are calculated using the following relations [36],

$$\text{SP} = \frac{I \times V}{m}$$  
$$\text{SE} = \frac{I \times t \times V}{m}$$

Where, SP is specific power in KW.kg$^{-1}$ and SE is specific energy in Wh.kg$^{-1}$. The above expressions shows the discharge current (I) in amperes, voltage range (V) in volts, discharge time (t) in seconds and mass of the electroactive material (m) in kilograms. The coulombic efficiency is calculated using the following equation [37],

$$\eta = \left(\frac{t_D}{t_C}\right) \times 100$$

Where, $t_C$ and $t_D$ represent the time of charging and discharging, respectively.

![Experimental setup for charge-discharge study](image)

Fig. 3.9 (c): Experimental set up for the charge-discharge study.
3.B.2.3 Electrochemical Impedance Spectroscopy (EIS) Study

Electrochemical impedance spectroscopy (EIS) is a helpful experimental tool to characterize frequency response of a device. The electrochemical impedance measurements were conducted with WonaTech made electrochemical workstation (ZIVE SP5).

Special equipment is required to apply a small AC voltage and measure the changes in magnitude and phase over a range of frequencies. The frequency range used was from $10^{-2}$ to $10^6$ Hz at open circuit voltage. The measurement proceeds by applying a low amplitude alternating voltage $\Delta V$ to a steady-state potential $V_s$, with $\Delta V(\omega) = \Delta V_{\text{max}} e^{i\omega t}$, where $\omega$ is the pulsation and $\Delta V_{\text{max}}$, the signal amplitude. This input signal leads to a sinusoidal output current $\Delta I$, with

$$\Delta I(\omega) = \Delta I_{\text{max}} e^{i(\omega t + \phi)}$$

where $\phi$ is the phase angle of the current versus the voltage and $\Delta I_{\text{max}}$ the signal amplitude. The electrochemical impedance $Z(\omega)$ is defined as

$$Z(\omega) = \frac{\Delta V}{\Delta I} = |Z(\omega)| e^{-j\phi} = Z' + jZ'',$$  \hspace{1cm} 3.15

where $Z'$ and $Z''$ are respectively the real part and the imaginary part of the impedance, defined as

$$Z'^2 + Z''^2 = |Z(\omega)|^2$$  \hspace{1cm} 3.16

Complex impedance analysis is a powerful tool to describe capacitors or supercapacitors, a more suitable way is proposed by analysing frequency behaviour by complex capacitance modelling of impedance data [38, 39].

3.B.3 Results and Discussion

3.B.3.1 Cyclic Voltammetry

In order to study, the cyclic voltammetry of RuO$_2$, PANI-RuO$_2$ composite and PANI electrodes were prepared by the CBD method. Fig. 3.10 gives cyclic voltammograms of (a) RuO$_2$, (b) PANI-RuO$_2$ composite, and (c) PANI electrodes with scan rate of 5 mV.s$^{-1}$. The potentials window was $-0.2$ and $+0.8$ V vs SCE for PANI and PANI-RuO$_2$ composite and 0 to $+1$ V vs SCE for RuO$_2$. The potential window of RuO$_2$ is different from the PANI and PANI-RuO$_2$ composite thin film as the area under curve of these materials is larger in their respective potential window. The CV curve of RuO$_2$ shows the pseudocapacitive behavior. Also it can
be observed that the shapes of the CV curves of PANI and PANI-RuO₂ composite are fewer rectangular within the measured potential window. It is pointed out that the CV curves for the composite reveals redox peaks with enhanced current background than the PANI and RuO₂ electrode materials. The specific capacitances of RuO₂, PANI-RuO₂ and PANI electrode were found to be 186, 830 and 591 F.g⁻¹, respectively at the scan rate of 5 mV.s⁻¹. The enhanced specific capacitance was observed for the PANI-RuO₂ composite material than the RuO₂ and PANI electrode material. The PANI-RuO₂ composite shows enhanced specific capacitance of 830 F.g⁻¹ which can be attributed to synergistic effect between PANI and RuO₂. Zhang et. al. reported the enhanced specific capacitance of PANI-MnO₂ composite due to synergistic effect [40].

![Graph](image-url)

**Fig.3.10:** The CV curves of (a) RuO₂, (b) PANI-RuO₂ composite, and (c) PANI electrodes.

**3.B.3.2 Effect of Film Thickness**

The effect of deposited weight on supercapacitive behavior of the PANI-RuO₂ composite electrode was studied in 1 M H₂SO₄ electrolyte at the scan rate of 5 mV.s⁻¹. Fig. 3.11 shows the typical cyclic voltammograms of PANI-RuO₂ composite electrode for different deposited weight. The area under CV curve goes on increasing with increase in deposited weight of material. Two pairs of redox
peaks corresponding to leucoemeraldine to emeraldine salt conversion (first pair \( P_1 \) and \( P_4 \)) and emeraldine salt to pernigraniline conversion of PANI are clearly observed (second pair \( P_2 \) and \( P_3 \)) [41,42]. The CV curve reveals a redox behavior of PANI-RuO\(_2\) composite electrode different from electrical double layer capacitance. The CV curve shows the increase in current density with increase in deposited weight upto 0.12 mg.cm\(^2\).

![Current Density vs. Voltage (V vs. SCE)](image)

**Fig. 3.11:** The thickness dependent CV curves of PANI-RuO\(_2\) composite electrode at 5 mV.s\(^{-1}\).

The variation of interfacial and specific capacitances with thickness is given in Table 3.2. It is observed that specific capacitance increased from 221 to 830 F.g\(^{-1}\) and the interfacial capacitance increased from 0.007 to 0.09 F.cm\(^{-2}\) with the increase in film thickness upto its 0.12 mg.cm\(^{-1}\), above which there is decrease in the values of both the capacitances. Patil et. al. reported similar type of increasing trend for interfacial and specific capacitances with deposited weight [43]. The interfacial capacitance is proportional to the specific surface area of PANI-RuO\(_2\) composite material. At lower value of film thickness, there are small number of active sites present for protonation process which results into low specific capacitance value. When the weight of the electrode increased more than
0.12 mg.cm\(^{-2}\), the inner layers became inactive and remained as the dead volume [44] [49].

<table>
<thead>
<tr>
<th>Thickness (mg.cm(^{-2}))</th>
<th>Specific capacitance (F.g(^{-1}))</th>
<th>Interfacial capacitance (F.cm(^{-2}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.033</td>
<td>221</td>
<td>0.007</td>
</tr>
<tr>
<td>0.077</td>
<td>332</td>
<td>0.02</td>
</tr>
<tr>
<td>0.12</td>
<td>830</td>
<td>0.099</td>
</tr>
</tbody>
</table>

### 3.B.3.3 Effect of Scan Rate

The voltammetric responses of PANI-RuO\(_2\) composite electrode at different scan rates are shown in Fig. 3.12. It was found that the current under curve is slowly increased with scan rate. This showed that a voltammetric current is directly proportional to the scan rate of CV, indicating pseudocapacitive behavior [45]. The cyclic voltammograms at high scan rates do not show redox peaks over the potential range, due to the slow kinetics of the surface redox reaction of the electrode as well as the limited proton diffusion migration than at the low scan rate [46].

The specific and interfacial capacitance values are decreased from 830 to 255 F.g\(^{-1}\) and 0.099 to 0.03 F.cm\(^{-2}\), respectively, as the scan rate was increased from 5 to 100 mV.s\(^{-1}\). The decrease in capacitance with the scan rate is attributed to the presence of inner active sites, which cannot precede the redox transitions completely at higher scan rate of CV, probably due to the diffusion effect of proton within the electrode [47]. The maximum specific capacitance of 830 F.g\(^{-1}\) is obtained for PANI-RuO\(_2\) composite thin film at lower scan rate of 5 mV.s\(^{-1}\). Patil et. al. obtained a maximum specific capacitance of 73 F.g\(^{-1}\) for RuO\(_2\).H\(_2\)O on the stainless steel substrate by CBD method [48]. Hu et. al. reported a maximum specific capacitance of 100 F.g\(^{-1}\) for RuO\(_2\).H\(_2\)O electroplated on to a titanium substrate by CV from an aqueous solution [49]. Nam et. al. [50] observed that the specific capacitance of 708 F.g\(^{-1}\) by electrodeposition of PANI on the hydrous RuO\(_2\).
However, we have observed the maximum capacitance of 830 F.g⁻¹ for the PANI-RuO₂ composite electrode, higher than reported values of PANI-RuO₂ composite.

![Graph](image.png)

**Fig. 3.12:** The CV curves of PANI-RuO₂ composite thin films at various scan rates.

Fig. 3.13 shows the variation of specific capacitance of (a) RuO₂, (b) PANI-RuO₂ composite and (c) PANI thin films, respectively. Fig. 3.14 shows the variation of interfacial capacitance of (a) RuO₂, (b) PANI-RuO₂ composite and (c) PANI thin films, respectively. From the Figs. 3.13 and 3.14 it is observed that the specific and interfacial capacitances of RuO₂, PANI-RuO₂ composite, and PANI electrode decreased with the increased scan rates. The decrease of specific capacitance value with the increase in scan rate has been attributed to the resistance of ion diffusion, which becomes significant under relatively high scan rate. In addition, the proportion of inaccessible sites also increased with increasing the scan rate of CV, therefore a decrease in the specific capacitance is observed accordingly [51].
3.3.4 Stability Study

Long cycle life is a crucial parameter for supercapacitor electrode materials. Stability of PANI-RuO$_2$ composite electrode was tested by cyclic voltammetry.
Fig. 3.15 shows the CV curves of PANI-RuO\textsubscript{2} composite electrode at the scan rate of 100 mV.s\textsuperscript{-1} within the voltage range -0.2 to +0.8 V vs. SCE for the 1\textsuperscript{st} and 5000\textsuperscript{th} cycles. The specific capacitance for the 1\textsuperscript{st} cycle was 255 F.g\textsuperscript{-1} and it was decreased upto 217 F.g\textsuperscript{-1} for 5000\textsuperscript{th} cycle. The current under curve is decreased by 15% up to 5000\textsuperscript{th} cycles. We found that PANI-RuO\textsubscript{2} composite electrode exhibits stability of about 85% without a significant decrease in the capacity. The small amount of decrease in specific capacitance value is observed due to the loss of active material with the cycle number. Hence, it illustrates the fairly stable nature of PANI-RuO\textsubscript{2} composite electrode in energy storage application.

**Fig. 3.15:** The CV curves of PANI-RuO\textsubscript{2} composite electrode at 1\textsuperscript{st} and 5000\textsuperscript{th} cycles at the scan rate of 100 mV.s\textsuperscript{-1}.

Fig. 3.16 shows the specific capacitance as a function of cycle number of (a) RuO\textsubscript{2}, (b) PANI-RuO\textsubscript{2} composite and (c) PANI electrodes. It is observed that the PANI-RuO\textsubscript{2} composite shows the 85% stability over the 5000\textsuperscript{th} CV cycles.
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Fig. 3.16: Variation of specific capacitances of (a) RuO\(_2\), (b) PANI-RuO\(_2\) composite and (c) PANI thin film with cycle number.

3.B.3.5 Charge-Discharge Study

The charge–discharge behavior of the RuO\(_2\), PANI-RuO\(_2\) composite and PANI thin films examined by galvanostatic charge-discharge in the potential range of -0.2 to 0.8 V vs. SCE at 0.5 mA.cm\(^{-2}\) current density is shown in Fig. 3.17. (a), (b) and (c), respectively. The charge-discharge curve of RuO\(_2\) shows linear charging and discharging with time, indicating supercapacitor behavior [52].

The charge-discharge curves of PANI-RuO\(_2\) composite and PANI thin films showed a potential drop, while discharging. The potential drop for PANI-RuO\(_2\) composite film is less as compared to the PANI thin film. This result reflects that the internal resistance of PANI-RuO\(_2\) composite is smaller than the PANI. Low internal resistance is of great importance in energy storage devices, as the less energy would be wasted to produce unwanted heat during the charging–discharging processes [53]. The parameters such as specific power (SP), specific energy (SE) and columbic efficiency are calculated using the relations described in section 3.B.2.2. The specific power, specific energy and columbic efficiency estimated from the charge-discharge plots are given in the Table 3.3: The supercapacitor parameters of PANI-RuO\(_2\) composite are larger than the PANI electrode showing more suitability of composite for the supercapacitor application.
Table 3.3: Supercapacitive parameters of RuO$_2$, PANI-RuO$_2$ composite, and PANI thin film electrodes.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>RuO$_2$</th>
<th>PANI-RuO$_2$</th>
<th>PANI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific Power (S.P.) kW/kg$^{-1}$</td>
<td>2.77</td>
<td>4.16</td>
<td>3.84</td>
</tr>
<tr>
<td>Specific Energy (S.E.) Wh.kg$^{-1}$</td>
<td>65</td>
<td>260</td>
<td>40.05</td>
</tr>
<tr>
<td>Coulombic Efficiency (η) %</td>
<td>93</td>
<td>95</td>
<td>87</td>
</tr>
</tbody>
</table>

Fig. 3.17: Galvanostatic charge-discharge curves of (a) RuO$_2$, (b) PANI-RuO$_2$ composite, and (c) PANI thin film electrodes.

3.B.3.6 Electrochemical Impedance Spectroscopy (EIS) Study

The typical Nyquist plane plots between real ($Z'$) and imaginary ($Z''$) parts of impedance data of (a) RuO$_2$, (b) PANI-RuO$_2$ composite, and PANI electrodes are shown in Fig. 3.18. The PANI-RuO$_2$ composite thin film shows semicircle in the high frequency region and in the low frequency region the linear region leans more toward the imaginary axis (shows the vertical line) and this indicates good capacitive behavior [54]. On the other hand in case of RuO$_2$ this semicircle is very small and its linear part in the low frequency region is inclined to $\sim 45^\circ$ to the real axis [55]. PANI thin film shows the semicircle in the high frequency region and
nearly vertical line in the low frequency region similar to PANI-RuO\(_2\) composite electrode. Inset of Fig. 3.18 shows enlarged view of semicircles of material. From the EIS study, it observed that the ESR for the PANI-RuO\(_2\) composite thin film (9 \(\Omega\)) is smaller than the ESR’s (22 \(\Omega\)) of RuO\(_2\) and (20 \(\Omega\)) PANI electrodes.

**Fig.3.18:** Nyquist plots of (a) RuO\(_2\), (b) PANI-RuO\(_2\) composite, and (c) PANI electrodes.

### 3.B.3.7 Conclusions

A new, simple chemical bath deposition method has been used to prepare PANI-RuO\(_2\) composite electrode for supercapacitor application. The cyclic voltammetry study shows that PANI-RuO\(_2\) composite electrode has supercapacitive performance in the potential window of -0.2 to +0.8 V vs. SCE. The deposited PANI-RuO\(_2\) composite electrode exhibits a maximum specific capacitance of 830 F.g\(^{-1}\). PANI-RuO\(_2\) composite electrode exhibits a good cycling performance and keeps 85% of initial capacity over 5000\(^{th}\) cycles. The electrochemical impedance study reveals the supercapacitive behavior of the all the material in the low frequency region as the vertical lines nearly inclined to 45\(^\circ\). From the comparative supercapacitor study of RuO\(_2\), PANI-RuO\(_2\) composite and PANI shows that formation of composite material enhances individual supercapacitive performance of pure materials.
Section C

Ammonia (NH₃) Gas Sensor Properties of PANI–RuO₂ Composite Thin Films

3.C.1 Introduction

The detection, measurements and control systems for hazardous, harmful, pollutant and toxic gas emissions are nowadays very important for an ecologically responsible development. Another aspect is the control of the technological process, where dangerous substances are used as technological gases [56]. Ammonia (NH₃) is one of the most important substances encountered in our daily lives. The major industrial application is in agriculture, specifically in the production of fertilizers [57]. In the food industry ammonia is also an important indicator [58].

Ammonia (NH₃) is highly toxic. Inhalation of NH₃ at high level may cause respiratory distress or failure. Therefore, detection of NH₃ is important in the industrial, medical, and environmental applications [59]. The NH₃ gas sensors have been fabricated by many techniques, such as Langmuir-Blodgett technique [60], spin coating [61], thermal evaporation [62], chemical vapor deposition [63], and reactive sputtering [64]. Although these techniques have been used in the fabrication of NH₃ gas sensors, these techniques have disadvantages such as low productivity, high cost, complicated and long-time operations, and low reliability.

To overcome the problems, we have adopted the low cost and reliable CBD method for the preparation of NH₃ gas sensor. This section discusses the NH₃ gas sensing performance of PANI-RuO₂ composite thin films. The effect of thickness and concentration has been discussed. The selectivity of PANI-RuO₂ over the different gases is studied.

3.C.2 Experimental Setup of NH₃ Gas Sensor

The NH₃ gas sensing properties of PANI-RuO₂ thin films were studied in the gas sensor assembly as shown in the Fig. 3.19 (a) and photograph of actual experimental setup is as shown in Fig 3.19 (b). Before the target gas was introduced into the chamber, the chamber was purged with dry air to remove any residual gas molecules which might influence the gas sensing behavior. The target gas used in this work was NH₃. The gas sensing characteristics of PANI-RuO₂
composite thin film was investigated by measuring the electrical resistance across the film at room temperature by exposing the different concentrations of NH$_3$. Princeton Applied Research Potentiostat (Model 263) was used to measure the electrical resistance of PANI-RuO$_2$ composite thin film sensor. For electrical measurement, silver paste contacts of 1 mm$^2$ were applied at the edges of the PANI-RuO$_2$ composite films separated by 1 cm.

The gas sensor set up consists of heater block that is contained in an airtight stainless steel enclosure having a volume of 250 cc. It also contains a pair of spring-enabled pressure contacts made of silver rods. The upper ends of which are connected to potentiostat. The electrical resistances of PANI-RuO$_2$ composite thin film in air ($R_a$) and in gas atmosphere ($R_g$) were measured at room temperature (300 K) to evaluate the gas response defined using relation 2.10. The selectivity of the PANI-RuO$_2$ composite sensor was studied under the exposure of different gases at room temperature.

![Gas sensor assembly](image)

**Fig. 3.19 (a):** Gas sensor assembly for the studying the gas sensing properties of PANI-RuO$_2$ composite thin films.
Fig. 3.19 (b): Photograph of experimental setup for gas sensor study (Inset shows the mounted sample of PANI-RuO₂).

3.C.3 Ammonia Sensing Properties of PANI–RuO₂ Composite Thin Films

PANI is a special conducting polymer since its doped state can be controlled by acid/base reactions. This is widely used to detect acidic and basic gases. When exposed in ammonia gas, PANI undergo dedoping by deprotonation,

\[
\text{PANI}^+ + \tilde{\text{NH}}_3 \rightarrow \text{PANI}^0 + \text{NH}_3^+ \quad \text{Adsorption}
\]

\[
\text{PANI}^0 + \tilde{\text{NH}}_3 \rightarrow \text{PANI}^+ + \tilde{\text{NH}}_3 \quad \text{Desorption}
\]

The protons on –NH– groups are transferred to NH₃ molecules to form ammonium ions while PANI itself turned into its base form. This process is reversible, and in fact, when ammonia atmosphere is removed, the ammonium ion can be decomposed to ammonia gas and proton. The formation of new N-H bonds between the hydrogen atoms and nitrogens can reduce the resistance of PANI [65, 66].
The resistance of PANI-RuO$_2$ composite thin film increases upon exposure to NH$_3$, a reducing agent acting as an electron donor. Upon interaction with NH$_3$ some electrons are added into the valence band of the PANI p-type semiconductor, and as a result the conductance of PANI is decreased. The n-p contacts between RuO$_2$ nanoparticles and PANI matrix give rise to variety of shallow donors and acceptor levels increasing the physical adsorption sites for gas molecules thus enhancing the gas sensitivity [67].

3.C.4 Effect of Film Thickness

Fig. 3.20 shows the gas response of PANI-RuO$_2$ composite thin films as a function of different film thicknesses, under the exposure of 20 ppm NH$_3$ gas at room temperature (300 K). It is evidenced from the figure that the gas response increases from 20% for a thickness of 0.033 mg. cm$^{-2}$ to the maximum gas response of 49% for a thickness of 0.095 mg.cm$^{-2}$. It is well known that the gas response of the metal-oxide semiconductor sensors is mainly determined by the interactions between the target gas and the surface of the sensors. So it is obvious that for the greater surface area of the materials, the interaction between the adsorbed gas and the sensor surface is stronger, i.e. gas response is higher [68].

![Graph showing the thickness dependent gas response of PANI-RuO$_2$ composite thin film sensor to 20 ppm NH$_3$ gas concentration.](image)

**Fig. 3.20:** The thickness dependent gas response of PANI-RuO$_2$ composite thin film sensor to 20 ppm NH$_3$ gas concentration.
3.C.5 Effect of Gas Concentration

The resistance response curves for maximum thickness of 0.095 mg.cm$^{-2}$ with time under the exposure of different NH$_3$ gas concentrations is shown in Fig. 3.21. It is revealed from Fig 3.21 that the resistance of sensor increased as the NH$_3$ gas concentration was increased from 20 to 80 ppm. On initial exposure of the NH$_3$ gas, PANI-RuO$_2$ composite sensor displayed a sharp increase in the resistance, indicating that the PANI had been deprotonated by the NH$_3$ gas to the conducting emeraldine base form [69]. On subsequent injections of NH$_3$ gas, the PANI-RuO$_2$ composite sensor displayed rapid increase in resistance and sharp decrease when the chamber was vented. It is observed that with increase in the gas concentration from 20 to 80 ppm, the resistance increased gradually indicating that the increasing gas response from 49 to 85%. Further, it is seen from the figure that, almost the same time (70 s) was taken to reach the maximum response for different concentrations of NH$_3$ gas and the NH$_3$ gas response dropped (110 s), when the NH$_3$ gas was removed from testing atmosphere indicating that the sensor has good response and recovery at high concentrations of gas. Fig 3.22 shows the variation of gas response for the (a) PANI and (b) PANI-RuO$_2$ with gas concentrations. The PANI-RuO$_2$ composite sensor showed maximum gas response of 85 % than the PANI gas response of 50 % to 80 ppm NH$_3$ gas concentration at 300K
Fig. 3.21: Resistance response curves of PANI-RuO$_2$ composite thin film to different NH$_3$ gas concentrations.

Fig. 3.22: The gas response of (a) PANI and (b) PANI-RuO$_2$ composite thin films to different NH$_3$ gas concentration.

3.C.6 Selectivity Study

The ability of a sensor to respond to a certain gas in the presence of other gases is known as selectivity. Selectivity of PANI-RuO$_2$ composite thin film was
studied under the exposure of different gases CO₂, N₂, NH₃ and LPG at room temperature. The histogram (Fig. 3.23) shows the gas response of PANI-RuO₂ composite thin film gas sensor to different gases. The PANI-RuO₂ composite thin film showed strong selectivity towards NH₃ gas and much weaker responses to CO₂, N₂, and LPG gas. Furthermore, it is observed that PANI-RuO₂ composite thin films sense lower concentration of NH₃ with higher sensitivity value as compared to large concentration of other gases. This may be due to the correlation with the interaction strength between the testing gas and sensing layer [70].

![Fig. 3.23: The gas responses of PANI-RuO₂ composite thin film to different gases.](image)

3.C.7 Conclusions

The low-cost CBD method was used for the deposition of PANI-RuO₂ composite thin films. The NH₃ sensing properties of the PANI-RuO₂ composite films were dependent on film thickness. The PANI-RuO₂ composite thin films of a thickness of 0.095 mg cm⁻² exhibited the maximum gas response of 85 % at 300 K under the exposure of 80 ppm NH₃ gas concentration. The PANI-RuO₂ composite thin films exhibited good gas response (70 s) and recovery (110 s) characteristics towards the reducing NH₃ gas. The comparative gas response study of PANI and PANI-RuO₂ composite sensor showed PANI-RuO₂ composite sensor has high response than the PANI. Further, it showed selectivity toward NH₃ than the other gases.
## References

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Reference</th>
</tr>
</thead>
</table>


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