Nanoparticles

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Modular Synthesis of a Dual Metal–Dual Semiconductor Nano-Heterostructure**

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***Abstract:** Reported is the design and modular synthesis of a dual metal–dual semiconductor heterostructure with control over the dimensions and placement of its individual components. Analogous to molecular synthesis, colloidal synthesis is now evolving into a series of sequential synthetic procedures with separately optimized steps. We detail the challenges and parameters that must be considered when assembling such a multicomponent nanoparticle, and their solutions. This multicomponent nanosystem, Ru-CdSe@CdS-Pt, was designed to achieve charge carrier separation and directional transfer across different interfaces toward two separate redox catalysts. This heterostructure may potentially serve as a nanometric closed circuit photoelectrochemical cell.*

Hybrid nanostructures can exhibit several synergistic features and deliver more than one function simultaneously. The increasing interest in functional metal-semiconductor hybrid heterostructures has spurred the design of more complex and sophisticated structures.[1–4] This advancement was enabled by the exceptional improvement in the protocols for controlling the size,[5] shape,[6–11] and composition[12–14] of solution-grown nanocrystals, which pushed the realm of nanoparticle colloidal production into a branch of synthetic chemistry. Analogous to molecular synthesis, colloidal synthesis is now evolving into a series of sequential synthetic procedures with separately optimized steps, where multicomponent structures are assembled in a predictable manner for specific applications.[15–19] This approach facilitates the construction of nanoparticles of increasing chemical complexity.[20–27]

We demonstrate a modular synthesis of a hybrid heterostructure with control over the dimensions and placement of its individual components. This report details the challenges and parameters that must be considered when assembling such a multicomponent nanoparticle, and their possible solutions. The principles herein can be applied to most other procedures for the growth of nanoparticle heterostructures.

We synthesized an anistropic core–shell semiconductor heterostructure decorated with differet metal nanoparticles at distinct sites. Our multicomponent nanosystem was designed to achieve charge carrier separation and directional transfer across different interfaces toward two separate electrodes. This heterostructure serves as a nanometric closed circuit photoelectrochemical cell, with potential application as a photocatalyst for direct solar to fuel conversion.

For the light absorption and charge separation events we chose a cadmium sulfide (CdS) nanorod with a cadmium selenide (CdSe) quantum dot embedded within it, similar in fashion to the state-of-the-art seeded rod structure.[1,4,21–23,28] The structure further includes a platinum (Pt) nanoparticle reduction catalyst placed on one end of the CdS rod.[29,30] Prior work has shown that the CdSe@CdS-Pt combination is highly active for hydrogen production.[29,31] However, future applications have been hampered by photo-oxidative instability of the chalcogenide, which requires the use of hole scavengers. Since hole trapping is responsible for degradation of the chalcogenide we designed our system to rapidly tunnel the hole to an oxidation catalyst. The addition of a counter electrode adjacent to the CdSe seed is expected to enhance the stability of the structure, because of the electrodes ability to scavenge the holes from the sensitive semiconductor.[32] For this task, we selected Ru (with a partially oxidized surface)[33,34] to serve as the oxidation electrode. Our structure, illustrated in Figure 1, demonstrated remarkable photochemical stability under prolonged illumination (3 weeks) in pure water, without the addition of any hole scavengers.

The combination of CdS with Pt and an oxidation catalyst such as RuO_2 was studied previously in stochastic arrangements and demonstrated the potential for overall water splitting.[33] The longer-term goal here is to study this well-known system when the components are more precisely placed with respect to each other.

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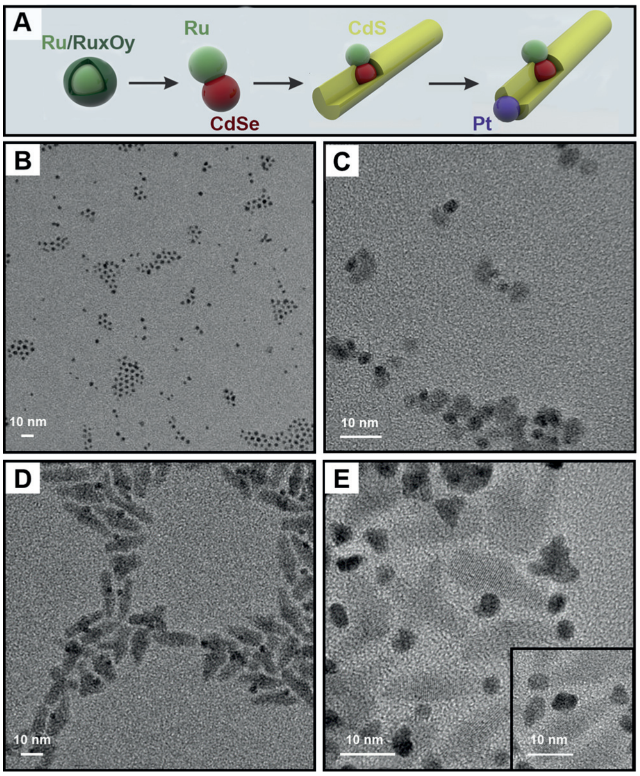

Figure 1. A) Illustration of the multistep synthesis. TEM micrographs of the different building blocks from which the heterostructure is composed: B) Ru@Ru$_x$O$_y$, C) CdSe-Ru dimers, D) Ru-CdSe@CdS nanorods, E) Ru-CdSe@CdS nanorods with Pt tips.

Figure 1 includes an illustration and TEM micrograph of the complete structure as well as the sequential synthetic steps leading to its formation. The synthesis commenced with production of the Ru nanoparticles (light green, Figure 1 A,B) which have an oxidized surface (dark green). Next, a CdSe quantum dot (red; Figure 1 A,C) was grown on the metal oxide electrode, thus forming a Ru-CdSe dimer. These dimers served as seeds for the growth of CdS nanorods (yellow; Figure 1 A,D), which grew exclusively on the CdSe portion of the dimer. Finally, the rods were tipped with a Pt nanoparticle (purple; Figure 1 A,E) on one end of the rod.

Ruthenium nanoparticles with an oxidized surface were synthesized using a modified procedure for metalic Ru nanoparticles, as developed by Hoefelmyer and co-workers.[35] The procedure included thermal decomposition of triruthenium dodecacarbonyl [Ru$_3$(CO)$_{12}$] in a mixture of hexadecylamine (HDA) and trioctylamine (TOA), while bubbling oxygen through the solution. Different oxidation protocols, including the use of chemical oxidizing agents such as trimethylamine oxide, were tested. The oxidation process, and in particular duration and onset with respect to the Ru growth affected the size of the resulting Ru@Ru$_x$O$_y$ particles. Longer in situ oxidation (see Figure S1 in the Supporting Information) resulted in smaller diameters compared to postpartum oxidation of preformed metallic Ru nanoparticles. Different shapes of metallic Ru were synthesized by adjusting the temperature and ligand ratio (Figure 2; for more information see the Supporting Information). For simplicity, only spherical nanoparticles were used in the following steps. The faceted and branched metallic Ru nanoparticles may prove to be interesting for catalysis.

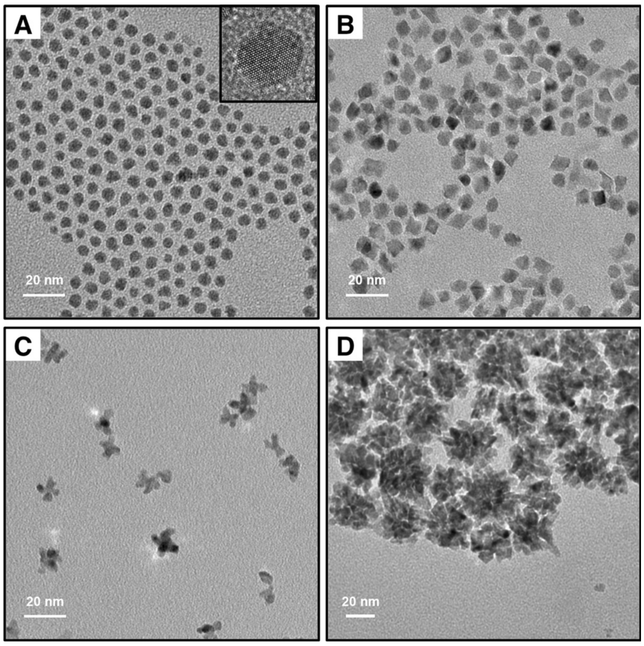

Figure 2. TEM micrographs of Ru nanoparticles of different shapes.

X-Ray diffraction (XRD) analysis confirms a composition of metallic Ru with some evidence of Ru oxide formation, presumably at the surface (see Figure S2 in the Supporting Information). The formation of Ru oxide species was also confirmed using X-Ray photoelectron spectroscopy (XPS), where changes in the oxidation state of Ru were monitored in the Ru 3d region (see Figure S3 in the Supporting Information).

A protocol for growing CdSe onto the Ru@Ru$_x$O$_y$ nanoparticles was developed. Ru@Ru$_x$O$_y$ nanoparticles were dissolved in 1,2-dichlorobenzene (DCB) and mixed with selenium (Se) powder and oleylamine. Injection of this mixture into a hot solution of cadmium oleate produced dimers of CdSe attached to Ru (denoted CdSe-Ru). In the process of CdSe growth, the Ru$_x$O$_y$ shell seems to be reduced to metallic Ru. XPS revealed the disappearance of a signature feature of RuO$_2$ at 281 eV and a red-shift of the Ru 3d$_{5/2}$ peak to that seen in metallic Ru nanoparticles (see Figure S3).[36–38]

Despite the reduction of the Ru$_x$O$_y$ shell, it was found to play a key role in the dimer formation, thus affecting the quantity and location of CdSe deposition. Variations in the oxidation conditions applied gave us control over the hybrid morphology, with formation of a core–shell structure, a flower-like decoration, or a dimer with a single CdSe dot on the Ru nanoparticle (Figure 3). In the absence of the oxide shell, growth on metallic Ru nanoparticles resulted in multiple CdSe dots on the surface (Figure 3 A), eventually reaching full coverage and a core–shell structure. Our findings suggest that the metallic Ru acts as a catalyst for the nucleation of CdSe. When, however, the Ru surface is partially oxidized, the CdSe nucleation is restricted (Figure 3 B–F). Oxidation of the Ru nanoparticles after their formation resulted with

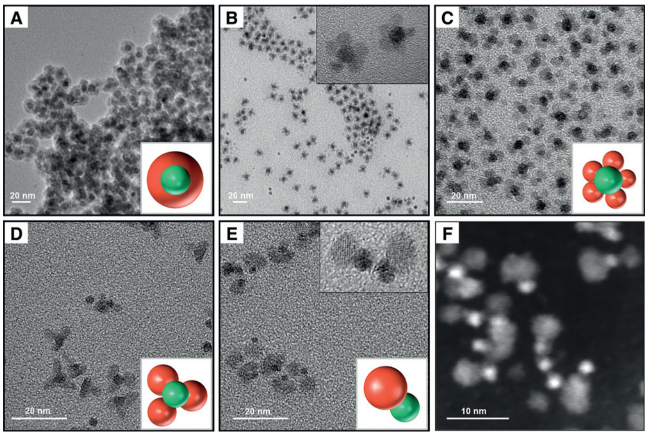

Figure 3. Variety of hybrid CdSe-Ru@Ru_xO_y nanostructures attained when CdSe was grown on Ru nanoparticles of different levels of oxidation.

flower-like decoration (Figure 3 B,C). Hence, longer in situ oxidation maximized the yield of dimers. For more information on the oxidation conditions see the Supporting Information.

The size and shape of the CdSe nanoparticle can be further tuned by varying the concentration of the ligands, oleic acid, and oleylamine (Figure 3 C–F). We focused on optimizing growth conditions for the formation of dimers with only one CdSe dot per Ru nanoparticle, as these seeds afforded the greatest control in the subsequent CdS growth. It should be noted that attempts to grow Ru onto preformed CdSe nanoparticles proved unsuccessful.

When using dimers as seeds, rather than simple quantum dots, separate attention should be given to the deposition process on each of the dimer components. A delicate balance must be attained between the optimized reaction conditions of the two alternative growth routes to allow selective deposition. Thermal mechanistic aspects of the growth on the desired component are intertwined with care for the stability of the other. Ligand compatibility considerations are entangled with their mutual effect on the growth kinetics. Prior to growing CdS on the CdSe-Ru dimers we studied the growth of CdS on Ru nanoparticles to better understand how to impede such undesirable deposition.

One particular challenge with regard to the utilization of dimers as seeds was dimer stability. It appears that the stronger binding phosphonic acids displace the original ligands on the CdSe-Ru dimers during CdS rod growth, and that this can potentially lead to separation and dissolution of the CdSe dots from the Ru nanoparticles.[39] Displacement of the dimer ligands in a controlled and gradual fashion was found to stabilize the dimers and minimize such detachment. Hence, a solution of propylphosphonic acid was directly added to the dimers prior to CdS rod growth. This issue of ligand compatibility was found to be central for increasing the yield of rods with incorporated CdSe-Ru dimers (Figure 1 C).

The Ru component of the seed served as a visual marker, thus indicating the location of CdSe within the CdS rod. Its presence enabled us to attain control over the location of the CdSe (dimer) within the CdS rod. Such control was achieved by tuning the kinetics of CdS nucleation and growth on the seed by careful selection of the ligands. Varying the chain length of the phosphonic acid (from propyl to hexyl), added to the dimers after the CdSe growth, altered the position of the CdSe within the CdS, as seen by the TEM micrographs in Figure 4 A,B.

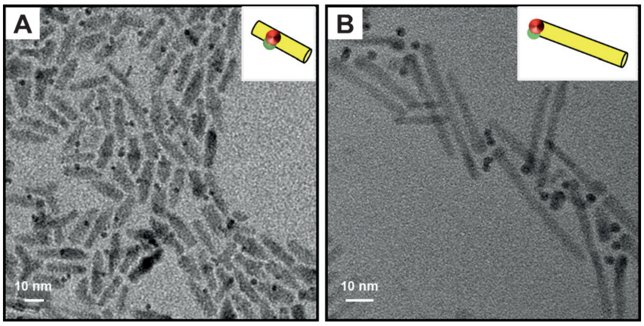

Figure 4. Control over the location of the CdSe (dimer) within the CdS rod was achieved by varying the chain length of the phosphonic acid ligand.

The design of the hybrid seed strongly affects the final heterostructure morphology. Utilization of CdSe-Ru nanoparticles with more than one CdSe dot resulted in multiple CdS arms (see Figure S8 in the Supporting Information). The size and shape of the CdSe component are also expected to be of significance.

Lastly, Pt was grown onto the CdS nanorod by an established protocol of thermal decomposition of $[Pt(acac)_2]$ using 1,2-hexadecanediol (HDD) as a reductant.[30] Indeed, the vast majority of our multicomponent heterostructures seem to have localized Pt nanoparticles grown selectively at one end of the rod. An example of such structure after Pt tipping can be seen in Figures 1 E and 5, and Figure S9 in the Supporting Information. Evidence of the Pt deposition onto the Ru was found on a low percentage of rods. This secondary metal deposition is a sensitive parameter, as one can easily lose control over distinct metal nanoparticle placement on a multicomponent structure.

Confirmation that all four materials (Ru, CdSe, CdS, and Pt) are present in distinct positions of the hybrid heterostructure is seen in the elemental analysis (Figure 5 and Figure S9). Our design schematic was successfully executed with several tailored synthetic steps. Similar to advanced organic synthesis, this multistep assembly of colloidal building blocks is challenged by low yields. The limiting step appears to be the successful growth of CdS rods on the CdSe-Ru dimers. Nevertheless, this structure represents advancement in the controlled assembly of hybrid heterostructures.

The nanoscience community has gained impressive control over the production of separate building blocks. We expect that in the near future the focus will gradually shift to skillful assembly of multicomponent structures. Assembly in sequential steps adds a dimension of freedom to the design and production of sophisticated structures. In designing a hybrid heterostructure, issues such as surface characteristics, ligand compatibility, stability of preformed components,

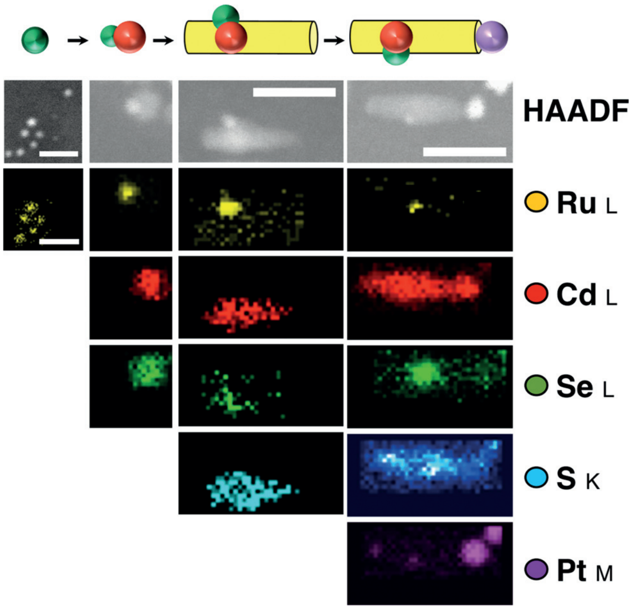

Figure 5. HAADF and elemental analysis of the different components within the heterostructure. Scale bar: 10 nm for Ru and 20 nm for the rods.

redox nature of the reaction, and growth chronology, must be addressed. Attention should also be given to alternative potential outcomes of each successive chemical transformation, such as material depositing in unwanted locations.

The boundaries of what is achievable with colloidal synthetic techniques are constantly being redefined. We believe the work presented here signifies an important milestone in this journey.

Experimental Section

All syntheses and sample manipulation were done under Argon. Thermolysis of 90 mg of [Ru$_3$(CO)$_{12}$] in 4 mL of TOA, 1 g of HDA and a 20% O$_2$/Ar flow at 200 °C for 1 hour at 100 mL min^{-1} produced Ru@Ru$_x$O$_y$. About 10^{-7} mol Ru@Ru$_x$O$_y$ dots were redispersed in 1 mL of DCB and 0.5 mL OLAm and 20 mg Se powder added. A 125 mg/1 mL DCB solution was prepared. Cd-oleate was formed at 210 °C using 64 mg CdO, 1 mL OAc and 5 mL octyl ether. The Ru/Se mixture was rapidly injected into the Cd-oleate at 200 °C and cooled after 4 min. The dimers were collected after the PPA/DCB solution was injected at 150 °C, then washed and redispersed in trioctylphosphine for CdS growth using a protocol by Talapin et al.,[28] with modifications. Pt tipping of the CdS nanorod was done using a protocol by Habas et al.[30] Further details are given in the Supporting Information.

Keywords: nanoparticles · quantum dots · semiconductors · synthetic methods · water splitting

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