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Recent Developments in Nano Based Hair Dye Formulations and their Characterizations

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ABSTRACT:

The recent developments in nanoscience and nanotechnology have opened up new possibilities for permanent dye hair applications. Since 2000, a lot of reports are coming on the synthesis of nano-based hair dye formulations. Mainly, three strategies are involved in the synthesis of nano-based hair dyes: (i) Nanoparticle based hair dyes, (ii) Graphene and carbon nanotube-based hair dyes and (iii) Melanin biomimicking based hair dyes. Nanoparticle based dyes, due to their increased surface area, can penetrate well into hair follicles. There are reports of gold, silica and PbS nano particle-based hair dye formulations, but their potential commercial application as hair dyes is limited due to various factors like multiple synthesis steps, time needed for developing color and low color fastness.Even though, graphene based hair dye is promising, the color range is limited. Development of hair dye formulations by biomimicking melanine synthesis by chemoenzymatic methods has recently received attention by the scientific community.Considerable amount of work has so far been carried out with polydopamine (one of the synthetic eumelanines) based multicolor systems for hair dyeing.

Keywords: Nanoparticle, melanine, biomimicking, hair dyes.

INTRODUCTION:

Hair is an important part of human body. It is an indicator of culture and ethnicity and also it protects our outer body. As people's interest to stay youth and beautiful increasing day by day, hair dyeing has become part and parcel of both men and women. According to a report published during Covid-19 crisis, the global hair color market is estimated to reach a revised size of US$36.1 Billion by 2027[1].Based on their chemistry, hair dyes are classified in to: oxidative (permanent and demi permanent) and non oxidative (semi-permanent and temporary) [2-4].Main components of oxidative hair dyes are oxidizing agent like H_2O_2[5-8], aromatic primary intermediates like para-phenylenediamine(PPD), para-toluenediamine(PTD), orthoaminophenol, and para-aminophenol [8-12] and coupling agents like m-aminophenols, m-hydroxyphenols, or resorcinol along with alkaline agents like ammonia or monoethanolamine [4,12].Small aromatic dye precursors diffuse deeply into the core of hair fibers at an alkaline pH and react with couplers. These alkalizers raises pH, swells the hair cuticle to allow better penetration of dye precursors, and destabilizes hydrogen

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peroxide to liberate oxygen. The released oxygen destroys the hair's natural melanin (i.e., lightens hair) and also oxidizes the dye intermediates and allows them to react with the couplers within the hair shaft to form a colored molecule [12-15].

Permanent hair dyes are the commonly used for dyeing because of greater efficacy of dyeing, resistance to shampoo washes, availability of wide variety of shades, ability to both lighten and darken the hair, entirely cover grey hair and producing a completely new color. However, the hair shaft can undergo oxidative damage with permanent hair dye use. Ancient Greek and Roman civilizations applied nanotechnology in human hair dyeing by growingPbS nanocrystals inside hair fibers giving black color to hair. The recent developments in nanoscience and nanotechnology have opened up new possibilities for permanent dye hair applications. Since 2000, a lot of reports are coming on the synthesis of nano-based hair dye formulations. Mainly, three strategies are involved in the synthesis of nano-based hair dyes: (i) Nanoparticle based hair dyes, (ii) Graphene and carbon nanotube-based hair dyes and (iii) Melanin biomimicking based hair dyes.

HUMAN HAIR STRUCTURE:

Human hair fiberis approximately 30-120 μmin width and consists of four parts- cuticle, cortex, medulla and cell membrane complex. The outer cuticle is the protecting layer which comprises of the outer membrane - epicuticle and the cysteine rich, cross linked exocuticle and the low cysteine endocuticle beneath. Most of the fiber mass is concentrated in the cortex composed of macro fibrils, microfibrils and matrix which contributes the swelling behavior of hair. The central part of the hair fiber is called medulla which comprises of keratin fibrils and is responsible for the shining of hair. Cell membrane complex is made up of cell membranes and binding materials and it opens routes for diffusion of molecules through hair fiber [16,17].

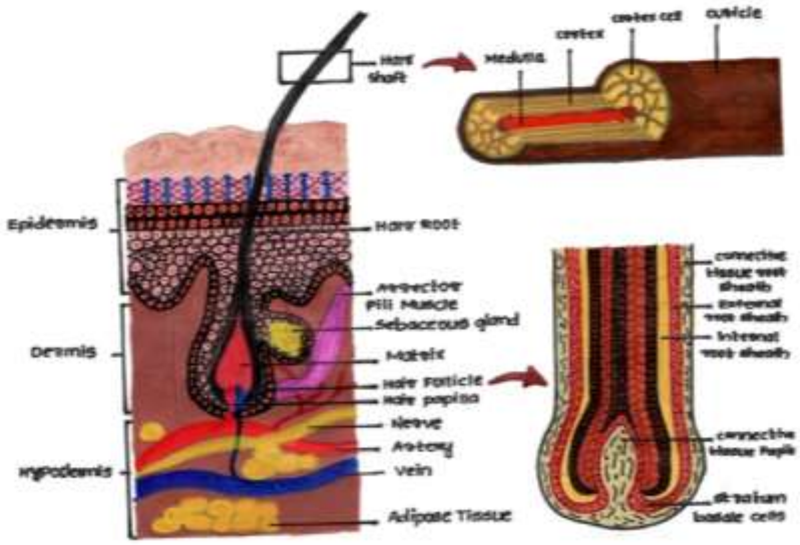

Fig. 1. Human hair structure

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NANOPARTICLE BASED HAIR DYES:

Nanoparticles with a larger surface area can make better contact and interact with hair, resulting in a longer- lasting black color. Nanoparticles, in particular, are well-known for their efficacy in delivering bioactive compounds to the skin and hair. Dye containing nanoparticles, penetrate significantly deeper into hair follicles and are kept in the hair follicles for much longer time.In 2006, the first report on the production and characterization of PbS nanocrystals inside hair, as well as their potential use as a hair dye, was published by Philippe et al. [18]. They used a hair dyeing recipe described in text dating back to Greco-Roman times, which involves mixing PbO, slaked lime and water to form a paste at a pH 12.5.It is then applied to the hair, resulting in the formation of PbS nanocrystals where lead from the paste reacts with Sulphur from the amino acids of keratin. As a result of the creation of PbS inside hair, Pb-based hair coloring chemicals produce a type of melanin substitute.The composition and supramolecular organization of keratins can govern the formation of PbS nanocrystals inside the hair, according to the authors.They were able to verify using X-ray fluorescence spectroscopy and X-ray diffraction experiments that the α-helical coiled structures in keratin proteins were retained followed by the blackening reaction.The three-dimensional distribution of Pb in hair was examined using a scanning confocal electron microscopy and a high-resolution transmission electron microscopy to observe cross sections and longitudinal sections.

S.Sampaio et al have successfully devised a new process for coloring human hair fibers with colored silica nanoparticles of 206 nm size [19].In this study, silica nanoparticles were made by combining an aqueous Telon Red MBL acid dye solution with a conventional sol gel reverse emulsion of sodium metasilicate in ether petroleum.The dye was attached to nanoparticles by using silane crosslinker (3-glycidoxypropyl trimethoxy silane).Transmission Electron Microscopy,Dynamic Light Scattering and Fourier Transform Infrared Spectroscopy were used to characterize the dye on the nanoparticles. The size of colored silica nanoparticles, as well as their dyeing efficacy on hair fibers, were determined using FTIR spectroscopy and TEM. The SEMstudies indicate the presence of silica nanoparticles in the outer portions of the hair structure especially the cortex and the inner layers of the cuticle. The two possible pathways for diffusion of materials through hair fiber are transcellular - applicable for small hydrophilic species and intercellular - mainly applicable for large hydrophobic species. The present study reveals that the preferred pathway for colored silica nanoparticles to diffuse into hair is the intercellular pathway through non- keratinous sections of hair, such as the cell membrane complex.The silica nanoparticles were discovered to be physically entrapped in the hair fibers, with the results indicating good shampoo fastness.

In another work, the cationic groups of *p*-Phenylenediamine (PPD) and the anionic groups of poly(ϒ-glutamic acid)(PGA) were used to make PPD-incorporated nanoparticles [20].Glycol chitosan was added to strengthen PPD/PGA ion complexes.Field emission scanning electron microscopy, FTIR spectroscopy, dynamic light scattering, and Powder X-ray diffractometry

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were used to analyze PPD embedded nanoparticles.Ion complex synthesis between hair color and poly (ϒ-glutamic acid) (PGA)/chitosan was used to make PPD- incorporated nanoparticles. Dynamic light scattering (DLS), Fourier transform infrared (FTIR),Powder X-ray diffractometry (XRD), and field emission scanning electron microscopy were used to investigate the physicochemical features of PPD-incorporated nanoparticles. Furthermore, human skin keratinocyte cells were used to assess the cytotoxicity of PPD incorporated nanoparticles.

The first report of the synthesis of gold nanoparticle (AuNPs) inside human hair involves treating hair fiber with alkaline solution of $HAuCl_4$ at a pH12.5[21]. As a result, a colorshade from golden to brown was produced but it took almost two weeks for the development of the color. With the help of Scanning Transmission Electron Microscopy (STEM) and Energy Disperse X-ray Spectroscopy (EDS), the authors were able to locate AuNPs in the cuticle and cortex of treated hair.Higher density of gold was present in the outer cuticle than the inner cortex. Based on spectroscopic evidences, they claim that AuNP is formed in situ inside the hair by the reducing action of amino acids, especially cysteine on $HAuCl_4$. Even though the authors claim that the color is stable for repeated shampoo washings, the prosperous application of this nanoparticle for hair dyeing is limited since it involves strong alkaline medium which may be harmful to hair fiber.

The encapsulation of dyes into nanoscale tubular containers assembled on hair has achieved good results [22,23].In another work, melanin extracted from cuttlefish ink was encapsulated in tiny lipid capsules for hair delivery via micro-needling inside the follicles, thus darkening grey hair. [24].

Para phenylene diamine (PPD) incorporated hyaluronic acid (HA) spherical nanoparticles with 300 nm sizeas potential candidates for new permanent hair dyeswere generated by ion-complex formation between the amine group of PPD and carboxy group of HA [25]. Because HA is an anionic polysaccharide, cationic dyes, such as PPD, may react with it and create nanoparticles.PPD can form ionic complexes with PGA and glycol chitosan, and this combination can generate nanoparticles that act as permanent hair dye carriers, according to the authors.Furthermore, a powder- X-ray diffractogram (XRD) analysis showed that the intrinsic crystalline peak of PPD was lost as a result of the synthesis of nanoparticles with HA nanoparticles.In a drug release trial, increased PPD concentrations resulted in a faster nanoparticle release rate. At MTT and apoptosis assays, PPD-incorporated nanoparticles demonstrated lower intrinsic toxicity against HaCaT human keratinocyte cells.

Recently, a hair dyeing solution was devised, that can be used for the hair blackening, inspired by iron gall ink, which has been utilized since Middle Ages [26].The formulation’s components, such as tannic acid, gallic acid, and iron, have all been certified as cosmetic ingredients (D-gluconate). The formulation doesn’t need any toxic oxidizing agents like hydrogen peroxide because the Fe(II) cations attached to tannins are oxidized spontaneously

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when exposed to air, forming a blackish Fe(III)- tannin nanocomplex that coats hair securely.On the exposure of sunlight for at least 3 months as well as after shampoo washing, dyed hair colorhave not diminished, according to the study.This natural blackening of hair mixture has the potential to have a big influence in the cosmetics business.The utilization of the Fe(II) – tannin complex as a precursor for nanomaterial-based hair dyeing was investigated in this study, and it was found to be superior to the traditional, direct synthesis of Fe(III)-tannin complex.The authors also discovered that L-ascorbic acid (vitamin C) helped with black hair coloring.The addition of L-ascorbic acid (1mM) to the formulation enhanced efficiency, though quantities more than 1mM reduced dyeing effectiveness, most likely because to its antioxidizing, inhibitory action on the oxidation of Fe(II) to Fe(III).

GRAPHENE AND CARBON NANOTUBE BASED HAIR DYES:

There are reports of dyeing hair black using carbon nanotube surface coating, which not only eliminates the use of toxic organic dyes but also sustain brushing and washing [27-29]. Recently, water-based graphene dyes have been reported as potential candidate for generating brown to black and gradient colors to hair [30]. They reduced graphene oxide with ascorbic acid and the colorant, reduced graphene oxide (r-GO) was dispersed in chitosan gel which serves as a binder. The dye formulation was characterized by UV, SEM and AFM spectroscopic methods. The authors claim that the formulation is safe, can be applied either by spraying or combing and the procedure is fast and does not need any pretreatment. Moreover, the performance studies indicates that this dye formulation is comparable to permanent hair dyes and it improves the antistatic and heat dissipation properties of hair.

The potential use of nanotubes loaded with medications or dyes for coloringand as a coating for hair care has been proposedin another work [31]. Chemically modified carbon nanotube (CNT) dispersions especially peptide-based CNT colorants find application in dyeing grey hair to black color, but they there is concern over their toxicological effect [32,33]. In this context, less toxic and comparatively cheaper Halloysite clay nanotube (HNT) is a competent substitute for CNT.The potential application of HNT based self - assembly for hair dyeing is explored in a recent study [34]. They loaded 2- hydroxyl-1,4- naphthoquinone (lawsone), the main coloring component of henna extract(*Lawsoniainermis*) into the nanotube and resulted in brown hue when applied on grey hair.Clay nanotube can be loaded with water soluble dyes or dyes in organic solvents and once the formulation is complete, the colored nano pigment is applied from aqueous dispersions [35,36].

MELANIN BIOMIMICKING BASED HAIR DYES:

Melanin is a natural biomaterial widely distributed in the animal and plant kingdom from microorganisms to higher species [37,38] and as the very name suggests (melanos, Greek word means black), these are pigments [39]. Besides, they find diverse applications including free radical quenching, UV protection and thermal regulation [40].The pigment melanin

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present as granules of nanometer size in the cortex and medulla, imparts color to hair [41]. Melanocytes, the pigment producing cells produce two types of melanin, viz, eumelanin- the major component with spherical structure which is brown to black colored and the rod shaped pheomelanin with color varying from blonde to red [42].With ageing, the tyrosinase activity which is necessary for melanogenesis decreases and hair starts greying. Recently, three more variants of melanin-allomelanin, pyomelaninand neuromelanin have been identified [43]. Melanin may be natural (in vivo) or synthetic (in vitro), depending on its method of generation. Even though the properties of natural and synthetic melanin are similar, they differ widely in their structures [44].

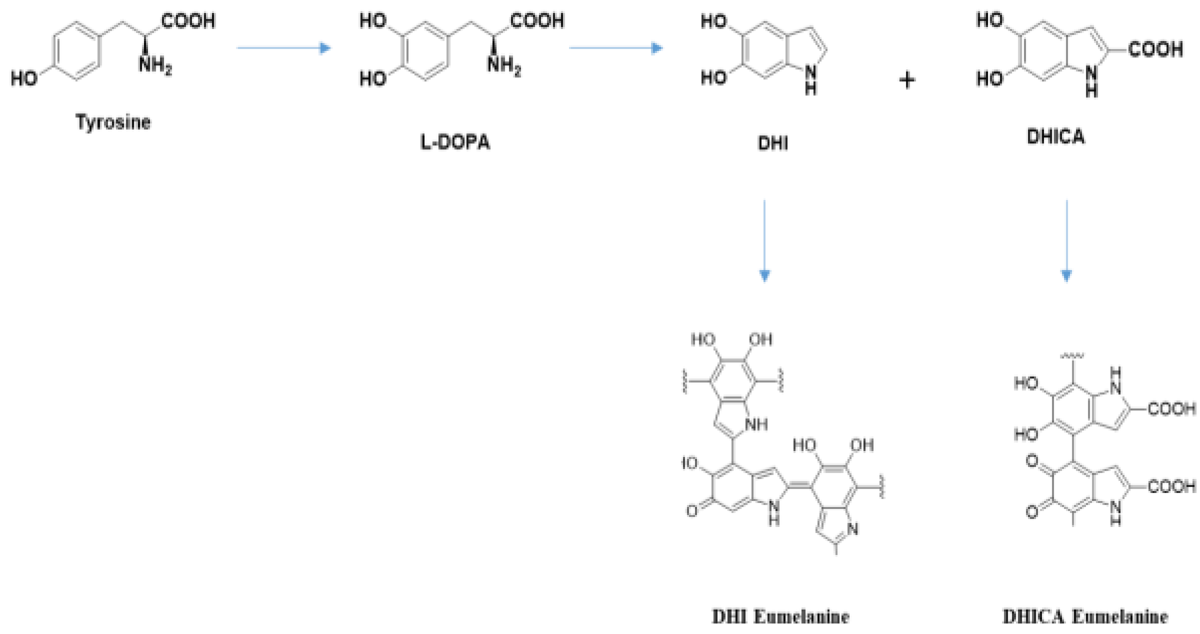

Fig.2. Biosynthetic pathway of eumelanin synthesis

Eumelanin biosynthesis starts with tyrosine which on hydroxylation in presence of the enzyme tyrosinase, first gets converted into 3,4- dihydroxy phenyl alanine, DOPA and on further oxidation to dopaquinone. Dopaquinone on a series of reactions, gets converted into indolequi none which on oxidative polymerization, eumelanin is formed. The intermediate compounds formed includes 5,6-dihydroxyindole-2-carboxylic acid (DHICA) and 5,6-dihydroxyindole (DHI).Synthetic eumelanin includes polydopamine, polydopa, poly DHI and poly DHICA. Biosynthesis of pheomelanin starts with condensation between dopaquinone and sulphur containing amino acid, cysteine followed by enzymatic oxidation and polymerisation leading to a polymeric structure composed mainly of benzothiazine and tetrahydroisoquinoline units.

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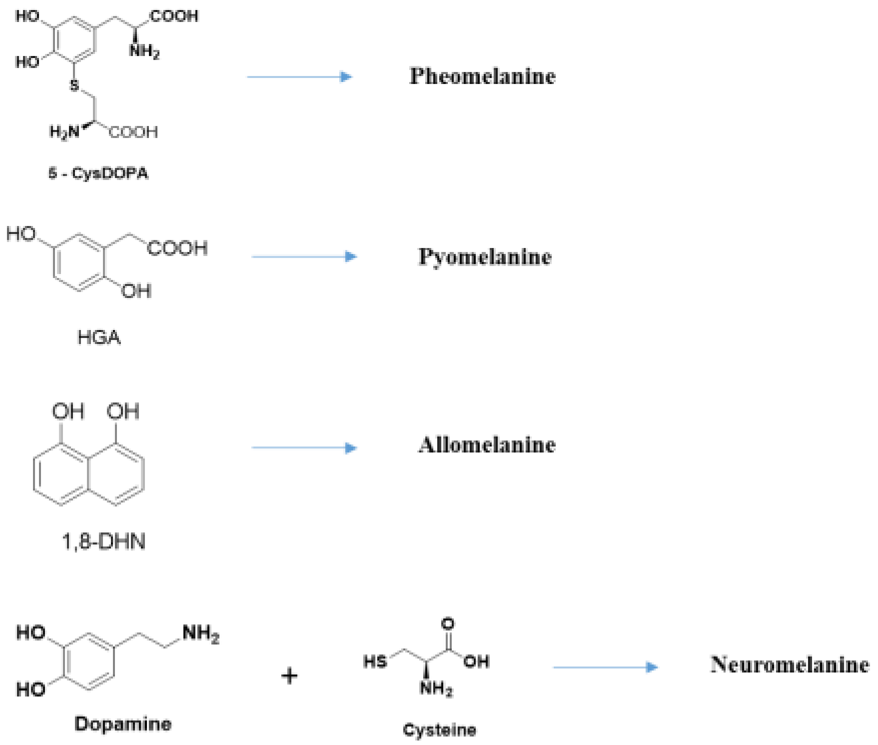

Fig.3: Precursors of melanin biosynthesis

Poly dopa -cysteine resembles pheomelanine. Neuromelanin, synthesized in brain is believed to be made up of indole and benzothiazine units and is related to neurodegenerative diseases [45]. Polydopamine- cysteine and polydopamine- lysine are synthetic variants of neuromelanine. Another type of natural melanin is allomelanin of plant origin, consists of 1,8- dihydroxy naphthalene (DHN) and catechol.PolyDHN resembles allomelanin. Allomelanin and pyomelanin are nitrogen free melanins mainly found in fungi and bacteria. Pyomelaninoriginates from the catabolic activity of tyrosine and phenyl alanine and is believed to be derived from the monomer, homogentisic acid (HGA). Melanin structure is not yet fully understood due to various factors like presence of extensive crosslinking which leads to complex structures,their poor solubility insolvents, wide variety of starting materials for synthesis etc.

There are recent reports of biomimicking melanin synthesis inside hair which opens up a new era in the hair dye synthesis. Polydopamine, eumelanin derived from dopamine precursor, has recently attracted the attention of scientific community due to the ease of synthesis, monodispersity and tailoring of particle size [46,47]. There are reports of imitating biosynthesis of eumelanin using other precursors like tyrosine, DOPA and its soluble esters, DHI, DHICA, epinephrine, norepinephrine etc.[48-55] but a systematic study of comparison of the resulting eumelanin structures is yet to come.There are large number of reports of developing structural colors using polydopamine [56-63]to produce brown, black to blonde color but the pigment formed disperses throughout the hair rather than deposition of granules

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which limits the efficiency of natural process [64,65].Even though, polydopamine is regarded as a biomimetic of eumelanin, recent spectroscopic evidences, especially EPR studies point out that polydopamine is rich in DHI whereas natural eumelanin mainly consists of DHICA units.

Synthetic pheomelanin is made by the oxidative polymerization of DOPA and cysteine using enzymes like tyrosinase, catalase or oxidizing agents like $KMnO_4$ in presence of catalyst like zinc ions [66-70]. There are reports of neuromelanin synthesis by the oxidative polymerization of dopaminewith cysteine and lysine [71-73]. DHN is used as the precursor for the synthesis of allomelanin [74]. Both chemoenzymatic method involving the enzyme laccase and chemical methods using oxidizing agents like $KMnO_4$ and $NaIO_4$ are reported for the synthesis of allomelanin [75,76]. There are recent reports of synthesis of pyomelanin like pigments by the autoxidation of homogentisic acid in alkaline medium [77,78].

Table 1: Synthetic variants of different types of melanins

Synthetic Melanins	
Name	**Variants**
Eumelanin	polydopamine, polydopa, poly5,6-dihydroxyindole (DHI),poly5,6dihydroxyindole-2-carboxylic acid (DHICA)
Pheomelanin	poly dopa -cysteine
Neuromelanin	polydopamine- cysteine and polydopamine- lysine
Allomelanin	Poly1,8-dihydro naphthalene (DHN)
Pyomelanin	homogentisic acid (HGA)

Synthetic melaninshas tunable colors and remarkable properties like UV visible absorption, free radical quenching, antioxidant capacity etc. It is biocompatible and nontoxic which are added qualities for using them as a dye. The first report of using polydopamine based hair dyeing formulation came in 2017 by Im et al [79]. They synthesized polydopamine by the oxidative polymerization of dopamine hydrochloride in presence of tris HCl buffer and grey hair was dipped in this formulation with different metal ions such as ferrous ion, ferric ion, Cu^{2+} and Al^{3+} ions for one hour. It was observed that polydopamine-ferrous ion system produced black coloration to grey hair and the color varied with metal ions suggesting the formation of different chromophore structures. Based on EPR, SEM and IRspectroscopic evidence, the authors confirmed the formation of ferrous ion cross links which binds polydopamine units with each other and also with keratin surface of hair. Another work demonstrated that the heat dissipation properties of hair enhance on polydopamine surface coating [80].

In a recent work, the fabrication of synthetic melanin based multicolor dyes with color ranges from red, brown to black is discussed [81]. The dye formulation was prepared by the

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oxidative polymerization of dopamine and dopamine - cysteine mixture with sodium periodate yielding eumelanin with brown to black color and pheomelanin with red hue. By varying the thickness of the surface coating, time of coating and the composition of the starting compounds, the desired color can be fabricated in a fast and non toxic method and the authors claim that this surface coating is comparable to permanent dyes in their UV protection and color fastness. The biomimetic melanin coating was characterized by SEM, ATR- FT IR and XPS techniques and the multicolor effects is attributed to change in absorption properties with conversion of hydroxyl groups of dopamine to carbonyl and carboxyl groups in polydopamine during oxidative polymerization.

In another recent work, C. Battistella et al developed a mild and efficient method of dyeing hair to give brown, black and even golden shades by the self oxidation of dopamine in mild alkaline conditions which is comparable to commercial hair dyes [82]. Golden orange color was developed in presence of minute amount of hydrogen peroxide. This not only eliminates the use of metal chelating agents and harsh oxidizing conditions but also the synthesis takes place at ambient temperature and the color developed resembles natural hair color. Morphological analysis of dyed hair using TEM, SEM and ATR-FTIR clearly indicates the presence of polydopamine nanoparticle on the surface of hair.

Most dyeing processes are carried out under alkaline conditions because the cuticle swells under this condition leading to higher penetration of the dye into inner layers and it may cause damage to the hair shaft. In an interesting work, C. Battistella et al adopted chemoenzymatic method to mimic melanin biosynthesis by the action of the enzyme tyrosinase on L-tyrosine under neutral pH condition [83]. Through a series of oxidative steps, they were able to synthesize brown to black eumelanin like artificial melanin. In addition to impartingcolor, they were found to act as UV screens for hair. Spectroscopic studies revealed that melanin was distributed as nanoparticle as well as elongated deposits and are mainly concentrated on the surface of hair rather than penetrating into the cuticle, thus causing less harm to hair.

Tyrosine hydroxylase catalyzed polymerization of dopamine hydrochloride in presence of metal ions at room temperature resulted in eumelanin like nano assemblies and their potential application as hair dye is discussed in a recent report [84]. The enzyme catalyzed process was so fast that the dyeing process could be completed within 5 minutes. Different metal ions were employed as chelating agents and better dyeing efficiency was achieved with Fe^{3+} ions compared to Fe^{2+} and Cu^{2+} ions, preferably due to higher oxidizing and coordinating capacity of ferric ion. Morphological studies using TEM and SEM points out the presence of rice shaped polydopamine nanoparticles on the surface of hair which closely resembles natural eumelanin. Even though, this enzyme assisted protocol of melanin synthesis is taking place under mild conditions without using strong oxidizing agents or alkali, multicolor dyeing cannot be achieved.

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CONCLUSIONS:

Nano based hair dye formulations are promising candidates for hair dyeing applications due to their increased surface area, effective penetration into hair follicles and comparatively less toxicological effects. A lot of research is going on in developing and marketing nanobased hair dyes. Commercial application of nanoparticle and graphene based hair dyes are limited due to many reasons which include multiple steps involved in synthesis, time taken for developing color and limited range of colors.Melanin biomimicking is a recent innovative method for making hair dye formulations. There are reports of synthesis of polydopamine based hair formulations with varying color shades by chemoenzymatic methods involving mild reaction conditions. The dying efficiency is comparable to permanent dyes and the dying process is less time consuming. Amongst the five known melanins, considerable work has been done only with polydopamine based eumelaninfor developing color. The potential application of melanin biomimicking synthesis for other variants of melanin and their characterization is yet to be explored.

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