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Self assembly process in graphite (pencil) powder and pani/pencil powder by mechanical mixture method - ohmic behavior

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ABSTRACT

Lead graphite-pencils have been associated in our daily life but it could be an easy source for understanding many unexplained properties of graphite based materials. The present work shows that lead pencils belong not only to the class of heterogeneous materials but also exhibited good soft ferromagnetic properties at room temperature. The structural, morphological, optical and electrical properties such as X-ray diffraction (XRD), scanning electron microscopy (SEM), optical absorption, photoluminescence (PL) were studied. Ohmic nature of the material was confirmed by electric conductivity studies.

Introduction

A **pencil** is a writing implement or an art medium usually constructed of a narrow, solid pigment core inside a protective casing. The case prevents the core from breaking, and also from marking the user's hand during use. Pencils create marks via physical abrasion, leaving behind a trail of solid core material that adheres to a sheet of paper or other surface. They are noticeably distinct from pens, which dispense liquid or gel ink that stain the light color of the paper.

In England, pencils continued to be made from whole sawn graphite. Henry Bessemer's first successful invention (1838) was a method of compressing graphite powder into solid graphite thus allowing the waste from sawing to be reused pencil manufacturing. The top sequence shows the old method that required pieces of graphite to be cut to size; the lower sequence is the new, current method using rods of graphite and clay "Sir Henry Bessemer".

Pencil lead contains the element carbon in the form (allotrope) of graphite. The powdered graphite is mixed with a clay binder. Most of the pencil cores are made up of graphite mixed with a clay binder, leaving grey or black marks that can be easily erased. Graphite pencils are used for both writing and drawing ***(ie..."B" for black and "H" for hard***). Pencils graded using this system is used to measure the hardness and resistance of varnishes and paints. The resistance of a coating (also known as its pencil hardness) is determined as the grade of the hardest pencil that does not mark the coating when pressed firmly against it at a 45 degree angle.

Now a day there are different types of pencil are available in the market. Namely the graphite pencils, Solid graphite pencils, Charcoal pencils, Carbon pencils, Colored pencils, Grease pencils, Watercolor pencils, Stenographer's pencil and Golf pencil. Pencil shapes are Triangular, Hexagonal, Round and bendable (flexible plastic).

Graphite is a crystalline solid of black-grey colour with a metallic sheen, whose structure, described by *Hull* *et.al*, corresponds to a stacking of planes of carbon atoms that are bonded to each other by covalent bonds with sp_2 hybridization. Due to its electronic structure, graphite shows a high electrical conductivity. Each year, large volumes of high-purity graphite powders are used worldwide in many applications. These applications include electrochemical storage systems, like batteries and fuel cells, friction materials, carbon brushes for electric motors, refractory, lubricants and iron powder metallurgy. The unique properties of conducting polymers not only provide great scope for their applications but also have led to the development of new models to explain their observed properties, particularly various mechanisms of charge transport. Among different conducting polymers, polyaniline are the most extensively studied material and also known as a P-type semiconductor.

This work has been initiated with a curiosity to investigate the elemental composition and magnetic response of different grades of lead pencils (6B, 2B, HB, 2H, and 5H) that people use in day today life. Interestingly, experimental results landed with a great achievement of observing soft magnetism in lead pencils indicating a wide scope of magnetic tuning for room temperature. The applications of the pencil powder are ferro magnetism, super capacitors and batteries **[1]**.

Experimental Method

Apsara platinum extra dark pencils were purchased from Hindustan Pencil Ltd., Mumbai, India. The lead-graphite core of the pencil was carefully taken out and made into powders using agate mortar and pestle. Subsequently, the collected grained pencil powders are taken for the basic studies.

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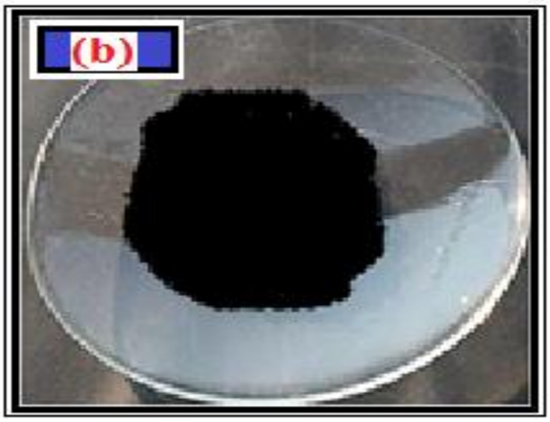


Fig 1 (a) Purchased Apsara pencil (b) Self assembled mechanical mixture pencil powder

Synthesis of PANI/pencil powder

In the process of synthesis, 0.2 M of aniline monomer is added to 100 ml of distilled water, and then 1M of Hydrochloric acid dopent to the above solution and pencil powder is mixed with slowly stirred for 30 minutes. After 15 minutes, Ammonium peroxide sulfate (APS) prepared in 50 ml of di-ionized water is added drop wise for a period of 30 minutes into solution mixture with constant stirring. The polymerization is carried out for 16 hours under constant stirring. Then Polyaniline/pencil powder is filtered out under vacuum condition and washed with methanol, Acetone and distilled water several times to remove the impurities present. The samples are then dried for a day at 60˚C in vacuum oven.

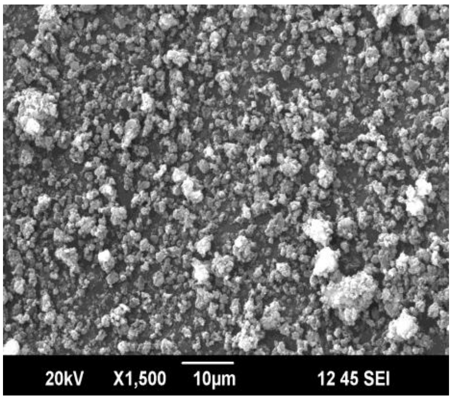
Characterization Techniques

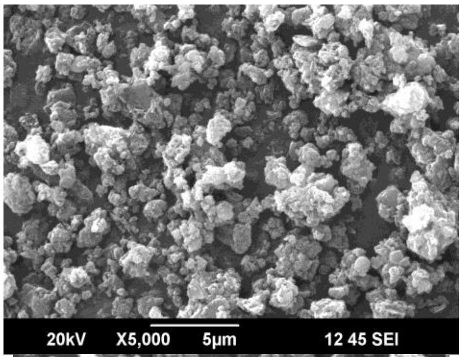
The prepared pencil powder was characterized by UV-vis spectroscopy and FT-IR spectroscopy. FT-IR spectra were recorded using Thermo Nicolet V-200 FT-IR spectrometer by KBr pellet method in the region 400 to 4000 cm^{-1}. Optical absorption spectrum was taken using JASCO V-530 dual beam spectrophotometer in the wavelength region 200 to 800 nm with a scanning speed of 400 nm/min. X-ray diffraction patterns of the coatings were obtained by employing JEOL JDX Services diffractometer using CuKα (Kα =1.54056 Å) radiation. The diffractometer was operated at 40Kv and 50mA. The electrical resistivity measurement for pencil powder was done by using four probe methods.

Result and discussion

Surface Morphology studies (SEM)

AJEOL JSM - 5610 Scanning Electron Microscopy was used to study the surface morphology of Apsara pencil powder prepared by mechanical mixture method.





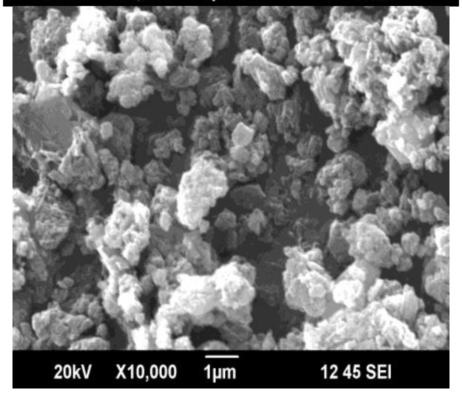
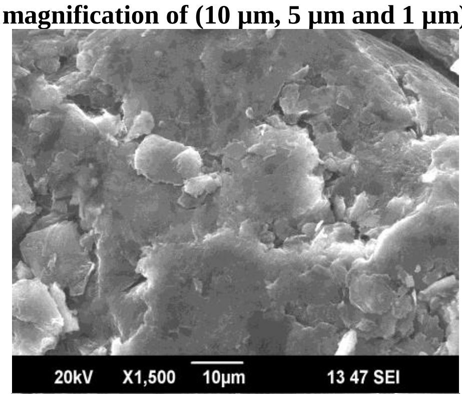
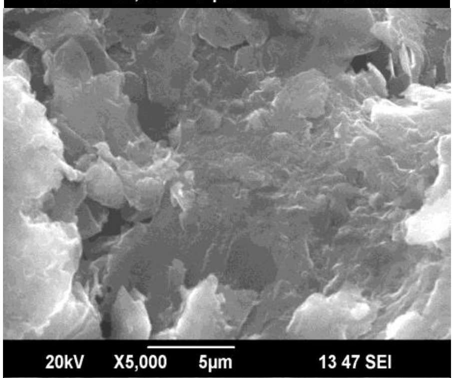


Fig 1. SEM images of pencil powder and different magnification of (10 μm, 5 μm and 1 μm)





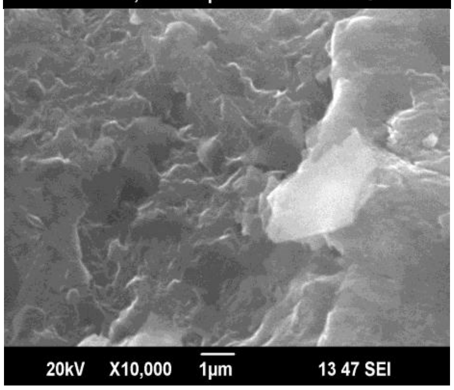


Fig 2. SEM images of Aniline doped pencil powder and different magnification of (10 μm, 5 μm and 1 μm)

Fig 1. (Low magnifications of 1µm) shows a spongy pattern of bulbous microstructure. A few spherical and some clusters were observed in the SEM image (Fig. 1 µm). The composite has mixture of agglomerated and cracking flat thin layers in (Fig. 2). Relatively uniform surface with few scattered granules is observed in the Aniline doped graphite pencil samples in different magnification (fig 2) **[8].** The defects in the chain owing to mobility of the charge carries on easily move **[2]**.

Energy-dispersive x-ray spectro-scopy analysis (EDAX)

The composition of the powder were investigated using an energy dispersive analysis by X-ray EDAX set up attached with scanning electron microscopy. The EDAX spectra of the prepared samples were recorded in the binding energy 0-10 KeV as shown in Fig 3& 4

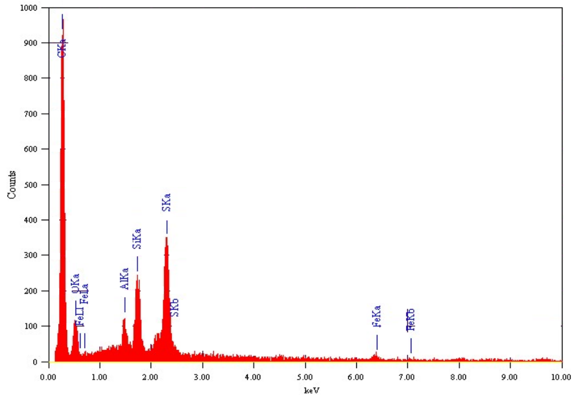


Fig 3. EDAX Spectrum of pencil powder

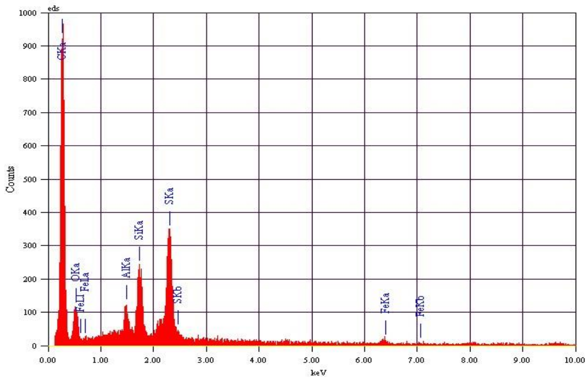


Fig 4. EDAX Spectrum of ANILINE + APP

EDAX results show (Fig 3&4) that the composition C, Si, O, Al, Fe is found for the major elements of lead pencils elements in the prepared samples (in table 1 &2).

Table 1: Presence of Elements Mass % and Atom % Apasara pencil powder

Element	(keV)	Mass%	Atom%	K
C K	0.277	76.63	88.37	1
O K	0.525	3.07	2.65	0.3805
Al K	1.486	1.89	0.97	0.2878
Si K	1.739	5.17	2.55	0.292
S K	2.307	11.82	5.11	0.3582
Fe K	6.398	1.42	0.35	0.8958
Total		100	100	

Table 2: Presence of Elements Mass % and Atom % of Aniline +APP

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The basic information is that iron (Fe) concentration decreases, where as the Silicon (Si) and Oxygen (O) increases with the increase of Clay content in graphite. A significant amount of Fe (Iron) and Al (Aluminum) is also noted and their concentration increases with the increase of clay content. The (Aniline + APP) EDAX results were depicted in (tab 1 & 2)The basic trend of varying the elemental composition of graphite (Carbon) and clay in lead pencils is identical in both XRD and EDX**[1]**.

X - ray diffraction pattern of Apsara pencil

X-ray diffraction patterns of pencil powder were recorded using an X-ray diffractometer with CuKα radiation (λ=1.54A˚). Fig 5. Shows a peak around 2θ= 26˚ and 55˚ reveals the crystalline nature of the lead pencils powder. The XRD spectra of pencils (e.g., 6B, HB, 5H) matched to hexagonal crystal structure with space group of standard graphite. The'd' spacing values are mentioned in the fig 5. The impurity phase of clay in graphite matrix of the lead pencil was within the back ground when intensity of the spectrum was plotted in linear scale **[3]**.

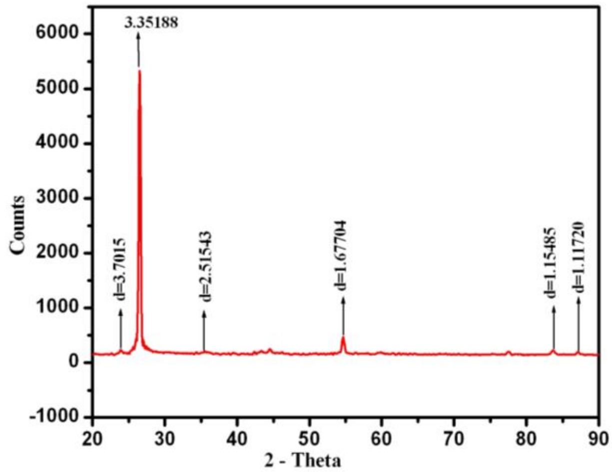

Fig 5. XRD pattern of apsara Pencil powder

FT-IR Spectrum

The FT-IR spectra of the prepared the samples were recorded between the ranges 400 to 4000 cm^{-1} using thermo Nicolet V-200 FT-IR Spectrometer.

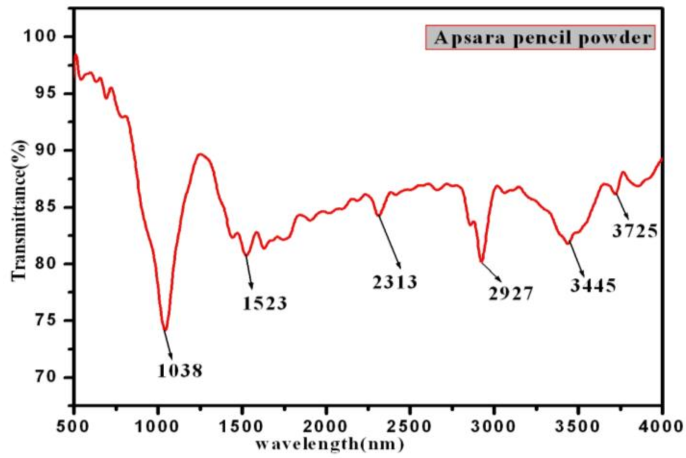

Fig. 6 FTIR Spectrum of apsara Pencil powder

FT-IR spectra indicate in the (fig 6.) shows the peaks at 691, 1038, 1523, 2313, 2927, 3445 and 3725 cm^{-1}, respectively. The characteristic peaks at 676cm^{-1} (S-O stretch) **[4, 5]**, 1038.49 cm^{-1} (N-H in-plane deformation), 1523cm^{-1} were assigned to the C N stretching mode for the quinoid rings **[6]**. It also exhibits distinct peak at 2927 cm^{-1}, which is assigned to the aromatic C-H stretching. The peak at 3445 cm^{-1} assigned to N-H stretching vibrations **[7]**.

UV-VIS absorption spectrum

The UV-visible spectrum of pencil sample was recorded employing Jasco V-530 dual beam spectrometer.

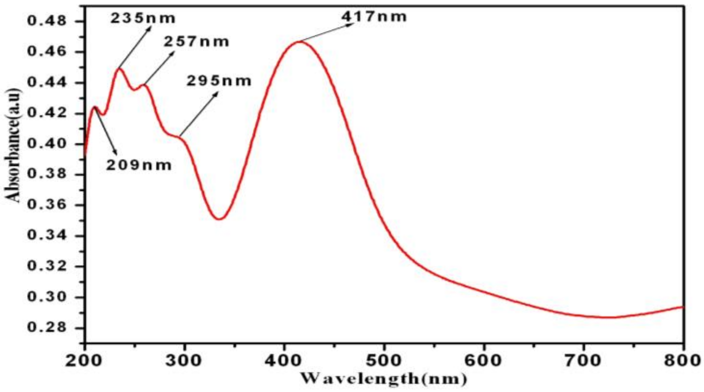

Fig 7. UV-vis Spectrum of apsara Pencil powder

The characteristic absorption band edge of pure pencil particles was observed over the wavelength range from 200 to 800 nm. As shown in Fig 7, the characteristic absorption peaks of the composite were observed at approximately 235, 295 and 417 nm. The peaks were observed at 235 and 295 nm was assigned to the π→π* transition or the exaction transition. The broad absorption bands located at approximately 417 nm should be assigned to the polaron-π* transition from the charged cationic species.

Photoluminescence Spectrum

The PL property of the pencil powder was studied using FP-6500 spectrofluro meter- 67 at room temperature (30°C). Fig 8 shows the two excitation shoulder peaks of the wavelength 330 nm, 391 nm. The broad additional emission peak at 510nm is attributed to green emission. From the PL Studies; the emission spectrum is found to be shifted towards longer wavelengths than the excitation spectrum.

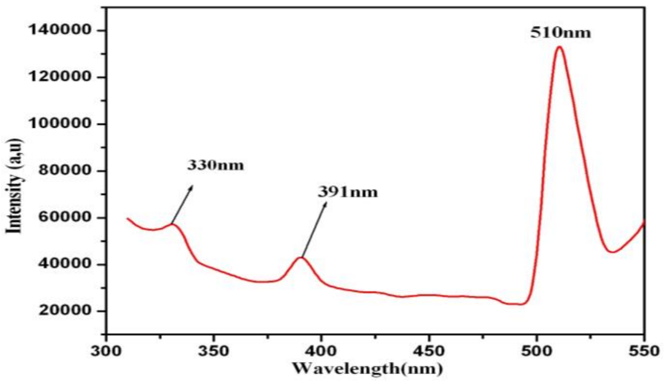

Fig 8. PL Spectrum of apsara Pencil powder

The direct band gap of the powder was calculated by using the formula Eg= hc/λ, where, h is a constant, C is velocity of light and λ is emission wavelength in photoluminescence spectrum. The direct Band gap energy of the pencil powder is found to be 3.74eV, 3.18eV and 2.44eV. Unlike the excitation at 330 nm showed a cumulative effect on the visible PL ranging 510 nm (see figure 8.). The mechanism of the green emission has been suggested to be mainly due to the concentration of free electrons, and the existence of various point defects identified.

Conductivity

The conductivity study of pencil powder was done by using Four Probe Setup (DFP-03). It has four individually spring loaded probes. The probes are collinear and equally spaced. The probes are mounted in a Teflon bush which ensures a good electrical insulation between the probes. A Teflon spacer near the tips is also provided to keep the probes at equal distance. The probe arrangement is mounted in a suitable stand, which also hold, the sample plate. To ensure the correct measurement of sample temperature, the RTD is embedded in the sample plate just below the sample. This stand also serves as the lid of the temperature controlled oven. Proper leads are provided for the current and voltage measurements.

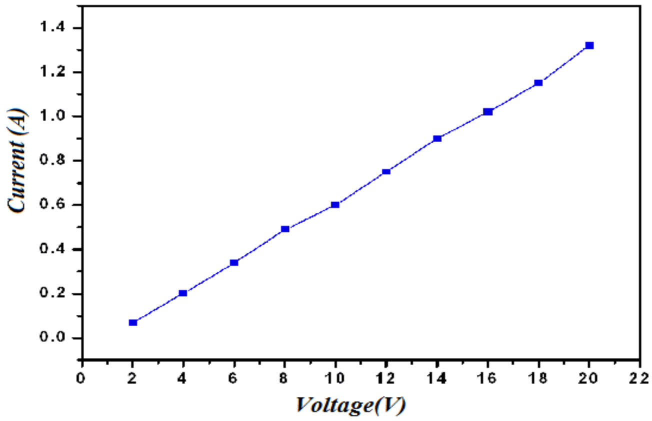

Fig 9. Conductivity measurement of Apsara Pencil powder

Since, potential difference V is proportional to the current I, from the fig. 9 it is concluded that I is linearly there with increase in voltages (V). V and I is a linear behavior for a conductor. Ohm's law holds well only when a steady current flows through a conductor.

Conclusions

Lead graphite-pencils have been associated in our daily life but it could be an easy source for understanding many unexplained properties of graphite based materials. Its ferromagnetic parameters are largely controlled by grain boundary disorder and heterogeneity existing in the material. The PANI/pencil composite has mixture of agglomerated and cracking flat thin layers. The presence of magnetic impurity Fe is acting as the catalyst for further enhancement of soft ferromagnetic parameters with increasing moment. Some of the lead pencils have been identified to be extremely useful component for making magnetic particles. Ohmic nature of the material was confirmed by conductivity studies. PANI/pencil powder is established to this part of the work.

Acknowledgement

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