Pitch-Black Nanostructured Copper Oxide as an Alternative to Carbon Black for Autonomous Environments

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Light detection and ranging (LiDAR) systems are becoming crucial for measuring the distance and creating a point cloud of the local environment, critical data for artificial intelligence to enable collision-avoidance mechanisms. However, LiDAR utilizes radiation in the near-infrared (NIR) region of the electromagnetic spectrum, which is prone to complete absorption by typical dark (such as painted by carbon black) colored objects, leading to loss of timely data points. Till date a very limited number of solutions have been put forward to address this. Herein, nanocrystallites of copper (II) oxide with specific prevalence of crystal facets that create nearly perfect black material at visible wavelengths are proposed. The sharp transition of absorbance near 700 nm wavelength light is attributed to the near-unity ratio of (−111)/(111) the crystal facets and a crystal size of around 100 Å for the (−111) plane. Although indistinguishable from carbon black and with the same degree of measured blackness (M, value 135.5), the nanocrystalline CuO shows 1500% better detectability by LiDAR. The study paves the way for the unconstrained use of dark objects in future society and infrastructure, moving a step closer toward fully autonomous operation of vehicles and robots.

1. Introduction

In the near future, self-driving cars and robots are set to heavily rely on a continuous stream of data and information originated from reflection of light detection and ranging (LiDAR) laser readings of distance from other objects to safely navigate in an autonomous environment[1] In recent years, despite the development of this core mobility technology on the aspects of electronic architecture and algorithms,[2] it is still challenging for LiDAR sensors to detect dark-tone objects, such as black vehicles, infrastructure, and pedestrians in its way.[3,4] This is because commercial LiDAR technology utilizes near-infrared (NIR) laser of around 905 nm, which is completely absorbed by the standard carbon black material used in paint. Even other colors such as dark gray, dark red, and blue hues are rendered using a significant amount of carbon black material or other absorptive materials, resulting in reduced detection by LiDAR sensors to an unsafe level.[4] The inability to detect another object may result in compromised mapping of the autonomous vehicle’s environment.

One approach to address this challenge is to leverage LiDAR-detectable black coatings using stacking paint layers; e.g., LiDAR-transparent black perylene is sprayed as base coat on top of a white reflective primer layer.[5] This approach requires an unconventional painting application process and complicated paint system design, which is not suitable for applications in all scenarios. Consequently, there is a need for a durable and inexpensive carbon-black-like earth-abundant material that perfectly absorbs the visible wavelength of light yet stays reflective at the LiDAR wavelength. Such a material should also be easily integrable into a standard painting process with little or no alteration. To that end, a class of complex inorganic materials based on mixed metal oxides such as chromium iron oxides, chromium green-black hematite, and chromium iron nickel black spinel, also known as “cool black” pigments, are common materials that show high absorption in visible light yet reflect near-NIR light.[5] However, these products are not considered “pure” black material in the paint industry as they show shades of blue or brown attributed to their crystallite phases.[7] Therefore, new materials with a combination of nearly 100% absorption in the visible spectrum yet high reflectivity at NIR wavelengths are an important attribute for both esthetics and safety requirements in autonomous environments (Figure 1a).

Toward this, materials with bandgap energy near the LiDAR detection wavelength (905 nm) or 1.37 eV and sharp transition at the visible edge (700 nm) are promising candidates. Cupric (II) oxide (CuO) is a monochromatic p-type semiconductor with a fundamental bandgap of indirect nature.[8] The experimental values of its indirect bandgap lie in the range of 1.2–2.2 eV.[9,10] CuO compounds are studied widely in areas such as solar energy materials,[10–13] gas sensors,[14] magnetic media,[15] optical devices,[16] batteries,[17] and catalysts[18,19] as well as constructing junction devices and superconducting materials.[19,20] It has also been emphasized that the bandgap of CuO is tunable by means of different approaches such as dopants, synthesis solvent and stoichiometry, nanoparticle size, and the shape of the...
most of the bandgap-engineering studies of CuO focus on optimum optical response to solar radiation and its catalytic behavior, however, ways to tailor its near full absorption in the visible and reflection in the NIR range remain limited. There have been efforts to improve the blackness of CuO by physically tailoring the particle size via ball milling or other techniques. However, by these means CuO could not reach the blackness level of carbon black.

In this study, we report synthesis of a type of nanocrystalline CuO particle (denoted as N2–CuO–A) as a replacement for carbon black that show superior blackness in the visible region while keeping high infrared reflectivity. The N–CuO–A was synthesized via the scalable precipitation–pyrolysis route, with proper selection in precipitating agents at a certain concentration range, followed by a well-defined sintering process. Structural and chemical composition studies show the evolution from precursor to extracted precipitates, and to final nanocrystalline CuO particles at various process stages. Here, we identified two key indicators in X-ray diffraction (XRD) spectra to guide the experimental conditions toward the desired crystal structure and resultant optical contrast in both the visible and NIR range. Painted panels prepared by incorporating N–CuO–A particles in a paint medium confirmed the blackness behavior and LiDAR-sensing operation in comparison to carbon black.

2. Results and Discussion

As shown in Figure 1b, with limited alternation in the current coating structure, N–CuO–A particles can be used as pigment directly dispersed in the base coat resin between the primer and protective clearcoat in a vehicle. The incident visible light will penetrate through the transparent clearcoat usually made of polyurethane or acrylic polymers and get fully absorbed by the N–CuO–A particles underneath in the base coat, while NIR light will be reflected from the surface of the N–CuO–A particles to the LiDAR sensor. Figure 1c shows photographic images of the nanostructured N–CuO–A particles in comparison to commercial carbon black particles (MONARCH900 carbon black, Cabot Corporation, USA) under visible light (top) and NIR light around 850 nm (bottom). N–CuO–A particles appear the same as carbon black visibly, yet show highly reflective properties in the NIR region.

The reflectance behavior of the four different samples is shown in Figure 2a, namely 1) the synthesized N–CuO–A particles as well as the morphology. At present, most of the bandgap-engineering studies of CuO focus on optimum optical response to solar radiation and its catalytic behavior, however, ways to tailor its near full absorption in the visible and reflection in the NIR range remain limited. There have been efforts to improve the blackness of CuO by physically tailoring the particle size via ball milling or other techniques. However, by these means CuO could not reach the blackness level of carbon black.
Figure 2. a) UV−vis−NIR reflection spectra of paints incorporated with carbon black, commercial “cool black” pigments, commercial CuO nanocrystals (N−CuO−C), and N−CuO−A particles (this study), respectively. The gray dotted line indicates the use of a LiDAR laser at 905 nm wavelength. b) Blackness $M_y$ value of paints incorporated with carbon black, commercial “cool black,” commercial N−CuO−C, and N−CuO−A pigment, respectively. The insert photo reveals the blackness difference of these four samples. c) SEM image of N−CuO−A pigments (scale bar: 10 μm). The insert figure shows a magnified image (scale bar: 1 μm). Both show that the morphology the N−CuO−A sample is that of a well-defined spherical particle with a diameter of ≈3 μm with a rough surface. d) XRD profiles of N−CuO−A, N−CuO−B, and commercial N−CuO−C. Planes of (−111) and (111) are the major planes for analysis as they have the highest peak intensity. e) Evaluation map of samples using the following two indicators: crystallite size of (−111) and relative intensity ratio of (−111)/(111). Both are obtained from the XRD spectra. The insert shows raw particle samples, from left to right, N−CuO−A, N−CuO−B, and commercial N−CuO−C, respectively. f) High-resolution transmission electron microscope image of N−CuO−A (scale bar: 5 nm). The bottom-right insert is the zoom-out figure of the N−CuO−A sample (scale bar: 2 μm). The TEM figure demonstrates crystalline lattice features in the N−CuO−A sample. The top insert is the SAED pattern recorded from an area containing a large number of nanoparticles of N−CuO−A. g) High-resolution transmission electron microscope image of N−CuO−B (scale bar: 5 nm). The bottom-right insert is the zoom-out figure of the N−CuO−B sample (scale bar: 1 μm). The top insert is the SAED pattern recorded from an area containing a large number of nanowires of N−CuO−B. h) XRD spectra of the obtained precipitates from different precipitate agents, in comparison to the references of pure CuCO$_3$. CuCO$_3$.Cu(OH)$_2$, and Cu(OH)$_2$. The material synthesized using the Na$_2$CO$_3$ precipitating agent exhibited similar reflections to CuCO$_3$.Cu(OH)$_2$, whereas the material synthesized using the NaOH precipitating agent exhibited reflections similar to neither CuCO$_3$ or Cu(OH)$_2$. Instead, it shows similar peaks to CuO.
(this study), 2) commercial nanostructured CuO pigments produced by thermal treatment of minerals (denoted as "N–CuO–C"), 3) chromium iron oxide based NIR reflective black pigments HEUCODUR HD 910 obtained from Heucotech LTD (denoted as "cool black"), and 4) MONARCH900 carbon black from Cabot Corporation (denoted as "carbon black"). It clearly shows the paint sample incorporated with the synthesized N–CuO–A particles offers an elegant black color with nearly full absorption in visible light, which is similar to carbon black but retains NIR reflectivity with the maximum peak close to 905 nm. The measure of blackness is also confirmed by blackness $M_b$ with a value as high as 135.5 (Figure 2b), where $M_b$ is a measure of the degree of blackness used widely in the paint industry that directly relates to the reference provided by the instrument (see the Experimental Section).\(^{[25]}\) Comparatively, a paint containing carbon black exhibits very low reflectivity (less than 1%) throughout the visible and NIR wavelength, resulting in a high blackness value of around 135. Paints with commercial CuO have higher NIR reflectivity selectively between 900 and 1000 nm, but they show distinguishable reflection in the visible wavelength, particularly in red hue, resulting in the appearance of an obvious brownish tone, with a blackness value less than 130. In contrast, the “cool black” sample shows strong reflection at the deeper end of the NIR spectra greater than 905 nm yet does not sufficiently absorb in the visible wavelengths, with a blackness value of 128. The insert photo in Figure 2b reveals the difference in blackness of these raw pigment samples, which agrees well with the reflectance spectra in visible range as paint samples (Figure 2a). The scanning electron microscopy (SEM) image of the N–CuO–A particles reveals a hierarchical morphology comprising well-defined spherical agglomerates in a diameter of ≈1–3 μm with rough nanotops in tens of nanometers on its surface (insert figure) (Figure 2c).

To understand the origin of the significantly higher blackness and NIR reflection in N–CuO–A, we compared different CuO particles obtained from the precursor Cu(NO$_3$)$_2$ with different alkaline bases generally used, namely, a weak base Na$_2$CO$_3$ for N–CuO–A and a strong base NaOH for the other CuO particles (denoted as N–CuO–B), following the same sintering conditions in a conventional oven (300 °C for 3 h). Commercial nanostructured CuO (N–CuO–C) was used as reference. Figure 2d shows XRD profiles of these nanostructured CuO samples. It reveals that all the samples are pure cupric (II) oxide with a monoclinic structure, and approximately correspond with JCPDS No. 03-065-2309. The diffraction peaks at 2θ values of 33.5, 35.5, 38.2, 48.7, 54.2, 58.3, 62.5, 66.4, 68.2, 73.4, and 75.6° are observed for all of the samples, which correspond respectively to the lattice planes of (110), (–111), (111), (–112), (–202), (020), (202), (–113), (220), (311), and (–222). Among those planes, the intensity of the (–111) and (111) peaks is much stronger than those of other peaks, which indicates the preferred orientation of the formed nanocrystals along these directions. No peaks of impurity phases such as Cu$_2$O were detected. The relatively broad XRD peaks in N–CuO–A and N–CuO–B indicate that the size of crystals in both N–CuO–A and N–CuO–B is relatively small (≈100 Å) under the provided sintering conditions. Comparatively, the XRD profile of N–CuO–C shows much narrower and sharper peaks, indicating larger crystallite sizes (204 Å). Although N–CuO–A and N–CuO–B have similar crystallite sizes, a close look at the XRD spectra reveals that the relative intensity ratios between the two major lattice planes (–111) and (111) in N–CuO–A and N–CuO–B are significantly different. As shown in Figure 3a, N–CuO–A shows a relatively smaller ratio of (–111)/(111) than N–CuO–B. According to the calculated potential of the low-index surfaces of CuO using the density functional theory (DFT) method,\(^{[26]}\) the (111) plane has a valence band maximum (VBM) edge near 1.2 eV (or ≈1030 nm) with a bandgap energy of 1.5 eV, while (–111) plane has a slightly larger VBM around 2.1 eV (or ≈620 nm) with a slightly larger bandgap energy of 1.6 eV. Accordingly, visual observation indicates that the (–111) plane is the major cause for the visible reflection as it starts from a larger VBM around 620 nm. Therefore, the smaller ratio of (–111)/(111) or the smaller crystallite size of the (–111) plane would potentially lead to a higher blackness level, while a larger ratio and crystallite size would benefit NIR reflectivity. As shown in Figure 2e, N–CuO–A has the lowest ratio and smallest crystallite size, and it has the highest level of blackness but relatively weaker NIR reflectivity (left sample in the insert). Samples that have either larger crystallite size (e.g., N–CuO–C) (right sample in the insert) or a relatively higher ratio of (–111)/(111) (e.g., N–CuO–B) show brownish color (middle sample in the insert). The NIR reflections in these two samples are higher due to the dominant (–111) plane (N–CuO–B) or the larger average crystallite size of the (–111) plane (N–CuO–C). This phenomenon has been found consistently in a series of experiments we have performed. Therefore, we concluded that these are two key indicators for experimental guidance, the ratio of (–111)/(111) planes in the crystalline phases and the average crystallite size of the resultant CuO nanocrystals. We found that maintaining a balance of the ratio around 1 and the crystallite size of (–111) around 100 Å are critical for achieving LiDAR reflectivity and visual blackness.

Figure 2f,g are high-resolution transmission electron microscopy (HR-TEM) images taken from synthesized N–CuO–A and N–CuO–B that reveal their dissimilarity in both agglomerates and smaller crystallites. N–CuO–A shows microspherical agglomerates made of connected nanospheres in a diameter of tens of nanometers (bottom insert of Figure 2f), while N–CuO–B is composed of nanorod-like aggregates in a width of tens of nanometers and length of 1 μm (bottom insert of Figure 2g). For N–CuO–A, several interplanar spacings in the primary N–CuO–A crystallites are indexed as 0.239, 0.250, and 0.234 Å, corresponding to the (111), (–111), and (200) planes, respectively (Figure 2f). The relative equal intensity ratio of (–111)/(111) is almost unity as specified by the XRD profile, which agrees with the observation of a few diffraction spots with relatively similar brightness in the selected-area electron diffraction (SAED) pattern (top insert of Figure 2f). In contrast, intensified spots in the SEAD pattern are observed in the case of N–CuO–B, which agrees with the relatively higher ratio of (–111)/(111) in the XRD profile, indicating a preferential orientation of the nanocrystals (Figure 2g). One of the dominant planes was indexed as the (–111) plane that contributes to the higher intensity of both the NIR and the undesired visible reflectivity. Nanocrystals of similar orientations are easy to connect and grow together; the aggregating rate at one preferred direction is...
faster than along other directions, leading to the formation of CuO nanorods in the case of N─CuO─B.

The evolution of the crystal structure and size was also studied, from the precursors to the extracted precipitates, and the final product N─CuO─A obtained after sintering. First, for comparison, different precipitating agents NaOH and Na$_2$CO$_3$ at a constant Cu/Na molar ratio of 0.65 were used. The XRD profiles of the extracted precipitates that formed right after precipitation from the solution prior to the sintering step are shown in Figure 2h. The XRD profiles of the pure chemicals Cu(OH)$_2$, CuCO$_3$, and malachite CuCO$_3$.Cu(OH)$_2$ as references are also presented. The precipitates were obtained by simple mixing rather than titration. The possible reactions involved, when Na$_2$CO$_3$ was used, are listed from reaction (1) to (4), where reaction (2) and (4) will lead to the formation of CuO. The extracted precipitate using Na$_2$CO$_3$ shows a lime-green color in the air and exhibits similar XRD peaks as the reference CuCO$_3$.Cu(OH)$_2$ with main peaks at 32°, which mainly follows reaction (1), whereas no peaks of CuCO$_3$ can be identified. Sintering at higher temperature is required for the malachite to become CuO according to reaction (2). In contrast, the extracted precipitate obtained using NaOH shows a brownish-black color, which exhibits similar XRD profiles as the final product N─CuO─B in Figure 2d. These characterizations confirm that the precipitation using NaOH follows reactions (5) and (6) in aqueous phase rather than reaction (7) in solid phase. Copper hydroxide Cu(OH)$_2$ is known to be metastable and it easily transforms into a more stable form copper (II) oxide. The kinetics of transformation to copper (II) oxide can be performed slowly in pure water at room temperature,\textsuperscript{[27]} but in the presence of hydroxide ions OH$^-$ in our case, it turns fast because the divalent copper ions are easily dissolved in the form of tetrahydroxocuprate (II) anions Cu(OH)$_4^{2-}$, followed by the precipitation of CuO in reaction (6).\textsuperscript{[27]} Here, the formation of CuO with the (−111) plane as the preferred growth plane was identified by XRD, which leads to high NIR reflectivity but visually brownish (Figure 2h). The subsequent sintering process at 300 °C would not reverse the ratio between the (−111) and (111) planes or change the growth direction, but rather increase the size of crystalline planes (Figure 2h).

$$\text{Cu}^{2+}_{(aq)} + \text{CO}_3^{2-}_{(aq)} + \text{H}_2\text{O} \rightarrow \text{CuCO}_3.\text{Cu(OH)}_2(s) + \text{CO}_2(g) \quad (1)$$

$$\text{CuCO}_3.\text{Cu(OH)}_2(s) \rightarrow 2\text{CuO} (s) + \text{CO}_2(g) + \text{H}_2\text{O} (g) \quad (2)$$

$$\text{Cu}^{2+}_{(aq)} + \text{CO}_3^{2-}_{(aq)} \rightarrow \text{CuCO}_3(s) \quad (3)$$

Figure 3. a) Demonstration setup using robot car equipped with 2D laser scanner at 905 nm, mimicking an autonomous driving car. The laser scanner is capable of sensing 360° and collects a set of data around the robot to use for SLAM and navigation. Tested paint panels were placed at the same angle and distance in front of the autonomous robot car each time. The insert shows the front-side view of the N─CuO─A-painted panel. b) Comparison of LiDAR intensity obtained by the robot car at 8° from painted panels incorporated with carbon black, N─CuO─A, N─CuO─B, commercial N─CuO─C, and cool black pigments, respectively. c) Demonstration of the robot car hitting the carbon-black-based painted panel with the threshold of LiDAR intensity set as 100. d) Demonstration of the robot car stopping in front of the painted panel incorporated with N─CuO─A pigment with the threshold of LiDAR intensity set as 100.
CuCO$_3$$_{(s)}$ → CuO$_{(s)}$ + CO$_2$$_{(g)}$  \hspace{1cm} (4)

Cu$^{2+}$$_{(aq)}$ + 2OH$^-$_{(aq)} → Cu(OH)$_2$$_{(s)}$  \hspace{1cm} (5)

Cu(OH)$_2$$_{(s)}$ + 2OH$^-$_{(aq)} → Cu(OH)$_2$$_{(aq)}$ + OH$^-$_{(aq)}$ + CuO$_{(s)}$ + H$_2$O  \hspace{1cm} (6)

Cu(OH)$_2$$_{(s)}$ → CuO$_{(s)}$ + H$_2$O$_{(g)}$  \hspace{1cm} (7)

In the case of using the Na$_2$CO$_3$ precipitating agent, in the synthesis step, the extracted precipitate is identified as CuCO$_3$$_{(s)}$. Cu(OH)$_2$$_{(s)}$. Thermogravimetry analysis (TGA) was used to assess the pyrolysis process of converting CuCO$_3$$_{(s)}$. Cu(OH)$_2$$_{(s)}$ to N–CuO–A. The mass loss of water and carbon dioxide separately generated from reaction (2) can be determined by TGA, as well as the critical temperature when the conversion starts. Here, the obtained CuCO$_3$$_{(s)}$. Cu(OH)$_2$$_{(s)}$ was sintered from ambient temperature to 600°C in the air via TGA. A major weight loss of malachite during the pyrolysis process was observed between 200 and 300°C due to the release of H$_2$O and CO$_2$. Visual observation indicates the malachite turns from the original lime-green color to orange color at about 200°C, then to jet-black color at 300°C, and to slightly brownish at higher temperatures. It is known that synthetic malachite decomposes thermally in a single step, which was also confirmed by the single-peak differential thermogravimetry (DTG). The DTG curve was generated as the first derivative of the weight with respect to ramping temperature (Figure S1b, Supporting Information)\(^{[28]}\). It became stable at around 300°C and above, as evident from the TGA analysis (Figure S1a, Supporting Information).

These measurements show that the decomposition of CuCO$_3$$_{(s)}$. Cu(OH)$_2$$_{(s)}$ into CuO mainly happened between 250 and 300°C, where significant weight change happens. The weight-loss value of 28.1% in total at 300°C indicates that the molar ratio of CuCO$_3$ to Cu(OH)$_2$ is nearly unity, which further confirms the formation of pure malachite rather than CuCO$_3$ or Cu(OH)$_2$. Further increase in the annealing temperature above 300°C would lead to negligible weight loss but growth of CuO crystallites (Figure S1a, Supporting Information). In contrast, the relative intensity of (111)/(−111) reduced significantly before 300°C during conversion from malachite to CuO and then became stable afterward. At 300°C, CuO particles synthesized from Na$_2$CO$_3$ (N–CuO–A) at the Cu/Na molar ratio of 0.65 have the highest blackness compared with their counterparts at higher sintering temperatures or commercial N–CuO–C (Figure S2a, Supporting Information), which agrees with the conclusion from Figure 2e. The representative SEM images reveal that the materials sintered at higher temperature maintain their size of spherical agglomerate shape in the same range of 1−3 μm, but the nanosized particles become more interconnected in the microspheres with nanoscale holes at a higher sintering temperature therefore their surface area decreases (Figure S2b, Supporting Information). Hence, the crystalline size of the nanocrystals, rather than the size of microspherical agglomerates, has the main impact on the optical properties, which show a consistent increase in visible reflection with increasing crystalline size. The observation of the growth of the crystal at higher sintering temperatures, with a decrease in surface area, was also reported by other researchers,\(^{[29,30]}\) which can be explained by the reduction in the numbers of vacancies of oxygen, vacancy clusters, and local lattice disorder along with crystal growth. Therefore, this superior blackness at smaller crystalline size may be attributed to the higher crystallographic disorder just at the completion of the conversion from malachite to CuO. Therefore, it is necessary to anneal malachite-originated CuO nanoparticles at the conversion temperature of 300°C and not higher.

With the same precipitate agent Na$_2$CO$_3$ but at different molar ratios of Cu/Na (or level of carbonate concentration), it is possible to change the nucleation growth route\(^{[31]}\) and to follow the other route via reaction (3) and (4) with CuCO$_3$ as the extracted precipitate. For this purpose, a series of samples was prepared by varying the Cu/Na molar ratio from 1.52 (carbonate deficiency) to 0.36 (carbonate surplus). The XRD profiles of the extracted precipitates with varying Cu/Na molar ratios formed prior to the sintering process are displayed in Figure S3, Supporting Information. The extracted precipitate samples with Cu/Na ratio of 1.52 and 0.82 exhibit peaks of CuCO$_3$ with negligible presence of CuCO$_3$. Cu(OH)$_2$. These measurements show that the synthesis of CuO at higher Cu/Na ratios (1.52–0.82), which corresponds to carbonate deficiency conditions, mainly follows reaction (3) and (4). The intensity of the CuCO$_3$ peaks decreases with further decrease of the Cu/Na ratio below 0.82 and new peaks of the malachite CuCO$_3$. Cu(OH)$_2$ start to appear. The samples with Cu/Na molar ratio of 0.76 exhibit peaks due to a mixture of CuCO$_3$ and CuCO$_3$. Cu(OH)$_2$, with the latter as the dominant species. The CuCO$_3$ peaks completely diminished for the extracted precipitates with Cu/Na molar ratio less than 0.65 and only pure malachite peaks were observed. There was no significant change in the XRD peaks with further decrease in the Cu/Na molar ratio (or in excess of Na$_2$CO$_3$) and the extracted precipitate materials only exhibit peaks due to CuCO$_3$. Cu(OH)$_2$.

Table S1, Supporting Information, summarizes the XRD profiles of the resultant CuO samples with varying Cu/Na molar ratio, in terms of the crystallite size of the (−111) plane and the intensity ratio of (−111)/(111). The crystallite size of CuO decreases with decreasing Cu/Na molar ratio until 0.53 and further decrease in the Cu/Na molar ratio leads to minimal change in the crystallite size. In contrast, there is no notable change in the (−111)/(111) ratio with changing Cu/Na molar ratio during the synthesis. All the samples exhibit the ratio of (−111)/(111) around 1.00 ± 0.05. SEM images of the CuO samples with varying Cu/Na molar ratio after the sintering are shown in Figure S4, Supporting Information. CuO samples with Cu/Na molar ratios 1.52 and 1.12 exhibits only flower-like morphology with sharp spikes. When the Cu/Na molar ratio decreases to 0.76, a mixture of flower-like morphology and microspheres is observed. At Cu/Na molar ratio between 0.7 to 0.65, the flower-like morphology disappears, and only microspheres are observed. Combined with XRD measurements, we concluded that the level of carbonate concentration would affect the nucleation and growth, as well as the formation of the precipitate. It is also clear that the formation of CuCO$_3$ during the precipitation leads to the irregular flower-like morphology of CuO products, while the formation of CuCO$_3$. Cu(OH)$_2$ malachite tends to result in nearly monodisperse microsphere CuO products. Notably, the samples with Cu/Na molar ratios less than 0.65 exhibit irregular morphologies, even though XRD measurements show that these extracted precipitates are composed of CuCO$_3$. Cu(OH)$_2$. Therefore, it is necessary to anneal malachite-originated CuO nanoparticles at the conversion temperature of 300°C and not higher.
precipitates only exhibit peaks of CuCO$_3$, Cu(OH)$_2$ (Figure S3, Supporting Information). Now the question is, why do final CuO products of Cu/Na molar ratios less and greater than 0.65 exhibit completely different agglomerate morphology? Further XPS measurements reveal that external impurity sodium ions were found in the extracted precipitates with Cu/Na molar ratios less than 0.65. (Figure S5, Supporting Information). Due to the remarkable differences in the size of the radius of Na$^+$ (1.02 Å) and Cu$^{2+}$ (0.73 Å) and in the valence charges, the presence of the external Na$^+$ impurity may affect the growth process of the crystal, leading to the dissimilar irregular morphology as observed in Figure S4, Supporting Information.$^{[23]}$ It is also found that the crystallite size decreases with the presence of a small amount of Na$^+$ (Table S1, Supporting Information).$^{[23]}$

The washing and filtration procedure after the precipitation is the same for all the samples synthesized in this study. Hence, decrease in the Cu/Na molar ratio during the synthesis leads to the presence of Na$^+$ in the CuCO$_3$, Cu(OH)$_2$ precipitate even after the washing and filtration.

Figure S6a, Supporting Information, shows a photographic image of the CuO nanoparticles with varying Cu/Na molar ratios over black and white backgrounds in the same order. As shown on the black background, the visual blackness of powders increases with decreasing Cu/Na molar ratio until 0.7, and then illegible change in the blackness is observed with further decrease in the Cu/Na molar ratio. However, the photo taken using an NIR camera indicates that the NIR reflectivity greatly reduces if the Cu/Na molar ratio reduces to less than 0.65, which implies the adverse effect of the Na$^+$ impurity on the crystal structures and the NIR reflectivity. A painted panel with incorporated CuO nanoparticles is shown in Figure S6b, Supporting Information, and we confirmed that the levels of blackness are the same irrespective of the background color of the substrate. The diffuse reflectance spectra of these paint panels are shown in Figure S6c, Supporting Information, and the corresponding indirect bandgap $\text{Tauc}$ plots based on the Kubelka–Munk function$^{[32]}$ are shown in Figure S6d, Supporting Information; the resultant bandgap values and blackness data are displayed in Figure S6e,f, Supporting Information, respectively. Similar to what was identified in the powder samples, with a decreased Cu/Na ratio, a redshift of the fundamental reflection edge in the prepared CuO paint samples is observed (Figure S6d, Supporting Information). Please note that the indirect bandgap energy of the CuO-painted samples of different Cu/Na ratios shows a significant reduction from 1.4 to 1.3 eV at the critical Cu/Na molar ratio of 0.65 (Figure S6d,e, Supporting Information). The blackness of the panels increases on decreasing the Cu/Na molar ratio from no greater than 130 at ratios between 1.52 and 0.76 to no less than 1.34 when the ratio is between 0.7 and 0.65. Further decrease in the Cu/Na molar ratio leads to a decrease in the blackness (Figure S6d, Supporting Information) as evidence from the brownish edges shown in the painted samples (Figure S6b, Supporting Information). The results indicate the impact of Cu/Na ratios and the impurity on the nucleation process, the formation of extracted precipitates, crystallite sizes, and agglomerate morphologies. It is concluded from both the blackness measurement and the bandgap estimation from the reflectance measurement utilizing Kubelka–Munk analysis that there is a narrow window in the Cu/Na ratio between 0.65 and 0.70 where a combination of pitch blackness and adequate NIR reflectivity can be achieved. However, we have not been able to derive a correlation between visible blackness and bandgap values as seen in Figure S6e, Supporting Information.

It is worth pointing out here that (after reviewing optical properties of over 100 samples) we have not seen evidence that the hierarchical surface features on the CuO nanoparticles (observed in Figure 2c) have played a role in selectively affecting reflectivity in the visible or IR region. However, it is imperative that the nanoscale roughness of the particles may have contributed to the reduction of the overall reflectance throughout the visible and IR regions, causing superior blackness appearance and at the same time reducing the IR reflectivity.$^{[13]}$ Therefore, we believe the crystallographic properties, namely, the ratio of dominant facets and the crystal size in the (−111) plane play a critical role in shaping the optical properties of the N–CuO–A sample.

To validate the LiDAR reflective performance of N–CuO–A synthesized as discussed earlier, a robot car (model TurtleBot 3 Burger) equipped with a 2D laser scanner at 905 nm was used to mimic an autonomous driving car. The laser scanner is capable of sensing 360° and collects a set of data around the robot to use for SLAM (simultaneous localization and mapping) and navigation, as well as performing stop when an obstacle is detected. Figure 3a shows the setup where a paint panel was placed in front of an autonomous robot car each time and the inset figure shows the prepared N–CuO–A-painted panel, which appears identical to carbon black paint. The intensity of the LiDAR sensor reflected by the panel and recorded on the screen, if the distance and angle are fixed, is solely proportional to the reflectivity intensity of the panels at 905 nm. The detected LiDAR intensity values on the sensor were recorded via Bluetooth in Figure 3b when the tested panels were placed in front of the robot car at a fixed distance of 6 in. and a fixed angle (8°). It clearly reveals that the N–CuO–A-painted panels have a significantly higher LiDAR intensity (nearly 1500%) than carbon black panels. Accordingly, the LiDAR reflectivity from the N–CuO–A paint sample is enough for the robot car to detect and perform an automatic "stop," while it would "bump" onto the carbon black panel due to near full absorption in NIR wavelengths (Figure 3c,d, and videos in the Supporting information).

3. Conclusion

Our study demonstrates that nanostructured copper oxide offers an effective solution to replace traditional carbon black pigments in the future autonomous environment. It shows superior blackness in the visible region while keeping IR reflectivity. We have identified that such a high contrast in optical reflectance around the edge of the visible wavelength is attributed to the specific crystal structures of copper oxide, mainly, the ratio of the two main crystallite phases and the crystallite sizes. The synthesis and optimization conditions to achieve such crystal structures are discussed in detail. Furthermore, mimicking autonomous driving test by a LiDAR-equipped robot, performed in the laboratory setting, confirmed that compared to carbon black, nanostructured CuO shows nearly 1500% better sensitivity to avoid a collision. These functional particles allow researchers and
engineers to expand the dark-color portfolios for future vehicles and robotics while still achieving the necessary level of LiDAR radiation detection.

4. Experimental Section

Analytic grade (AR) chemicals, namely, copper (II) nitrate Cu(NO₃)₂, sodium hydroxide (NaOH), and sodium carbonate Na₂CO₃ obtained from Sigma Aldrich, and deionized water, obtained from the laboratory, were used without any further purification.

CuO nanoparticles were synthesized by a coprecipitation method using Na₂CO₃ or NaOH as precipitating agent. In a typical synthesis, the required amount of Cu(NO₃)₂ was dissolved in 300 mL distilled water. Then, a known concentration of Na₂CO₃ or NaOH solution was added dropwise to the Cu(NO₃)₂ solution at room temperature with vigorous stirring. Then, the solution was stirred for 3 h and aged overnight before filtration. After the overnight aging, the precipitate was filtered and washed with 1000 mL of distilled water. The solid products are then dried at 120 °C overnight, followed by sintering from 300 to 600 °C for 3 h with a 5 °C min⁻¹ ramp rate. Further, control experiments were conducted following the same procedure to analyze the effect of base types, Cu/Na molar ratio, and sintering process on the crystal structure and morphology of CuO nanoparticles. Finally, a comparison of morphology and optical properties of these different systems to the representative sample, N=CuO–A, was presented. The crystallographic information of CuO nanoparticles was investigated using powder XRD (Japan Rigaku Miniflex 600) with Cu Kα radiation (λ = 0.1541 nm). The average crystallite size of the prepared particles was estimated from the measured width of their XRD diffraction curves using Scherrer’s formula.[14]

$$\tau = \frac{k\lambda}{\beta \cos \theta}$$  

Here, k is a dimensionless shape factor with a value close to unity. λ represents the wavelength of the X-ray radiation, β is the line broadening at half the maximum intensity (FWHM), and θ is the Bragg’s angle. The morphology and structure were determined by SEM (Japan Jeol JSM-7800FLV) equipped with energy-dispersive spectroscopy (EDS) and HR-TEM. TEM and small-area electron diffraction (SAED) were performed by EAG Laboratory. Samples were prepared by dispersing the powder in alcohol by ultrasonic treatment, positioning a drop onto a copper grid support, and then drying in the air.

For painted samples, if not specified, the CuO nanoparticles were mixed with polyurethane resin at a powder/resin ratio of 1:4 and then applied via a doctor blade with a wet-mixed alcohol by ultrasonic treatment, positioning a drop onto a copper grid support, and then drying in the air. The diffuse reflectance, R_d, of the sample by the relation

$$F(R_d) = (1 - R_m)^2/2R_m$$  

Here, R_m is the absolute value of reflectance and F(R_m) is equivalent to the absorption coefficient. The indirect bandgap of samples was estimated by plotting (F(R∞)hv)½ versus energy. The linear part of the curve was extrapolated to (F(R∞)hv)½ = 0 to obtain the indirect bandgap energy.[15]

The degree of blackness M_y of painted samples was evaluated by an X-Rite Ci7600 benchtop spectrophotometer (USA, X-Rite) that directly related to the reference provided by the instrument.[23]

$$M_y = 100 \log \left( \frac{Y_n}{Y} \right)$$

where Y_n = 100.000 is one of the CIE white point values for D65/10 conditions. Y is one of the CIE tristimulus values for the sample being measured.

X-ray photoelectron spectroscopy (XPS, USA PHI 5000 Versaprobe II) measurement was conducted using the Al Kα line as the excitation source. Charging of the catalyst samples was corrected by setting the binding energy of the adventitious carbon (C 1s) to 284.6 eV. The XPS analysis was performed at ambient temperature, and pressures were typically of the order of 10⁻¹ Torr. Before the analysis, the samples were outgassed under vacuum for 30 min. The TGA measurement (USA Thermal Science TGA Q500) was conducted in air with the test range from 25 to 600 °C and the heating rate was 5 °C min⁻¹. The surface area of CuO nanoparticles was measured by the single-point Brunauer-Emmett-Teller (BET) method through nitrogen adsorption/desorption analysis (3Flex, USA Micromeritics). Before the analyses, the samples were outgassed at 300 °C under vacuum (5 × 10⁻³ Torr) for 2 h.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

autonomous environments, carbon black, nanostructured copper oxide, near-infrared reflectivity, visible black

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[1] a) J. Hecht, Opt. Photonics News 2018, 29, 26; b) S. Royo, M. Ballesta-Garcia, Appl. Sci. 2019, 9, 4093.
[2] a) C. Debeunne, D. Vivet, Sensors 2020, 20, 2068; b) J. Fang, D. Zhou, F. Yan, T. Zhao, F. Zhang, Y. Ma, L. Wang, R. Yang, IEEE Robot. Autom. Lett. 2020, 5, 1931; c) J. Tachella, Y. Altmann, N. Mellado, A. McCarthy, R. Tobin, G. S. Buller, J.-Y. Tourneret, S. McLaughlin, Nat. Commun. 2019, 10, 4984.
[3] P. Hartzell, C. Glennie, K. Biber, S. Khan, ISPRS J. Photogramm. Remote Sens. 2014, 88, 147.
