Aqueous Phase Self-Assembly of Nanoscale p-n Heterojunctions

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Received: January 9, 2002

Methods, adapted from photographic microcrystal growth technology, are used to assemble organized ternary organo-inorganic, nanoscale heterostructures. The resulting ensemble consists of free-standing, oriented AgBr microcrystals, upon the $\langle 111 \rangle$ surfaces of which is self-assembled a monolayer of spectrally sensitizing dye, and upon the corners of the hexagonally shaped AgBr substrates are epitaxially grown nanoscale p-type CuSCN nodules. EPR spectroscopy and photophysical measurements are employed to show that the ensembles are capable of separating photogenerated geminate pairs. One of the remarkable features of this approach is that it utilizes the ultrafast kinetics of aqueous precipitation and, thus, allows the assembly of heterostructures at rates of 10^{10} /s·L, or greater.

Introduction

Nanoscale and monomolecular electronics hold great promise because of the possibility of reaching microelectronic device scales on the order of single molecules.¹ However, a significant challenge lies in creating methods for assembling or fashioning nanoparticles, or molecules, into "materials" capable of being fabricated into devices. Langmuir-Blodgett and self-assembly methods have been used to create organized two-dimensional molecular monolayers on a substrate.² However, discrete threedimensional assemblies of nanoparticles or molecules are generally much more difficult to "fabricate" and far fewer examples and methodologies have been reported. A further challenge of nanoscale and monomolecular technology is establishing methods for creating electrical contact between individual, or small groups, of atoms or molecules. Herein, we describe a methodology adapted from photographic microcrystal growth technology, and show the directed, aqueous phase, selfassembly of heterogeneous materials into organized, organicinorganic, nanoscale heterostructures. p-n heterojunctions thus created are capable of geminate pair separation, and outside of applications in the photographic process, may represent a natural bridge between conventional solid-state methods of device fabrication and the fabrication of organized nanoscale or monomolecular arrays.

Common commercial photographic film may contain as many as 10⁹ silver halide semiconductor particles per square centimeter, a density that is vastly greater than that currently found in the most advanced solid-state semiconductor devices. Silver halides share many features with solid-state semiconductors, such as doping to manipulate electronic properties,^{3,4} epitaxial growth of secondary phases,⁵ and dye-spectral sensitization.⁶ Silver halide microcrystals may be produced in large quantities with unprecedented size monodispersity and morphological control. We have adapted methods used in silver halide microcrystal growth to develop an approach to the self-assembly of ternary organic—inorganic heterostructures. The approach is depicted in Figure 1 and utilizes monodisperse, morphologically controlled AgBr microcrystals. Each microcrystal represents a discrete, free-standing "substrate" for further growth of heterogeneous materials. Onto the surfaces of the hexagonally shaped microcrystals is assembled a monolayer of spectrally sensitizing cvanine dye, capable of photoinduced electron transfer into the AgBr microcrystals with efficiencies near 1.0.6 The dye is known to J-aggregate (see ref 6) on the $\langle 111 \rangle$ surfaces of AgBr microcrystals, effectively blocking further growth on the surfaces, and directing any subsequent growth onto the corners of the microcrystals.⁵ We demonstrate the site-directed, epitaxial growth of the p-type semiconductor, CuSCN, onto the templated AgBr substrates. CuSCN is a wide band-gap p-type semiconductor and it has been shown that photographic cyanine dyes are capable of injecting holes into CuSCN with very high efficiencies.^{7,8} We use EPR spectroscopy to show that holes generated by band-gap irradiation of the AgBr substrate may be trapped in the CuSCN heterogrowths, and the intrinsic photographic properties of the AgBr substrate to show that the electrons are trapped in the substrate. The ensemble is, thus, capable of geminate pair separation. The aqueous precipitation method of assembling the composite is remarkably facile, capable of fabricating heterojunctions at a rate on the order of 10^{10} /s[·]L, or greater.

Experimental Section

To 0.50 mol of the AgBr microcrystals contained in 300 mL of water and 20.0 g of deionized gelatin, at a residual Ag concentration of pAg = 8.2 (where the $pAg = -\log [Ag^+]$) and a constant temperature of 40 °C, was added 25.00 mL of 0.1 M KI while the pAg was simultaneously adjusted to ca. 7.4 with 0.05 M AgNO₃. After the addition, 6.50 mL of 0.25 M NaSCN was added followed by 0.617 mmol of the magenta dye 5-chloro-2-(2-((5-phenyl-3-(3-sulfobutyl)-2(3H)-benzoxazolylidene)methyl)-1-butenyl)-3-(3-sulfopropyl)benzoxazolium. The contents were then allowed to stir at 40 °C for 20 min. The epitaxial growth was accomplished by initially doublejetting 4.0 mmol of AgNO₃ (0.25 M at 5.0 mL/min for 3.2 min) with 0.25 M NaSCN at 5.0 mL/min and then switching to 0.14 M CuSO₄ (which contained 0.55 mol ascorbic acid/mol Cu) for 32 min, while the flow of NaSCN was maintained. In total, 21 mmol of Cu and 25 mmol of SCN⁻ were added, while a

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Figure 1. Schematic illustration of the templating method used to prepare ternary organic-inorganic heterostructures.

constant residual silver ion concentration was maintained, pAg = 7.5. The contents were then cooled to 15 °C and kept refrigerated. All procedures were performed in the dark.

Electron paramagnetic resonance (EPR) measurements were made with a Bruker ESP300e spectrometer fitted with a helium gas flow cryostat of conventional design. Irradiations were performed in situ using a 200 W Hg/Xe source, the output of which passed through a $1/_8$ m monochromator and a combination of long-pass and band-pass filters. EPR experiments were carried out on dispersions that were evaporated to dryness under a stream of dry N₂.

Results and Discussion

Materials Assembly. The experimental approach for preparing the composite structures was adapted from Maskasky⁵ who showed that mixed silver halides and pseudohalides could be grown epitaxially upon AgBr. The substrate consists of oriented AgBr microcrystals with average particle dimensions of 4.2 μ m $\times 0.072 \,\mu m$ (the equivalent circular diameter of the hexagonal shaped disks and the disk thickness, respectively). The geometrical standard deviation of the equivalent circular diameter was 1.31 μ m. The microcrystals have their (111) surfaces oriented perpendicular to the thickness dimension. The microcrystal substrates are prepared for the growth of a secondary inorganic phase by the addition of an amount of cyanine⁶ dye sufficient to form a monolayer on their surfaces. Several authors have shown that various spectrally sensitizing dyes are strongly adsorbed onto AgBr $\langle 111 \rangle$ surfaces.^{5,6} The monolayer of dye thus formed serves two purposes. First, the J-aggregated dye is capable of absorbing visible light and transferring an electron into AgBr, thus "sensitizing" the AgBr (and CuSCN) to specific spectral regions. Second, the J-aggregated dye essentially strongly adsorbs to the $\langle 111 \rangle$ substrate surfaces and hence prevents further growth on the substrate surfaces, directing any subsequent growth onto the edges and corners of the AgBr microcrystals. We chose the magenta-colored dye shown in Figure 1 having an absorption in the green region of the visible spectrum (490-580 nm) with an absorption maximum at 545 nm. There exist many such dyes capable of sensitizing



Figure 2. SEM image of the AgBr microcrystals after the epitaxial growth procedure. The CuSCN epitaxy appears as capsule-like growths localized near the corners of the host grains, bar indicates $2.0 \ \mu m$.

throughout the visible and near-infrared spectral region.^{5,6} Prior to dye addition, a small amount of iodide ion is added to improve the adsorption of the dye to the $\langle 111 \rangle$ substrate surface and also, to further aid the inhibition of growth on these surfaces.⁵ The fast double jet addition of Cu⁺ and SCN⁻ ions then leads to the growth of CuSCN nodules, most typically on the corners of the grains. SEM images of the AgBr microcrystals after the procedure are given in Figure 2, and indicate capsule-like growths of CuSCN on the corners and edges of the AgBr microcrystals. Growth at corners is preferred over growth at edges, presumably because the corners contain a greater density of uncoordinated ions and hence sticking coefficients are greater there. We estimate the CuSCN nodule size to be on average 150 nm, which can be directly controlled by varying the amount of Cu⁺ and SCN⁻ added. The microcrystal population, having



Figure 3. Elemental EDAX map of a AgBr grain containing epitaxy prepared by the described method. The grain analyzed is shown in the top left-hand corner of Figure 2a. The subsequent frames represent elemental maps of the image area as measured by examining the X-ray fluorescence emerging from the image with (b) S, (c) Cu, (d) Br, and (e) Ag. The sulfur and copper mapping is largely limited to the epitaxial positions of the grain, while the Ag and Br mapping essentially reflects only the host grain.



Figure 4. 9.3 GHz EPR spectra of the substrate AgBr emulsion measured at 8 K. Black trace: background signal obtained before exposure to light. Blue spectrum: signal obtained at 8 K during exposure to 440 nm light. The background signal has been subtracted. Red trace: signal obtained after exposure to 440 nm light at 160 K showing no change in the signal assigned to Cu^{2+} in gelatin.

all six corners with CuSCN epitaxy, is estimated at 30%. We note that the capsule-like growths appear from SEM images to be oriented crystalographically with respect to the host microcrystals. An elemental EDAX map of the epitaxy (see Figure 3), clearly show that the Cu and S are localized to the epitaxial positions and that the Ag and Br maps are limited to the substrate positions, clearly indicating growth of CuSCN upon AgBr.

Photophysical Properties. An EPR spectrum of the substrate AgBr microcrystals is shown in Figure 4. The sample was examined prior to the adsorption of the magenta dye. Before light exposure, evaporated samples of this dispersion show weak

EPR signals typical of impurity Cu²⁺ bound to gelatin (black spectrum). A small amount of Cu²⁺ impurity is nearly always present in silver halide microcrystals prepared in gelatin. There is also a weak line at 333 mT possibly from Ag_n^0 centers also commonly found in silver bromide microcystals.9

Exposure to band-gap light (440 nm) at 8 K produces a cyclotron resonance signal from conduction band electrons (indicated by the sloping baseline in the blue spectrum),¹⁰ and the hole signal assigned to Br_4^{3-} centers trapped at grain surfaces.¹¹ These signals are characteristic of a pure AgBr grain with a low concentration of lattice dislocations and point defects. Recombination destroys these intrinsic centers once the exciting light is quenched. Exposure to 440 nm light at higher temperatures produces more Ag_n^0 image centers and oxidized gelatin radicals, the latter formed by hole transfer from the AgBr grain surface to the peptizing polymer. The concentration of Cu²⁺ impurity ions in gelatin is unaffected by irradiation between 8 K and RT (e.g., see red spectrum in Figure 4).

EPR spectra of the emulsion containing the CuSCN epitaxy and the magenta dye before and after exposure to 440 nm light are given in Figure 5. CuSCN has a band gap of 3.6 eV,8 while the band gap of AgBr is 2.68 eV,¹² thus the 440 nm (2.82 eV) exposure produces photogenerated geminate pairs in the substrate AgBr microcrystals, but produces few, if any, electrons or holes by direct light absorption in the CuSCN heterogrowths or the J-aggregated dye. Prior to exposure, the sample shows a moderately strong Cu²⁺ spectrum (black spectrum). This signal is quite well resolved and shows the characteristics expected of a d⁹ complex with a $d_{x^2-y^2}$ ground state (i.e., $g_{\parallel} > g_{\perp} \ge 2$). Three of the four parallel hyperfine features from ^{63/65}Cu nuclides are observed on the low-field tail. The composition of the ligand shell is not revealed in this spectrum and thus we cannot distinguish between Cu²⁺ as an impurity in CuSCN or gelatin. There is also a weak signal at 333 mT, as found in the substrate spectrum and likely from Ag⁰ clusters or gelatin radicals. The exposure of this dispersion to 440 nm light at 8 K



Figure 5. 9.3 GHz EPR spectra measured at 8 K from the AgBr emulsion containing site-directed CuSCN epitaxy. Black trace: before light exposure. Red trace: after exposure to 440 nm light at 160 K, with the low-field region expanded in the insert. Background spectrum has been subtracted. The arrows indicate probable ^{63/65}Cu HF features.

produces no substantial change in the EPR spectrum. However, irradiation at 160 K generates a new set of features in the spectral region between 250 and 330 mT. The insert (red spectrum) in Figure 5 shows the change caused by light (i.e., the background signal has been subtracted). The position of the new EPR signal and the detection of poorly resolved HF features in the low-field tail (marked by arrows in the insert) suggest an assignment to Cu²⁺. We conclude that there is a substantial generation of a new Cu²⁺ center as the result of a thermally activated hole transfer mechanism. In the course of this process, a small population of holes is also transferred to the magenta dye and to the gelatin peptizer. The resultant oxidized dye and gelatin radicals produce new signals convoluted near g = 2 in Figure 5. Because the Cu²⁺ spectrum is not that observed from this ion bound to gelatin, we propose that the photosignals between 260 and 320 mT in Figure 5 are from holes transferred from AgBr to the CuSCN epitaxy.

Photographic Properties. The photographic process involves the photogeneration of electron-hole pairs within silver halide particles, and the subsequent detection and amplification of longlived trapped electron states, by developer chemistry.¹² Belloni et al.¹³ have recently brought attention to the fact that the salient loss mechanism of this process results from the fast recombination of some fraction of photogenerated geminate pairs. They further described an approach to minimizing recombination, which involves doping the silver halide grains with hole scavenger molecules, which upon trapping a hole, in turn, decompose to produce a secondary photoelectron. A similar approach has been described by Gould et al.14 The method described herein represents a unique approach to enhancing the yield of photoinduced electrons. The p-n heterojunctions created are capable of geminate pair separation, and therefore potential utilization of both the electron and hole as photographically active species. The heterojunctions are fabricated in standard photographic emulsion processing equipment, at rates compatible with silver halide precipitation itself, and in a directed manner at targeted sites on the silver halide grains.



Figure 6. Photographic response (density versus exposure) curve for the AgBr/CuSCN emulsion exposed by 365 nm light, each step represents a 0.15 log E increase in exposure.

The potential utility of photographic heterojunctions was first pointed out by Levy et al.,15 who showed that when semiconductor materials such as CdS, ZnO and PbO were physically mixed with silver halide emulsion grains, spectral sensitization, and increases in intrinsic photographic activity could be observed.15 The methods employed by Levy et al., however, proved ultimately unreliable or impractical from a processing standpoint. A more amenable approach requires direct aqueous precipitation of a semiconductor material onto the silver halide grains. The criteria for such heterogeneous growth upon AgBr are, indeed, enormously limiting. The more obvious criteria include aqueous compatibility, a solubility near that of AgBr, structural similarity, and/or a commensurate lattice parameter. In fact, perhaps 99% of all semiconductor materials can be eliminated based on these criteria alone. CuSCN meets many of these requirements and it has recently been shown that photographic cyanine dyes are capable of injecting holes into CuSCN with efficiencies near 0.90.7 CuSCN has a $pK_{sp} = 14.3$, comparable to that of AgBr ($pK_{sp} = 12.3$), and is soluble in thiosulfate allowing it to be fixed out of (i.e., removed from) an imaging system (a basic requirement of color photography).

The photographic response (density versus exposure) curve for the AgBr/CuSCN emulsion coated onto a cellulose acetate support in gelatin is given in Figure 6. The data indicate a rather typical photographic response with a high D-min level likely resulting from the ascorbic acid reducing agent used to produce Cu^+ in the preparation. Although the photographic response is by no means comparable to that of state-of-the-art commercial systems, the data do indicate that the method generates a viable imaging system, and the occurrence of normal photographic behavior indicates that conduction-band electrons generated by actinic irradiation are effectively trapped in the silver halide substrate. It is anticipated that considerable optimization of the system would be required to realize the full potential of the approach.

The EPR spectroscopy data show that holes generated by band-gap irradiation of the AgBr substrate may be trapped in the CuSCN heterogrowths, and the photographic properties of the ensemble indicate that the electrons are trapped in the substrate. These data, taken together, indicate that the ensemble is capable of geminate pair separation and provide indirect experimental evidence for the presence of p-n heterojunctions. Because, to our knowledge, values for the electron affinities and thermal work function of CuSCN are not yet known, it is impossible to precisely discuss the energetics of the junction interface. However, the experimental data herein suggests that, since holes are transferred to the CuSCN heterogrowths, the valence band of the CuSCN lies above that of AgBr, and would further suggest that, while electron transfer from the adsorbed dye molecules to AgBr occurs readily, electron transfer from dye molecule to CuSCN is higly unlikely.

Conclusions

We have used methods, adapted from photographic microcrystal growth technology, to assemble organized ternary organo-inorganic, nanoscale heterostructures. EPR spectroscopy and photophysical measurements are employed to show that the ensembles are capable of separating photogenerated geminate pairs. This approach may be applied, in photography, to enhance the yield of photogenerated electrons, and in principle, might allow both the electron and hole to be utilized as photographically active species. One of the remarkable features of this approach is that it utilizes the ultrafast kinetics of aqueous precipitation and thus, allows the assembly of heterostructures at rates of 10¹⁰/s, or greater. In this manner, molecular monolayers are assembled upon nanoscale features that are "constructed" upon micron scale crystals. The ensembles are threedimensional and free-standing and may represent a natural link between conventional methods of device fabrication and molecular approaches. The general approach depicted here may be extended to include other electronic materials, based upon the criteria outlined above, to assemble ternary organo-inorganic systems in unprecedented ways.

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