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ARTICLE

Environment-Dependent Optical Scattering of Cuprous Oxide Microcrystals in Liquid Dispersions and Langmuir-Blodgett Films[†]

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Optical properties of semiconductor materials are important for their broad applications, especially when the materials are nano and micrometer crystals. Here we show that cuprous oxide microcrystals have three extinction peaks in visible-near infrared regions that are environment sensitive. The extinction peaks show linear blue shift with the increase in refractive index of surrounding medium. The environment-dependent sensitivity of extinction spectra can also be observed for cuprous oxide in casting films and Langmuir-Blodgett films. The sensitivity of environment-dependent optical behavior depends on the energy of the extinction peaks. Both experimental work and theoretical calculation on the environment-dependent spectra of cuprous oxide microcrystals provide valuable knowledge on these functional semiconductor materials for various applications.

Introduction

Manipulating the properties of micro- and nanoscale materials has received increasing interests due to their potentials in various applications, such as high-efficiency catalysis,^{1,2} photovoltaics,^{3,4} lithium-ion batteries,^{5,6} ultra-sensitive sensors,^{7,8} and high-performance optic devices.⁹ The study on tuning optical properties, for example, can provide effective approaches in material optimization for desired optical behavior. General strategies of tuning optical properties include tuning the chemical compositions of the materials,^{10,11} changing the structures of the materials,¹² and altering the local environment surrounding the materials.¹³⁻¹⁵ There have been many reports on the optical properties of plasmonic materials which are mainly determined by the surface plasmon resonances of the materials.¹⁶⁻²⁰ These optical properties are highly sensitive to the structures of the materials as well as the dielectric constants of the surrounding media. Similarly, exploring new approaches to tune the optical properties of non-plasmonic materials is critical in designing novel materials with unique optical properties for various optoelectronic applications.

Non-plasmonic materials, such as semiconductor quantum dots,^{10,21} possess tunable optical behaviors in a broad spectral range. Approaches such as changing chemical compositions, doping impurities, and altering the nanostructures are utilized to change the semiconductor materials and thus tune their optical properties. For example, optical variation with reduced particle size was observed on quantum dots due to their size-dependent band gap.²² Nie and coworkers reported the widely tuneable optical properties via varying the composition of alloyed quantum dots.¹⁰ Carbon nanotube wrapped with DNAs also demonstrated structural

dependent optical properties in both experimental studies and theoretical calculations.^{23,24} Besides tuning the optical absorption, altering the scattering can also significantly affect the overall optical behavior of semiconductor materials. For nanomaterials with high refractive index (RI) and/or wavelength-comparable dimensions, optical scattering will be dominated in the overall extinction spectra. Tuning the scattering properties can be extremely important for certain semiconductor materials who have small Bohr exciton radii and hard to make nanoparticles experimentally with a comparable size. As far as we know, there are only few reports on tuning the scattering properties of semiconductor materials.^{25,26}

Cuprous oxide (Cu₂O), a typical p-type semiconductor material with a bulk band gap of 2.2 eV, has been intensively studied due to their potential applications in various areas such as photovoltaics,^{27,28} photocatalysis,²⁹⁻³² surface enhanced Raman scattering,³³⁻³⁶ and gas sensing.^{37,38} The optical properties of Cu₂O play an essential role in most of these applications. Since the Bohr exciton radius of Cu₂O is quite small (~0.7 nm),³⁹ the extinction spectra of Cu₂O particles are dominated by their scattering property when the sizes of particles are comparable to the wavelength of visible light.⁴⁰ There have been intense studies on tuning the scattering properties of Cu₂O particles by manipulating their morphology, orientation, and local environment. For example, Wang and coworkers tailored the scattering responses in visible and near infrared regions by tuning the radii of Cu₂O nanoshells and shell-in-shell structures with a method of Ostwald ripening.^{41,42} However, to the best of our knowledge, there is a lack of systematic study on environment-dependent scattering properties of Cu₂O micro-size particles. In this paper, we systematically study the solvent-dependent optical response of Cu₂O microcrystals via both

experimental approaches and theoretical simulations. Moreover, we investigate the optical behavior of Cu_2O microcrystals in various sizes and states (in dispersions and in thin films). Our study can promote the understanding of the optical response of semiconductor materials and thus advance our knowledge for materials design and device optimization.

Experimental Method

Synthesis and assembly of Cu_2O microcrystals: The Cu_2O microcrystals were synthesized according to a known method reported previously.³⁴ Typically, 0.825 g copper chloride dihydrate (Acros 99 %) was dissolved into 50 mL deionized water under constant stirring. Then, 10 mL solution of NaOH (6.0 mol/L) was added dropwise into the previous solution under different temperature (5°C, 10°C, 16°C, or 22°C) and such precursor mixture with blue precipitate was further continuously stirred for five minutes under controlled temperature. After that, the reaction mixture was heated to 70°C and kept stirring for 30 minutes before the addition of 0.200 g D-glucose powder (Acros). During this process, the precipitate gradually changed its color to brick red, indicating the formation of Cu_2O microcrystals. The reaction was then allowed to naturally cool down to room temperature. The obtained precipitates were centrifuged several times using deionized water and methanol before further processing and characterization. Cu_2O microcrystal dispersions in various organic medium were prepared by dispersing the Cu_2O precipitate with corresponding organics. Drop casting films were prepared by dropping a Cu_2O methanol dispersion onto a clean glass substrate and dry naturally. Cu_2O chloroform dispersion was used here to prepare Langmuir films at the air-water interface on a KSV2000 Langmuir-Blodgett (LB) trough and the Cu_2O LB films were fabricated at 45mN/m with a dipping speed of 1 mm/min.

Characterizations and simulation: Scanning electron microscopy (SEM) and UV-Vis spectroscopy were employed for the inspection of the morphologies and optical properties of Cu_2O microcrystals and their thin films. SEM micrographs were obtained on a Zeiss Supra40VP variable-pressure field-emission SEM. XRD study was conducted on a Rigaku Ultima IV powder X-ray diffractometer. The optical properties of the microcrystals were studied by examining the extinction spectra of colloidal dispersions in a 1 cm-path length quartz cuvette using either a Cary 5000 UV-Vis spectrophotometer or a Cary 50 UV-Vis spectrophotometer. Optical properties of Cu_2O thin films were also measured on these UV-Vis spectrophotometers when glass substrates were used to support the films. The software applied in the simulation studies is so-called metal nanoparticle (MNP) simulator, which is a GUI written by Guido Goldoni in Matlab.⁴³ The MNP, based on the Mie scattering theory, allows simulating the extinction, absorption, and scattering spectra of diverse nano- and micro- scale particles. In our simulation, the shape of Cu_2O microcrystals is simplified as a solid sphere and the size approximation is applied. The approximated diameters of Cu_2O crystals in our calculation are 900, 1300, 1400, 1700 nm, respectively. The organic mediums and their refractive indexes (at 589 nm) used in the work are as follows: methanol (1.328), water (1.332), ethanol (1.362), tetrahydrofuran (THF) (1.407), dichloromethane (1.424), chloroform (1.446), and styrene (1.519).

Results and Discussion

The size and morphologies of Cu_2O microcrystals were investigated using SEM and a typical SEM micrograph is shown in Fig.1a. The as-synthesized Cu_2O microcrystals are in polyhedron shape on the substrate with a uniform size in sub-micrometer scale. Digital photograph (inset) of the Cu_2O microcrystals in methanol dispersion

presents a reddish color, which is quite common for micron sized cuprous oxide particles. The dispersion is reasonably stable and uniform after a general shaking. Actually it is not a long-term stable system and the Cu_2O microcrystals can be precipitated when stored overnight. XRD study on the sample after drying gave a set of strong diffraction peaks that are consistent with the standard card for cuprous oxide powder (Fig. S1). Magnified SEM image (Fig.1b) illustrates that the microcrystals are cuboctahedral structures with the truncated (100) facets. This type of crystal structure is very typical for Cu_2O nano- and microcrystals, as being reported by others.^{44,45} The surface of microcrystals is, in general, clean and flat. The magnified SEM graphs also allow the size measurements for those microcrystals. We found that the average size, as defined by the distance between opposite facets of Cu_2O microcrystals, is around 900 nm. As shown in the inset of Fig. 1b, the size distribution is quite narrow with a standard derivation of 170 nm.

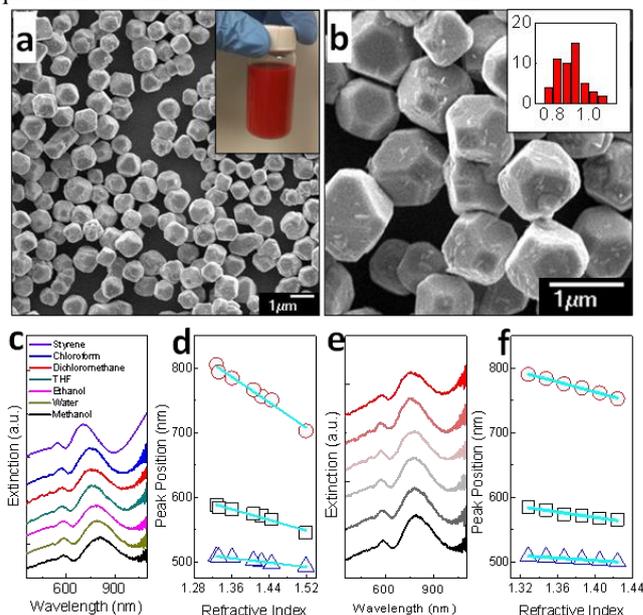


Figure 1. (a) SEM image of as-synthesized Cu_2O microcrystals (precursor at 22°C). Inset: digital photograph of Cu_2O microcrystals dispersed in methanol. (b) Magnified SEM image of Cu_2O microcrystals showing a corner-truncated morphology. Inset: size distribution of the Cu_2O microcrystals. (c) Extinction spectra of Cu_2O microcrystals dispersed in different mediums. (d) Graph of relationship between characteristic peak positions and refractive index of those mediums. (e) Extinction spectra of Cu_2O microcrystals dispersed in mixtures of methanol and dichloromethane. (f) Relationship between characteristic peak positions and refractive index of miscible mixtures.

To explore the environment-dependent optical properties on our material, we here investigated the visible extinction (absorption plus scattering) spectra of Cu_2O microcrystals dispersed in various dispersive mediums with different refractive indices. Centrifugation and re-dispersion processes were used to prepare the colloidal Cu_2O microcrystals dispersed in a variety of mediums: methanol, ethanol, water, THF, dichloromethane, chloroform, and styrene. The visible spectra of these dispersions give extinction curves with a similar shape. Three broad peaks were observed in the extinction spectra with 516 and 595 nm in the visible region and 805 nm in the near infrared (NIR) region, using methanol dispersion as an example. The peak at 805 nm is dominated and has a maximum intensity in the entire spectral region. Those peaks are tentatively assigned to the scattering, rather than the absorption of the cuprous oxide particles. It is believed that those peaks are originated from the phase-retardation effect.^{41,46} When the Cu_2O microcrystals were dispersed in different mediums, the peak positions were progressively shifted (Fig. 1c and Table 1). The extinction peaks of

the Cu_2O microcrystals appear a blue-shift in the spectrum when the crystals are dispersed into a medium with a larger refractive index. The major extinction peak around 800 nm in the NIR region has the most significant blue shift as compared to the other two peaks (around 500 nm and 600 nm). The relationship between the peak positions in the extinction spectra and the refractive indexes of the dispersion mediums was plotted in Fig. 1d. It is clearly demonstrated that blue shifts of extinction peaks for Cu_2O microcrystals occurred in all the mediums tested in our work. Furthermore, highly linear regressions were obtained when fitting the relationship between the peak positions and the refractive indexes. The slope for peaks around 800 nm is the largest among the three slopes and is about 496 nm per refractive index unit (RIU) (same as 2.500 eV/RIU). Our work reveals that the optical extinction of Cu_2O microcrystals is sensitive to their surrounding mediums.

Table 1. Characteristic extinction peak positions of Cu_2O microcrystals in a variety of dispersion medium.

Solvents	Peak wavelength/energy (nm/eV)					
	Peak I	Peak II	Peak III			
Methanol	509	2.436	588	2.109	806	1.538
Water	508	2.441	584	2.123	794	1.562
Ethanol	507	2.446	581	2.134	785	1.580
THF	502	2.470	575	2.156	767	1.617
Dichloromethane	500	2.480	572	2.168	757	1.638
Chloroform	497	2.495	566	2.191	751	1.651
Styrene	493	2.515	545	2.275	703	1.764

The environment-dependent extinction spectra can also be studied using a mixture of two miscible dispersive mediums with a controlled refractive index. We prepared the dispersive medium by mixing methanol and dichloromethane, and various volume ratios were used to precisely adjust the RI ranging from 1.328 to 1.426. In the mixture of methanol and dichloromethane, Cu_2O microcrystals also possess three extinction peaks (Fig. 1e). Similarly, we found that the peak positions appeared blue-shift linearly with the increase of the refractive index for the mixed dispersion (Fig. 1f). Overall, the environment-dependent optical extinctions of Cu_2O crystals are quite similar no matter if the dispersion mediums are individual chemicals or a mixture of mediums with various volume ratios.

To gain further insight into the extinction tunability and their complexity of extinction peaks shift, we conducted theoretical work which can model the absorption, scattering, and extinction spectra of Cu_2O microcrystals in different mediums using Mie scattering theory.⁴⁷ Geometry approximation and size estimation on microcrystals were applied in the theoretical calculation. We assumed that the cuboctahedral Cu_2O microcrystals were symmetrical spheres with the geometry parameters match the microcrystals fabricated in the experiments. The wavelength-dependent empirical dielectric functions of bulk Cu_2O ⁴⁸ was utilized, and the dielectric mediums in the surrounding of the microcrystals were matched with the experimental conditions. The first panel in Fig. 2a shows the calculated extinction spectrum of Cu_2O microcrystals in methanol. The spectrum exhibits multiple peaks in the visible and near-infrared region. The overall line shape and multi-peak feature of the calculated spectrum matched very well with the experimental spectral result. A detail study on splitting the absorption and scattering components in the extinction spectrum revealed that the extinction spectrum is dominated by scattering rather than absorption. Similarly, the extinction spectra of Cu_2O microcrystals in various dispersion mediums were calculated (Fig. 2a) and the domination of scattering was observed in all these theoretical extinction curves.

The overall extinction spectra of Cu_2O microcrystals in different mediums were summarized in Fig. 2b. Similar to our experimental results, the multi-peak feature in theoretical calculation

does not change too much when the microcrystals dispersed in different mediums, except the shift of peak positions. For all the peaks, a progressively red-shift occurred with the increase of RIUs of the dispersion mediums, which is consistent with the experimental results. The Mie scattering theory calculations provided strong evidence in demonstrating the correlation between the optical properties of Cu_2O microcrystals and their environments. We also noticed some discrepancies between the experimental spectra and calculated data, which might be due to the approximations in our calculation such as geometry simplification.

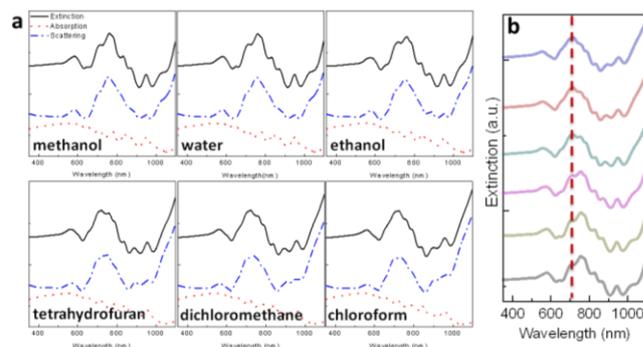


Figure 2. (a) Calculated extinction (absorption + scattering) spectra of Cu_2O microcrystals dispersed in different mediums. (b) Summary of extinction spectra of Cu_2O microcrystals from calculation.

The changes of extinction spectra of Cu_2O microcrystals have also been investigated when the microcrystals were attached to solid substrates. Two types of thin film were fabricated in this work, drop-casting films and LB films. The extinction spectra of Cu_2O microcrystals in these two solid states are shown in Fig. 3a, together with the spectrum of colloidal dispersion. The major extinction peak for Cu_2O microcrystals is located at 806, 786, and 767 nm for colloidal, casting film, and LB film, respectively. We tentatively attribute the blue shift of the extinction peak in solid states to the changes of the refractive index for the surround materials from methanol (RI: 1.328) to a combination of glass substrate (RI: 1.490) and air (RI: 1.000). Furthermore, the extinction peaks of LB films demonstrated a blue shift as compared to the casting films, which can be related to the different density of Cu_2O microcrystals in these two films. The density of Cu_2O microcrystals in the LB films is much higher than that of casting films so that the refractive index of surrounding mediums for individual microcrystals can be impacted. Shift of peak can be clearly observed as shown in the inset of Fig. 3a with the peak position of the major extinction for the Cu_2O microcrystals in colloidal, drop-casting film, and LB film, respectively. It is noteworthy that even for the two cases of Cu_2O crystals on solid substrates, the width of major extinction peaks are also slightly different. These phenomena of sensitive optical responses have been previously observed on gold and silver nanoparticles,^{17,20} where local surface plasmon resonances were highly relied on the structure, compositions, and surroundings of the nanoparticles.²⁰ While for semiconductor materials, the mechanism for such phenomena is still unclear and thus need further investigation. The blue shift and narrowing of extinction peaks were also observed for other weak peaks in the spectra, although the impacts are less significant than the major one.

The environment-dependent extinction spectra of Cu_2O microcrystals were explored in the forms of solid state thin films. Drop-casting films and LB films were placed in a 1 cm-path length quartz cuvette that filled with various dispersions for studying their extinction properties. Fig. 3b shows the extinction spectra of the Cu_2O microcrystal thin films in different dispersions whose refractive indexes ranging from 1.32 to 1.46. Similar to the case of

colloidal dispersion, the Cu_2O microcrystals in solid states also showed a high sensitivity to surrounding mediums with various refractive indexes. Furthermore, we found that the surrounding mediums do not cause noticeable permanent structural changes of the Cu_2O microcrystals and shift of extinction peaks were quite robust during the dispersion alternation. Fig. 3c represents the extinction spectra of the LB films immersed in methanol and chloroform alternatively. The Cu_2O microcrystal LB films demonstrated tuneable and repeatable extinction spectral characterizations. As shown in the inset of Fig. 3c, the reproducible change in the extinction spectra were observed when the peak positions were tracked during the dispersion alternation experiments with methanol and dichloromethane.

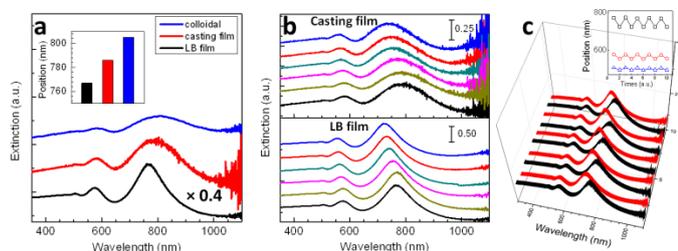


Figure 3. (a) Extinction spectra of Cu_2O microcrystals in colloidal dispersions and on solid substrates. Inset: peak positions of three samples. (b) Extinction spectra of Cu_2O microcrystal casting films and LB films (top and bottom) settled in different mediums. (c) Extinction spectra of Cu_2O microcrystal LB film settled alternatively in methanol and dichloromethane. Inset: Peak positions of Cu_2O microcrystal characteristic peaks.

The environment-dependent extinction spectra were further studied on Cu_2O microcrystals of other sizes and morphologies. Here we prepared Cu_2O microcrystals with morphologies ranging from cuboctahedral to octahedral (shown in Fig. 4a-4d) by controlling the temperatures during the precursor preparation. The SEM micrographs indicate the variations of microcrystals topographies as well as their sizes. The difference in crystal structures can be attributed to the changes in the seeding processes.⁴⁵ The sizes of the Cu_2O microcrystals increase with the decrease of temperature during the precursor formation. As we know, the accelerated growth rate under high temperature is favor for the nuclei formation of small crystals.⁴⁹ Our results are consistent with the previous study on the temperature dependence of Cu_2O syntheses.⁴⁹ We also collected the sizes information of those crystals (see Fig. S2). These Cu_2O microcrystals were utilized in exploring their environmental-dependent optical extinction properties. We found that all of these microcrystals exhibited extinction spectra with an overall multi-peak shape. Furthermore, the morphology and size dependences were clearly observed. Extinction spectra for those Cu_2O microcrystals in methanol were shown as insets in Fig. 4 and the scattering peaks were red shifted as the sizes of microcrystal increase. Such size-dependent optical property was also observed by other researchers when they studied the geometry-dependent properties for Cu_2O particles.^{41,42} It is noteworthy that our theoretical calculation gives similar extinction curves for those Cu_2O microcrystals (see Fig. S3).

The fact of different positions of the scattering peaks for Cu_2O microcrystals at various sizes and morphologies allows a systematic exploration of the environment dependent optical properties. We measured the extinction spectra of these Cu_2O microcrystals dispersed in various dispersions (See Fig. S4) and analyzed the positions of the extinction peaks. The relationship between peak positions and refractive indexes of disperse mediums was plotted (Fig. 5a and Fig. S5). Similar as what we found before, linear relationships between the positions and refractive indexes were

obtained for all sets of Cu_2O microcrystals. The scattering peaks clearly blue shifted with the increase of refractive indexes of the mediums. By comparing the slope of each fitting line, we found that the scattering peaks at lower energy (long wavelength) have faster blue shift than those of high energy peaks (Fig. S5a). It is worth noting that such trend is valid for all set of peaks, regardless the shape and morphology of the crystals in our study.

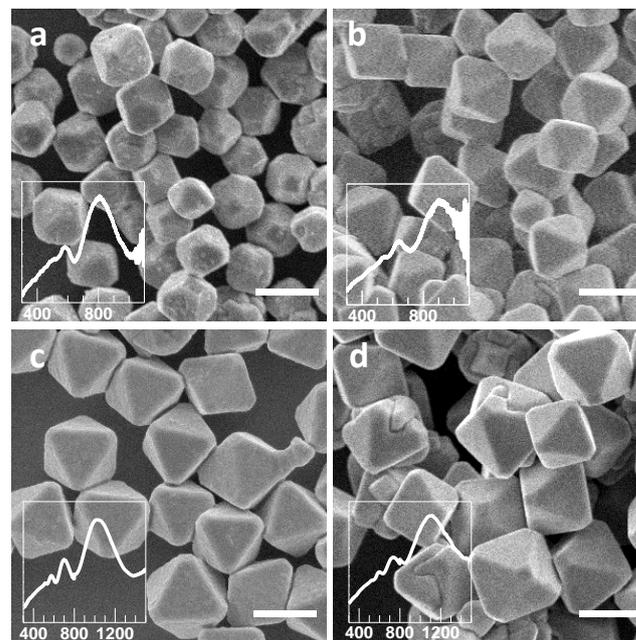


Figure 4. (a)-(d) SEM images of Cu_2O microcrystal with precursors at different temperature, (22°C, 16°C, 10°C, and 5°C), respectively. All scale bars are 1 μm . Insets: extinction spectra of corresponding Cu_2O microcrystals dispersed in methanol.

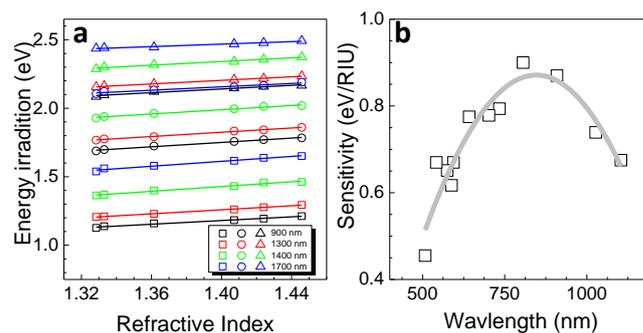


Figure 5. (a) Sets of extinction peak positions (in eV) variation in different disperse mediums. Same color code for one type of Cu_2O microcrystal and same symbols represent the correlation of the peaks. (b) Sensitivity of peak shift (slope) versus the starting positions of all extinction peaks of Cu_2O microcrystals (in methanol).

The slopes found in the fitted curve can indicate how sensitive of the extinction peak regarding the refractive index of the surrounding mediums. As shown in Fig. 5b, the slopes are in a range of 0.46 to 0.90 eV/RIU. We found that a maximum slope of 0.90 eV/RIU can be obtained for extinction peak at around 840 nm. This plot gives more interesting nature of the environment-dependent optical behaviour for cuprous oxide microcrystals, which cannot be simply revealed in the plot using a unit of nanometer (Fig.

S4b). To the best of our knowledge, it is the first time to observe the maximum sensitive change of the extinction peak for such environment-dependent Cu₂O microcrystals. We believe that this unique property could be related to the intrinsic structural parameters of Cu₂O microcrystals. A detail explanation of such linear relationship is subject to a future study, which is beyond the scope of this work. As shown in Fig. S4c, a similar curve was also achieved in the theoretical calculation using the Mie scattering theory. The discrepancies between our experimental spectra and calculated data, are related to the approximation in our calculation such as geometry simplification, and might be further improved with more complex simulations. Over all, both our experimental discoveries and theoretical calculations showed that the environment-dependent extinction spectra of Cu₂O microcrystals are size and geometry tunable, and their scattering behaviors are predictable. A further detail experimental investigation and more complicate modelling toward a better understanding of such optical properties will be essential for an intensive utilization of these functional semiconductor materials.

Conclusion

In conclusion, cuprous oxide microcrystal exhibits three major extinction peaks in visible-near infrared regions and positions of these peaks are environment dependent. With the increase of refractive index of surrounding medium, the extinction peaks show linear blue shift. The shifts of peak positions are consistent with theoretical simulations based on Mie scattering theory. The environment-dependent extinction spectra can be observed for cuprous oxide in colloidal dispersions, casting films, and LB films. The systematic study on microcrystals with different size and morphology revealed that sensitivity of environment-dependent optical behavior depends on the energy of the extinction peaks. A maximum slope of 0.90 eV/RUI was obtained with the extinction peak at around 800 nm. Our work on the environment-dependent spectra of cuprous oxide microcrystals provides valuable knowledge for these functional semiconductor materials.

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Notes and references

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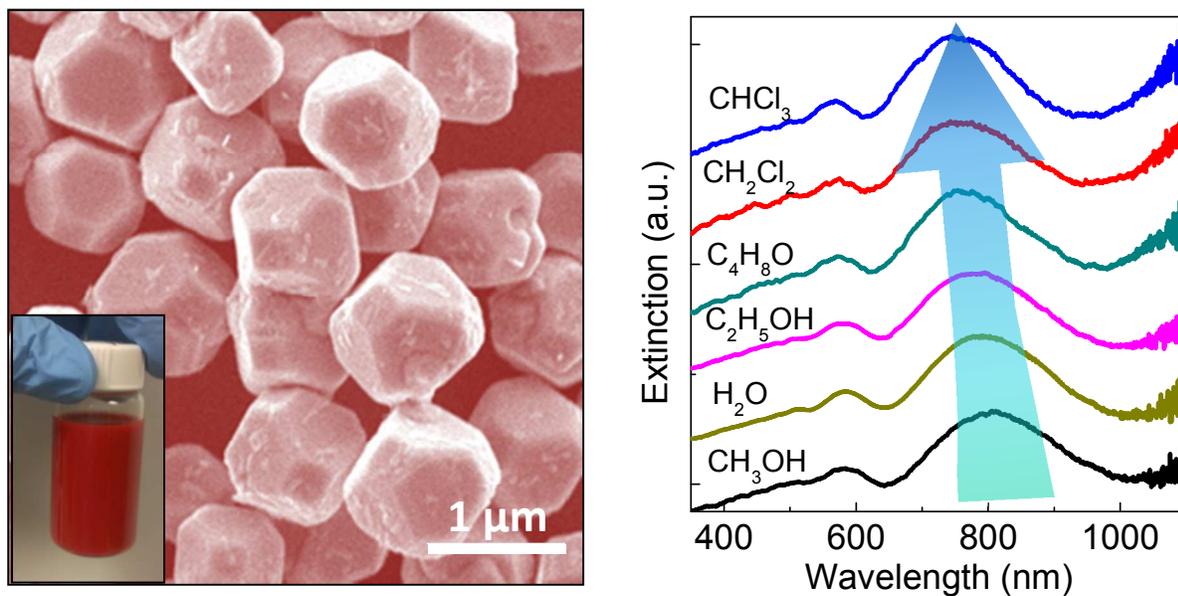
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Environment-Dependent Optical Scattering of Cuprous Oxide Microcrystals in Liquid Dispersions and Langmuir-Blodgett Films[†]

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Table of contents entry



Extinction peaks of cuprous oxide microcrystals are systematically blue shifted with the refractive index increase of their environment.