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Hybridization of thiol-functionalized poly(phenylacetylene) with cadmium sulfide nanorods: improved miscibility and enhanced photoconductivity†

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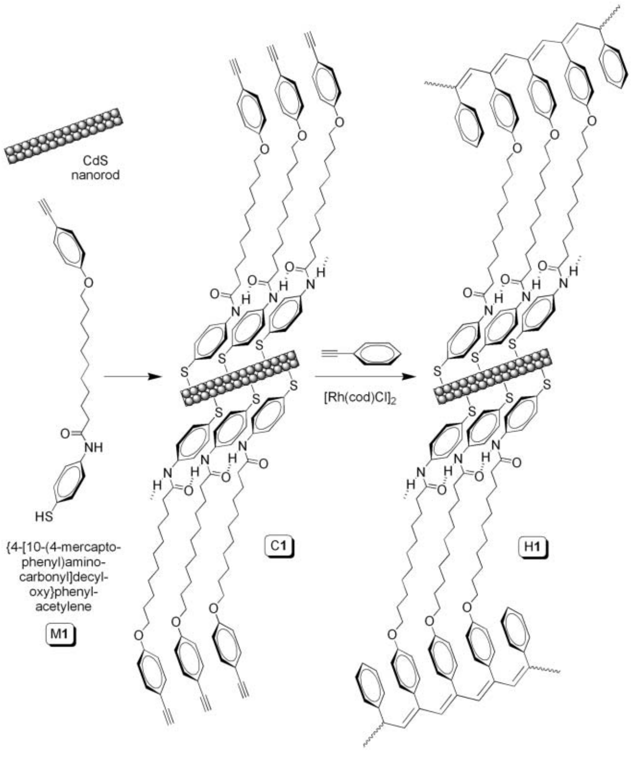
Molecules of a thiol-functionalized phenylacetylene derivative were assembled on the CdS nanorod surface and copolymerized with phenylacetylene, affording an inorganic semiconductor–conjugated polymer hybrid with excellent solubility and high photoconductivity.

Nanoscopic hybridization of inorganic semiconductors with organic polymers offers the possibility to create new hybrids with combined advantageous attributes from the two constituents (*e.g.*, high charge mobility of inorganics and ready processability of organics), which may find technological applications as active materials in the construction of advanced photoelectronic devices such as photovoltaic cells (PVCs) or solar cells for the generation of "green electricity" by harvesting light from the sun.[1] Promising results have been obtained along this line of research endeavor. CdSe nanorods, for example, were hybridized nanodimensionally with a soluble polythiophene derivative, whose PVCs exhibited high external quantum efficiencies.[1a] Nanocomposites of ZnO nanocrystals and a poly(phenylenevinylene) derivative were made and their PVCs showed impressive performance.[1b] Polyacetylenes are the best-known conjugated polymers,[2] but their hybridization with inorganic semiconductors remains an almost unexplored area of research.[3]

Inherently, inorganic semiconductors and organic polymers are mutually immiscible. Their mixtures tend to be nonuniform and inhomogeneous due to the detrimental processes involved such as self-aggregation and phase separation. In our previous work, we tackled this problem by taking advantage of the electrostatic interactions between metallic and ammonium ions and succeeded in the preparation of homogeneous films of perovskite–poly(1-phenyl-1-alkyne) hybrids.[3] In this work, we tried to develop a new approach. By utilizing the bonding interactions of a transition metal semiconductor with a thiol functional group,[4] we accomplished the hybridization of CdS nanorods with poly(phenylacetylene) (PPA) chains (Scheme 1). Nanorods, rather than nanoparticles, were used in this study because the former naturally provide a directed path for charge transport.[1] PPA is chosen as the parent form of polymer because it is a well-investigated photoconductive polyacetylene derivative.[5] It was envisaged that the nanohybrid of CdS and PPA would exhibit high photoconductivity. In this Communication, we prove this is indeed the case.

The CdS nanorods used in this study were prepared by a solvothermal reaction according to a published procedure (ESI†).[6] A phenylacetylene (PA) monomer carrying a thiol end group (**M1**) was synthesized *via* the multi-step reaction route shown in Scheme S1 (ESI†). The intermediate obtained in each reaction step and the final product (**M1**) were characterized by standard spectroscopic methods, from which satisfactory analysis data were obtained.



Scheme 1 Assembly of the molecules of monomer **M1** on the surface of CdS nanorod gives composite **C1**, whose copolymerization with phenylacetylene yields CdS–poly(phenylacetylene) hybrid **H1**.

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† Electronic supplementary information (ESI) available: Preparation and characterization data of **M1**, **C1**, **H1**, **B1**, **B2** and CdS; ^{1}H NMR spectra of **M1** and **H1**; MS spectrum of **M1**; absorption spectra of CdS, **M1** and **C1**; (HR)TEM images and EDX data of **C1**; TGA thermograms of PPA, CdS and **H1**; SEM and TEM images of **B1**; SEM images of **B2**; TEM image of **H1**; determination of CdS content in **H1** by elemental analysis; experimental procedures for the photoreceptor fabrication and photoconductivity measurement. See DOI: 10.1039/b617595c

We initially planned to prepare the hybrid by incorporating the CdS nanorods into preformed polymer of **M1**, as we did in our previous work on the perovskite system.[3] Monomer **M1** could, however, not be polymerized by the Mo-, W-, Ta- and Nb-based "classic" catalysts for acetylene polymerization[2] because of the "toxic" effect of its mercapto hydrogen on the transition-metal catalysts. While the monomer could be polymerized by rhodium-based catalysts such as $[Rh(cod)Cl]_2$ (cod = 1,5-cyclooctadiene), the polymerization product was completely insoluble in common solvents, possibly due to the "physical cross-linking" between the "free" thiol pendant groups.

We thus considered an alternative strategy: to allow molecules of **M1** to assemble on the CdS nanorod surface, for it should consume the active mercapto hydrogen of the monomer (*cf.* Scheme 1). The nanorods and the monomer were thus mixed in dichloromethane (DCM) and gently stirred for 24 h. The resulting nanocomposite (**C1**) was collected by precipitation and was then washed with DCM several times. The indelible binding of the **M1** molecules on the surfaces of the CdS nanorods and the complete removal of the unbound **M1** molecules were confirmed by chromatographic and spectroscopic analyses (ESI†).

Composite **C1** was soluble in organic solvents and could thus be used as a nanodimensional monomer to copolymerize with PA in the presence of a Rh catalyst of $[Rh(cod)Cl]_2$ (ESI†). The lack of an active mercapto hydrogen in **C1** enabled its copolymerization mixture to remain homogeneous during the whole reaction process. Moreover, the isolated hybrid (**H1**) was soluble in organic solvents such as chloroform, DCM and tetrahydrofuran. Thin films could be readily prepared by simply casting the hybrid solutions onto solid substrates.

The hybrid formation was confirmed by spectroscopic analyses (ESI†). A set of IR spectra is shown in Fig. 1 as an example. In the spectrum of **M1**, the ≡C–H stretching band is seen at 3293 cm^{-1}. This peak disappears in the spectrum of **H1** (Fig. 1B), indicating that the acetylenic triple bond has been completely consumed by the copolymerization reaction. On the other hand, absorption bands associated with the stretching of the methylene and carbonyl groups are observed at 2926–2851 and ~1675 cm^{-1}, respectively. These bands are absent in the spectrum of the PPA parent (Fig. 1C), confirming the integration of the **C1** unit into the hybrid structure.

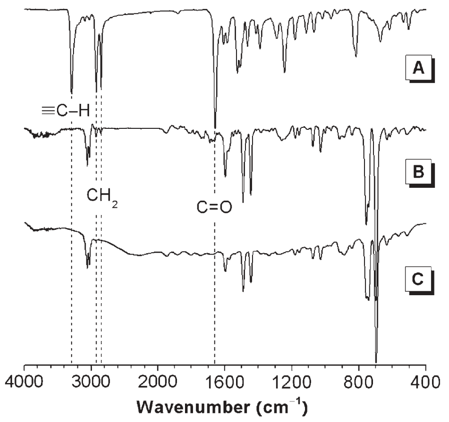

Fig. 1 IR spectra of (A) monomer **M1** and (B) hybrid **H1**. Data for PPA are shown in part C for comparison.

To verify the polymeric nature of **H1**, its molecular weight was estimated by gel permeation chromatography (GPC). To prevent the GPC system from potential damage by the inorganic nanorods, the hybrid was washed with concentrated hydrochloric acid to remove the inorganic component. After the acid pretreatment, the organic portion was subjected to GPC analysis, which gave a weight-average molecular weight of 72620 and a polydispersity index of 2.94, indicating that the acetylene polymerization reaction had proceeded as expected.

Upon excitation with UV light of 330 nm, the hybrid exhibits a fluorescence spectrum with emission maxima at 398, 458, 496 and 515 nm (Fig. 2). From the comparison with the spectra of its CdS and PPA parents, the photoluminescence of **H1** is clearly dominated by the attributes from its CdS component.[7] This is easy to understand, because PPA and its derivatives are known to be weak light emitters.[2]

The morphology of a thin film cast from an **H1** solution on an aluminum plate is characterized by a continuous surface decorated by discrete rod-like structures (Fig. 3A). According to the principle of electron microscopy, and by comparison with the morphology of the original nanorods used in the fabrication of **H1** (*cf.* Fig. 3D), the rod-like structures with high contrast can be assigned to the CdS nanorod component in the hybrid. The nanorods are dispersively distributed in the film: some of them lie parallel to the film surface, while others tilt from the surface normal. As can be seen from a deliberately generated fissure, the CdS nanorods are interspersed well throughout the film (Fig. 3B). In sharp contrast, the morphology of the film prepared by casting a solution of a blend of CdS and PPA (denoted as **B1**) features very large aggregates of the CdS nanorods, as manifested by its fluctuated, uneven surface (Fig. 3C). Evidently, the bonding interactions between the thiol groups in the polymer and the cadmium species in the nanorods have helped to enhance the miscibility of the two components, making it possible to uniformly disperse the CdS nanorods in the PPA matrix.

Thermogravimetric analysis (TGA) has been commonly used to estimate the weight fraction of a thermally stable component in a composite material.[3,8] The content of the CdS nanorods in the hybrid was estimated by measuring the TGA thermograms of **H1** and PPA (the thermogram of the nanorods was not taken because the sample was obtained by sintering the as-prepared CdS at

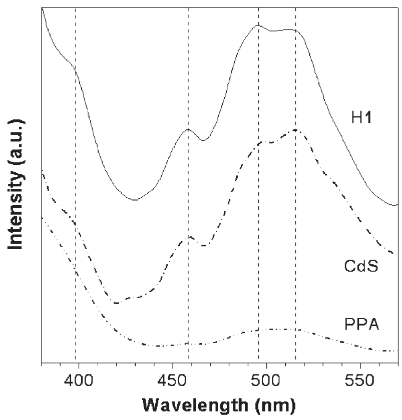

Fig. 2 Photoluminescence spectra of thin films of **H1** and CdS [blended with poly(methyl methacrylate) or PMMA]. Data for a PPA film are shown for comparison. Excitation wavelength: 330 nm.

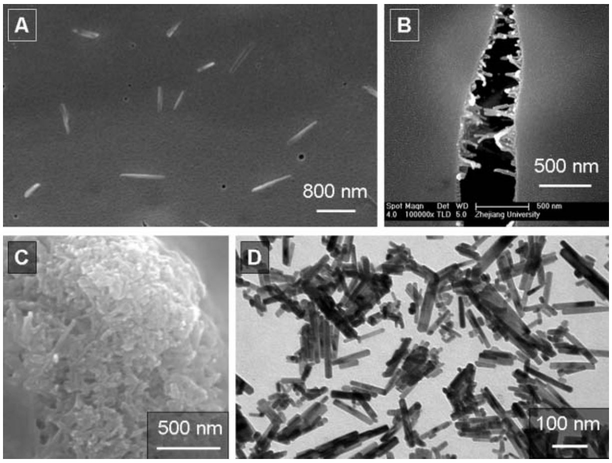

Fig. 3 SEM images of (A) an as-fabricated H**1** film, (B) an H**1** film with a deliberately torn fissure, and (C) a film of CdS–PPA blend (B**1**) that was prepared by the polymerization of phenylacetylene in the presence of the CdS nanorods. (D) TEM image of the CdS nanorods used in this study.

Table 1 Photosensitivity of the double-layered photoreceptor device prepared by using H**1**, CdS, PPA, B**1** or B**2** as charge generation material (CGM)[a]

CGM	V_0 (V)	R_d (V s^{-1})	V_r (V)	$t_{1/2}$ (s)	S (10^{-3} mm^2 (μW s)$^{-1}$)
H**1**	1027	25	317	2.63	34.3
CdS	749	22	308	4.74	19.0
PPA	891	25	308	3.67	24.5
B**1**	656	30	226	3.35	26.9
B**2**	675	35	252	4.30	21.0

[a] Exposed to a light with an intensity of 11 μW mm^{-2} from a halogen lamp. Abbreviations: V_0 = initial surface potential; R_d = dark decay rate; V_r = residual surface potential; $t_{1/2}$ = half discharge time under exposure; and S = photosensitivity. B**2** denotes a simple blend of CdS and preformed PPA.

~650 °C; ESI†). From the TGA data (ESI†, Fig. S6), the nanorod content was found to be *ca.* 10.8 wt%. Elemental analyses of the materials were also carried out (ESI†, Table S2), which gave a CdS nanorod content of ~9 wt%, very close to the value estimated from the TGA analysis.

Thanks to its solubility and film-forming capability, H**1** can be used as an active material to construct photoelectronic devices. A series of double-layered photoreceptors were prepared by a solution-casting process and their photoconductivities were evaluated by a photoinduced discharge technique (ESI†).[3a,5,9] Upon exposure to illumination by a halogen lamp, the initial surface potential of the photoreceptor using H**1** as CGM dropped quickly to its half value in as short a time as 2.63 s (Table 1, entry 1). Its photosensitivity (S) is 34.3 × 10^{-3} mm^2 (μW s)$^{-1}$, higher than those of all the devices using its parent forms of PPA and CdS as well as their blends (B**1** and B**2**) as CGMs.

In our previous study on the photoconduction in the devices prepared using polyacetylene derivatives as CGMs, we found that the introduction of phthalimido groups into poly(1-phenyl-1-alkyne)s as pendants can dramatically improve the performances of the devices due to the formation of charge-transfer complexes.[3a,10] Photoreceptors prepared from donor–acceptor nanocomposites are known to exhibit high photosensitivities owing to photoinduced charge transfers (PICT) between the donors and the acceptors.[9,11] As an *n*-type semiconductor, CdS works as an electron acceptor, while PPA functions as an electron donor in the hybrid. The PICT process takes place when the photoreceptor is illuminated. The strong bonding of the CdS nanorods with the PPA chains and the uniform distribution of the CdS nanorods in H**1** facilitate the PICT process and the successive charge separation and transport, hence enhancing its photosensitivity.

In summary, in this work we have developed a facile strategy for the hybridization of CdS nanorods with polyacetylene chains. Taking an approach of assembly plus copolymerization, we have successfully prepared a CdS–PPA nanohybrid that is fully soluble in common organic solvents and that can form homogeneous films when its solutions are cast on solid substrates. With the aid of the bonding interactions between the thiol groups and the cadmium atoms, the nanorods can be uniformly dispersed in the polymer matrix. The uniform distribution of the CdS nanorods in the hybrid film and the efficient PICT process between the *n*-type nanorods and the *p*-type polymer chains have synergistically boosted the photosensitivity of the hybrid photoreceptor. Noting that the thiol group can bond with metallic species in many other inorganic semiconductors, the process developed in this work may prove to be a versatile approach towards the fabrication of a wealth of inorganic–organic hybrids, using various combinations of different nanostructured inorganic semiconductors and conjugated organic polymers.

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