Preparation and Characterizations of Nanomaterial by Pulsed Laser Ablation in Liquid (PLAIL) as Friendly Environment Paint

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Abstract. In this research, silver oxide and nickel oxide were prepared as collide using Pulsed Laser Ablation in Liquid (PLAIL) method in the water. In all preparation case, the laser parameters were fixed at optimum conditions (laser energy 600 mJ with frequency 1 Hz at room temperature) and nanomaterial was added in several proportions (2%, 4%, 6%, 8%, 10%, 12%) to the local paint. Physical properties of the nano-collide were studied by Uv-visible spectroscopy, Scanning Electron Microscopy (SEM), Atomic Force Microscope (AFM), contact angle (CA). A colloid as core-shell (composite materials) was obtained when the two slices were placed together in the water and ablated them by laser. It has shown the best results compared to using its individual Ni or Ag. The local paint was tested in two cases: the first by adding nickel and silver as micro-scale, and in the other in nanoscale to compare which one the best in the self-cleaning. The nanomaterial at a percentage 12% showed the best results when it added to the paint; it for their properties such as adhesion strength and hardness strength, exposure to weather conditions of temperature, and humidity. The adhesive strength increased when adding the nanomaterial from 112 to 139 before exposure to the weather and from 58 to 108 after exposure. The hardness also increased from 77.9 to 86.5 before exposure to the surrounding environment and from 94.2 to 96.8 after exposure.

Introduction

Great efforts have made last year to prepare and investigate nanostructures. Materials with a generally defined nanostructure are solids consisting of structural elements (mostly crystals) whose distinctive size falls in the range of 1 - 100 nm [1] [2]. Nanomaterials are useful in a number of applications in physics, chemistry, engineering, and biology, depending on their size [3]. The control of the shape of metallic nanoparticles has received much attention in recent years due to the strong association between shape and chemical, physical, electronic, optical, magnetic, and catalytic properties of nanoparticles [4] [5]. Incorporation of non-physical substances into these products, such as resins, aerosols, and paints, may reduce the highly toxic additives that are considered hazardous to health. Appropriate anti-corrosion bonds are important in the manufacture of paints, which aim to protect structures prone to chemical or electrochemical corrosion due to pollution and marine atmosphere in populated areas and large coastal areas. Through photo stimulation of immaterial materials as additives, high phobia and self-cleaning ability may reduce surface

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contamination by degrading pollutants, in order to improve the quality and appearance of the structural surface [6].

The mechanism of the photosynthesis process for the decomposition of organic pollution is (accelerate photosynthesis by the presence of a photocatalyst in the process of photosynthesis activity). The catalyst material does not change by itself and is not consumed during chemical reactions. The photocatalytic process of semi-conductive metal oxide describes a process when semiconductor particles such as (NiO, TiO2, ZnO, WO3, etc.) are activated by exposure to visible UV light that suitable for their gap energy scope to stimulate oxidation and reduction reaction on its surface. The basic criterion for the efficiency of the photodiode semiconductor photocatalytic activity mechanism is that [the potential of a charged couple return, i.e. (e - h +), lies in the band gap range of the photocatalysis process]. The energy level at the bottom of the conduction band determines the reduced power of the photoelectrons while the energy level at the top of the valence band determines the oxidizing power of the holes generated by the image [7].

In the past few years, there has been a great deal of work to paint pollution resistant development. As a commercial product, its efficiency is high and its global market. Due to its use in many practical applications, from window panes to glass facades, solar energy systems, cement and pigment on textiles. The paint may become self-cleaning due to the very important economic cost. The self-cleaning paint is classified into two hydrophilic and hydrophobic types [8] [9].

Cleaning water-repellent coatings by wrapping water droplets that carry any dirt, while water-repellent coatings clean with a layer of water to remove dirt from the surface. In 2005, Parken et al. revealed that water-loving coatings are able to destroy organic materials absorbed in sunlight or UV radiation. The main factor distinguishing moisture is the constant contact angle of water, known as the inclination angle at which a drop of water rolls off the surface. The angle of contact with water depends on several factors such as surface energy, surface roughness, and cleanliness. If the liquid moistens the surface (indicated with a moisturizing liquid or a water-loving surface), the value of the water contact angle is 0 ≤ θ ≤ 90°, while if the liquid does not moisten the surface (indicated with a non-wet or hydrophobic liquid the surface) the value of the angle of contact with the water is 90° C and 180° C [10].

Most of the effective physical methods for nanofabrication of material is laser resection, it is a typical example of a top-down approach in the manufacture of nanoparticles, laser resection is the process of removing materials from a solid surface by illumination with a laser beam [11]. It has also been used to prepare nanoparticles: ablation laser is usually applied to in situ element analysis and the formation of a thin layer (pulsed PLD laser deposition). In particular, the temperature and pressure of plasma induced plasma by pulsed laser beams on the surface of a metallic target in a liquid is very high compared to a vacuum or atmosphere due to the confinement effect [12].

In general Ag NP’s are used for a number of applications due to the special electrical and biochemical properties [13] [14]. A large amount of industrial liquid waste contains the main sources of pollutants of synthetic dyes, which are dumped into the environment and lead to serious water pollution [15]. The efficiency of the photocatalytic activity of the decomposition of organic pollutants by semiconducting
metal oxide such as nickel oxide (NiO) is highly efficient since the nickel oxide (NiO) has high transparency considered to be a P-type semi-separator with a wide band gap around \( \sim (3.2 \text{ eV} - 4 \text{ eV}) \) \[1\]. Thin films of nickel oxide (NiO) with high photocatalytic activity, low cost of synthesis and low toxicity, high stability in physical and chemical properties, especially strong ability of highly decomposing organic pollution to non-harmful types such as (CO2, H2O, etc.) considers a promising material for self-cleaning \[7\] \[16\]. Finally, contact angle measurement was used to identify the type of surface if it was hydrophilic or hydrophobic for self-cleaning.

1. Experimental work

1.1. Materials and Methods

1.1.1. Materials. The weight ratio of chemical materials to prepare the local paint is shown in the in table (1).

| Chemical material       | Weight ratio % |
|------------------------|----------------|
| Alkyd resin            | 55             |
| Sliver-Nickel oxide    | 12             |
| Calcium carbonate      | 12.5           |
| Benton                 | 3              |
| Oil                    | 14.6           |
| Cobalt dryer           | 0.6            |
| Lead dryer             | 0.4            |
| Calcium dryer          | 1.2            |
| Oily grinding assistant| 0.5            |
| Anti-flake             | 0.2            |

1.1.2. Synthesize mix of Ag with Nickel nanoparticles. The silver oxide and Nickel oxide was obtained by laser ablation method using Nd: YAG laser with a wavelength of 1064 nm, laser energy (600) mJ, (100) pulses, and repetition rate 1 Hz. The laser ablation process was carried out in two cases: one put the target NiO and AgO individually and put them together in the other. In all cases, the target was placed horizontally in a glass baker filling with 2ml of distilled water; the laser beam was focused on metal targets with spot sizes of (1.2) mm. The target was a high purity (99.9%) AgO and NiO metal plate (1x1) cm, which was placed horizontally into a baker, and the plate of nickel and silver was submerged in DIW (2) cm above the AgO and NiO, total distilled water (30) ml with no surfactants was used as a medium, which was agitated by a magnetic stirrer during the experiments.
1.1.3. Preparation of local paint. The alkyd resin is weighed, then addition the oily grinding assistant and mixed well. The pigment is added to the alkyd resin, so it will be nano or microparticles. Calcium carbonate and Benton are added respectively, to the mixture and mix well after each addition. The mixture was left one day to moisturize the solids well with alkyd resin. On the second day, the solvents, dryers, and anti-flakes are added to the mixture and mixed them well after each addition.

1.1.4. The nickel-silver colloidal mixture with a percentage of 12% was added to the dye and mixes them well until become homogeneous by the magnetic mixer. And then the composite materials were mixed with a local paint, and pour the resulting mixture on the plates made of iron dimensions of 10 cm * 5 cm and left for a whole day till the dye dried up. Several assays were made including the hardness, paste, and color degree examination such as whiteness, brightness, and exposure to weather conditions (heat and moisture) to accelerate weather conditions impacts.

2. Results and Discussion

2.1. UV-visible spectrophotometer analysis of AgO NPs, NiO NPs and AgO-NiO nanocomposite

UV-Vis Spectrophotometer was used to study the absorption and Transmission spectra of the prepared samples in the wavelength ranging from 500-800 nm. Figure 1a shows the optical absorption spectra of AgO NPs, NiO NPs, and AgO-NiO nanocomposite as a function of wavelength. The absorption peak for NiO ranging between 510-520 nm refer to a high ratio of NiO nanoparticles as compared with AgO NPs and AgO-NiO nanocomposite. Figure 1b illustrates the Transmission of AgO, NiO, and AgO-NiO as a function of wavelength. It shows that silver oxide is higher than nickel oxide which is close to the transmission of the silver-nickel as a mixture.

2.2. SEM analysis of AgO NP’s, NiO NP’s, and AgO-NiO Nnocomposite

SEM images of the prepared AgO NPs, NiO NPs, and AgO-NiO Ncomposite was shown in Figure 2 a, b and c. All the images at the same magnification (at the same bar scale 200nm) which can give characterize the shape and size of prepared samples. Figure 2a shows particles in a spherical shape and uniformly distributed with the grain size equals 19.83 nm of AgO NPs which contains several nanoparticles with an
average size of about 15nm. Figure 2b shows a uniform distribution of NiO NPs; have a spherical shape with a grain size of 23.71nm, and an average particle size of 20nm. While the mixture of AgO and NiO core-shell as (composite materials) display a different shape; has a cubic shape and with average grain size larger than 30.91nm as shown in figure 2c.

2.3. **AFM analysis of AgO NPs, NiO NPs and AgO-NiO Nanocomposite**

The surface topology of the synthesized AgO, NiO, and AgO mixed with NiO nanoparticles in water distilled were studied by atomic force microscope (AFM) analysis as shown in figure 3 a, b, and c. It shows the top view of the surface for AgO, NiO, and AgO-NiO nanoparticles, with scan area (2×2) μm², respectively. For all synthesized samples, the results showed a uniform surface and indicated that the surfaces have a root mean square (RMS) or average roughness is equal to 30 nm. And also, can be measured the grain size of the samples by granularity cumulating distribution chart to be (63.42) nm for AgO and (54.93) nm for NiO as shown in figure 4a& b, while it increased the grain size of particles into (72.88) nm for AgO-NiO when mixing them together as shown in figure 4c.
Figure 3 a,b&c AFM images of the top view of the surface for a. AgO NPs, b. NiO NPs and c. AgO-NiO Nanocomposite. All samples prepared in distilled water.
3. Evaluate nanomaterial with paint

3.1. Adhesion

The bond strength of paint with nano AgO-NiO Nanocomposite was significantly higher than the paint with AgO-NiO micro for both cases, before exposure to weather condition (Ultraviolet, sun, and moisture) and after exposure to weather condition. The interface quality and adhesion strength at the interface determine the load transfer between the matrix and the nano-padding [16]. This improvement with nanoparticle content is listed in Table 2, and this is a positive result that can be attributed to the enhancement of good dispersion development and high compatibility between the coating and the nano-pre-phenotype. The importance of adhesion, the ability of a coating to resist removal from the applied surface, is self-evident [16].

| Sample          | Before exposure (psi) | After exposure (psi) |
|-----------------|-----------------------|----------------------|
| Paint with micro| 112                   | 58                   |
| Paint with nano | 139                   | 108                  |

3.2. Hardness test (shore B)

Known coating hardness and ability to resist permanent indentation and scratching, cutting, and penetration by a hard object [17]. There are different methods of assessing yield hardness for different results because they measure different types of materials. Figure 5 showed the improvement in hardness of the paint with nano AgO-NiO, as a result of excellent interaction between AgO-NiO nanoparticles with paint matrix. Besides good dispersion of particles, leading to an increase in the surface area of the filler. Based on these results, the mechanical properties of nanocomposites can be altered by various factors such as properties of the matrix, filler particle size, and morphology, particle loading and distribution, interfacial adhesion between filler particles and matrix [18]. Figure 6 shows increase the hardness values for both paint with nano and micro after exposure to weather conditions.
3.3. Contact angle results

When the contact angle increases to more than 90° from the contact surface, the surface is hydrophobic but is hydrophilic when it is less than 90°. In both cases, the surface is once unable to self-cleaning, but it has another possible benefit. That a complete photocatalyst works and has the ability to absorb pollutants and return them to nature, useful substances such as water and carbon dioxide. And once more, it is self-cleaning [19]. In our work with the presence of sunlight ultraviolet radiation, moisture and AgO-NiO nanoparticle convert surface contact angle from the hydrophilic surface to the super hydrophilic surface for paint with micro AgO-NiO. Here, was a decrease in contact angle after exposure to weather conditions for both types (paint with nano and paint with micro), resulting in making the surface hydrophilicity. Hydrophilicity depends on both the surface roughness and the chemical composition [19]. The hydrophilic surface is excellent for self-cleaning. With increasing surface energy as shown in figure7. The wet surface be beneficial for enhanced application, e.g. in the in self-cleaning which agrees with the reference [20].
4. Conclusions

The silver and nickel oxide nanoparticles mixture prepared by the pulsed laser ablation in the water gave good results. When adding it to the local dye when conducting several dye tests, including adhesive and hardness and contact angle. Examined the dye before it was exposed to weather conditions and after exposure in a micro-form once and in a nano, in the other, the adhesion strength and hardness increased with adding the nanomaterial.

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