

Hyperbranched polymers meet colloid nanocrystals: a promising avenue to multifunctional, robust nanohybrids

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Abstract Colloid nanocrystals (NCs) mainly include metal nanocrystals, semiconductor nanocrystals, and insulator nanocrystals, exhibiting interesting size-dependent electrical, optical, magnetic, and chemical properties that cannot be achieved by their bulk counterparts. However, there's a critical problem that NCs tend to aggregate, which induces degradation of their performance. Hyperbranched polymers (HPs) possess excellent attributes of three-dimensional topology, low viscosity, good solubility, and plenty of modifiable terminal groups. The combination of NCs and HPs to form nanohybrids cannot only endow NCs with multifunctionality, uniform dispersibility, and splendid solubility but also can impart extra properties to HPs. This article reviews the recent progress and state-of-the-art of the synthesis and applications of NCs-HPs nanohybrids (NHBs). NHBs can be obtained by three approaches: HPs first (i.e., NCs are formed with the stabilizer of HPs), NCs first (i.e., HPs are grafted on the surface of as-prepared NCs), and ligand exchange (the original ligand of NCs is replaced with HPs). Various HPs including hyperbranched poly(amidoamine), polyethylenimine, polyglycerol, polyester, polyamide, polyurethane, and poly(3-ethyl-3-hydroxy-methylloxetane), as well as sorts of NCs such as metals (e.g., Ag, Au, Pd, Pt, and Rh), quantum dots (e.g., ZnO, CdS, CdTe, CdSe, and SnO₂), magnetic oxides (e.g., Fe₃O₄), rare earth compounds, and so forth, have been used to obtain NHBs. The NHBs can be applied in nanocatalysis, antimicrobia,

biosensor, biological labeling, and other fields promising their bright future.

Keywords Hyperbranched polymers · Nanocrystals · Quantum dots · Dendritic polymers

Introduction

Nanoparticles, nanoclusters, and nanocrystals are the most frequently used terms of nanomaterials. Nanoparticles are routinely defined as particles with sizes between about 1 to 100 nm in two or three dimensions [1]. Nanoclusters are expected to be 1–10 nm with near-monodisperse size distributions ($\leq 15\%$) [2]. Nanocrystals (NCs) are single crystalline particles with at least one dimension between 1 and 100 nm [3]. Colloidal nanocrystals are solution grown, nanometer sized, inorganic particles that are stabilized by a layer of surfactants attached to their surface [4]. Due to their small size, large surface-to-volume ratio, and discrete electronic energy state, NCs show unique physical and chemical properties extremely different from both the corresponding single atom and macroscopic material [5]. From the electronic nature point of view, NCs mainly comprise metal NCs such as Ag, Au, Pt, Pd, Cu, Co, etc., insulator NCs such as Fe₃O₄, CuO, NiO, etc., and semiconductor NCs such as CdSe, CdTe, CdS, ZnS, ZnO, etc. As revealed in the published reviews, every kind of NCs has its own application fields [6–10]. For instance, metal NCs can usually be used as bactericide and nanocatalysts, and semiconductor NCs are generally used in biological field such as cell labeling as well as energy field such as solar cells and optical devices. Hence, NCs have aroused increasing interests of researchers in chemistry, physics, biomedical, material science, and other fields, as

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demonstrated by the rapid increase of the number of publications per year (Fig. 1).

The chemical methods have conspicuous advantages in controlling the size and shape of NCs, which would seriously influence the properties. In this respect, some critical reviews have been published [4, 11–14]. On the other hand, NCs show aggregation tendency because of strong interactions between each other owing to colossal surface energy, resulting in poor change of performance. Thus, besides the size and shape, dispersibility and stability of NCs are also crucial for their performance, functions, and real applications. Various stabilizers including inorganic ligands [15], small organic molecules [16, 17], linear polymers [18], and dendritic polymers [19, 20] have been used to improve the stability and dispersibility of NCs (Fig. 2). Among these stabilizers, dendritic polymers have globular structures and lots of intramolecular holes, showing superb capability in the synthesis of monodispersed, ultrastable NCs.

Dendritic polymers that chiefly consist of dendrimers and hyperbranched polymers (HPs) represent the new emerging polymer architecture following the conventional linear, chain-branched, and cross-linked polymer architectures [21]. Dendrimers have well-defined, regular-branched structures as well as monodispersed molecular weights, whereas they are only available through tedious multi-step synthesis protocol. The dendrimer-stabilized NCs have already been reviewed recently [19]. HPs have similar unique physical and chemical properties to dendrimers such as low viscosity, good solubility, intramolecular nanocavities, and plenty of functional groups. More significantly, HPs can be facilely and scalably produced by one-pot reaction. Therefore, they have been widely used for various purposes such as nanocapsules to encapsulate dyes and organometallics, nanoreactors for some reactions, scaffolds for fabrication of organic–inorganic hybrids, base for various coating resins,

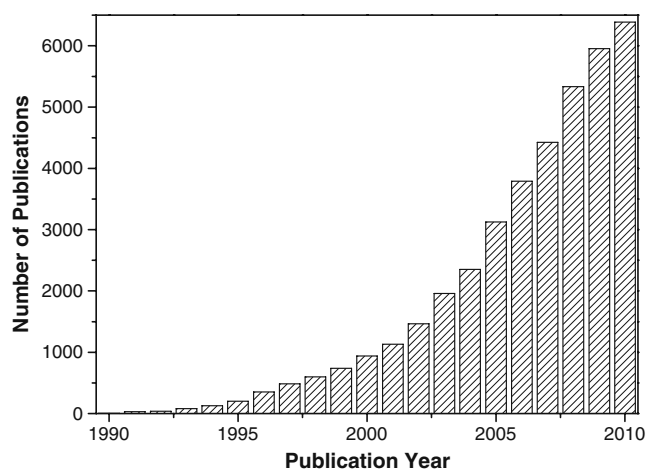


Fig. 1 Numbers of publications per year since 1990 with the topic of “nanocrystals” searched by ISI Web of Science

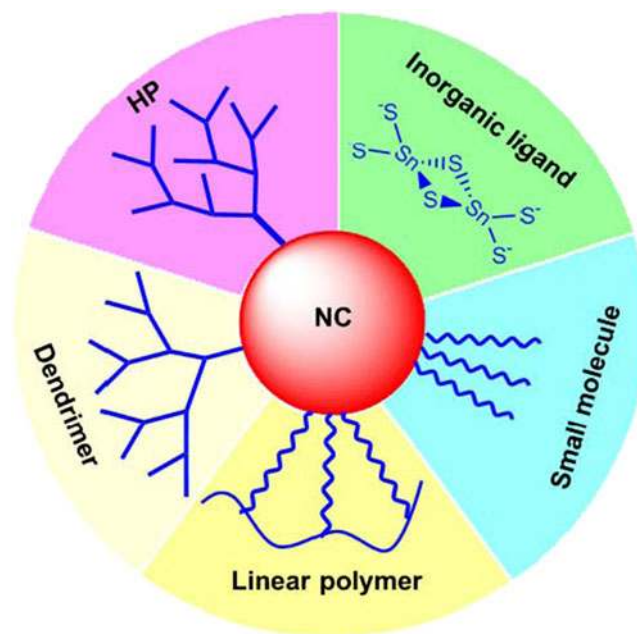


Fig. 2 Different kinds of stabilizers used to synthesize nanocrystals

modifiers and additives to improve performance of composites, and so on, which have been commented and summarized in many excellent reviews [21–27]. Here, we only focus our attention on the synthesis of nanohybrids (NHBs) composed of HPs and NCs. Applications of the obtained NCs such as Pt, Pd NCs as nanocatalyst for hydrogenation reactions, Ag NCs as bacteriostat, semiconductor CdTe NCs as coloring agent for cell labeling, iron oxide NCs as magnetic source in recycling catalyst, and so forth, are also discussed.

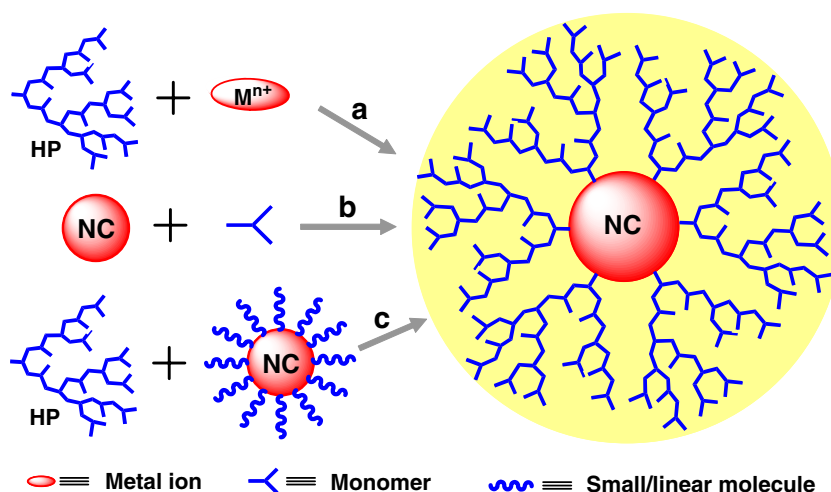
Synthesis

As shown in Fig. 3, three strategies have been developed to synthesize NHBs: (1) HPs first (or shell first), signifying HPs are used as stabilizer to directly synthesize NCs, (2) NCs first (or core first), which allows grafting or in situ growth of HPs on the core surfaces of preformed NCs, and (3) ligand exchange, denoting that NCs are initially prepared using small molecules or linear polymers as ligands/stabilizers, followed by ligand-replacing process with pre-synthesized HPs.

HPs first

The three-dimensional structure of HP provides large amount of nanocavities both intra- and inter-molecule, which can be used as boxlike container to encapsulate metal ions [21–27]. In the presence of HPs and metallic cations, metal and metal-contained NCs could be obtained by the addition of a

Fig. 3 Three strategies for the preparation of nanohybrids of nanocrystals and hyperbranched polymers: **a** “HPs first”, **b** “NCs first”, and **c** “ligand exchange”



reductant or corresponding anions. Furthermore, HPs possess abundance of functional groups, and some of them can complex with metal ions and then stabilize resulting NCs via multivalence mode of interactions. Various HPs have been used as stabilizers to prepare series of NCs (Fig. 4, Table 1). Notably, we call HPs as “stabilizer” instead of “template” since “template” is not such right that means the size of NCs can be well controlled through changing the size of HPs, but in fact it is not always true.

Hyperbranched poly(amidoamine) (HPAMAM)

HPAMAM is a chemical analog of the well-known poly(amidoamine) dendrimers. Four types of HPAMAM were tried as stabilizers for in situ formation of NCs, named HPAMAM-1 [obtained from tris(2-aminoethyl)amine and tris(2-di(methyl acrylate)-aminoethyl amine), HPAMAM-2 (synthesized from *N,N'*-methylene bis-acrylamide and *N*-aminoethyl piperazine), HPAMAM-3 (made from diethylene triamine and methyl acrylate), and HPAMAM-4 (prepared by reaction of ethylenediamine and methyl acrylate), respectively.

Marty et al. used HPAMAM-1 to synthesize Au [28, 29], Pt [30], and ZnO nanoparticles (NPs) [31]. In detail, Au NPs were fabricated in aqueous solution of HPs with NaBH_4 as the reductant [28]. Comparative studies of HPAMAM-1 and PAMAM dendrimer reveal that the obtained NPs are quite similar except for that larger average diameter of Au from HPAMAM-1. The average size of the NPs can be easily adjusted by changing the ratios of $[\text{HAuCl}_4]/[\text{polymer}]$ and $[\text{NaBH}_4]/[\text{HAuCl}_4]$ [29]. The functionalization of HPAMAM-1 with gluconolactone can improve the stability of Au NPs. Very recently, hyperbranched core-multishell structure [HPAMAM-1 as core, long alkyl chain as inner shell, and poly(ethylene glycol) (PEG) as outer shell] was designed to synthesize water-

soluble ZnO quantum dots (QDs) via decomposition of an organometallic precursor, dicyclohexyl zinc, in tetrahydrofuran [31]. The obtained ZnO QDs exhibited stable photoluminescent properties, and could be redispersed in various solvents such as water, toluene, and ethanol, implying the importance of fine structures of HPs.

HPAMAM-2 was used to synthesize Ag NPs with sizes of 10–40 nm by changing either the ratio of Ag^+ to amino groups or the reaction temperature [32]. Later, the influence of the HPs structure as well as molecular weight on size and size distribution of Ag NPs were investigated [33, 34]. Using HPAMAM-2 both as a stabilizer and a reductant, Yan and co-workers prepared Ag NPs with diameters from 4 to 15 nm by adjusting the N/Ag ratio [35]. Besides, a series of colloid Ag and Au NPs can also be obtained by employing methyl-terminated HPAMAM-2 as the stabilizer [36]. Similarly, HPAMAM-3 has also been used both as a stabilizer and a self-reducing agent to synthesize Ag NPs through one-step process [37]. The resulting NHBs can be utilized to improve antibacterial properties of cotton fabric.

Zhu and co-workers have constructed a double-hydrophilic HP by linking poly(ethylene glycol) mono-methyl ether arms and a water-soluble HPAMAM-4 core with pH-sensitive acylhydrazone bonds (Fig. 5) [38]. Then pH-responsive CdS QDs were formed in situ in the core-shell structure. The fluorescence intensity of QDs increased greatly with a decreasing pH of the solution, owing to the departure of PEG arms following with the break of acylhydrazone bonds.

Hyperbranched polyethylenimine (HPEI)

HPEI exhibits good water solubility due to its primary, secondary, and tertiary amino groups. For the preparation of inorganic NPs, both modified and unmodified HPEI were

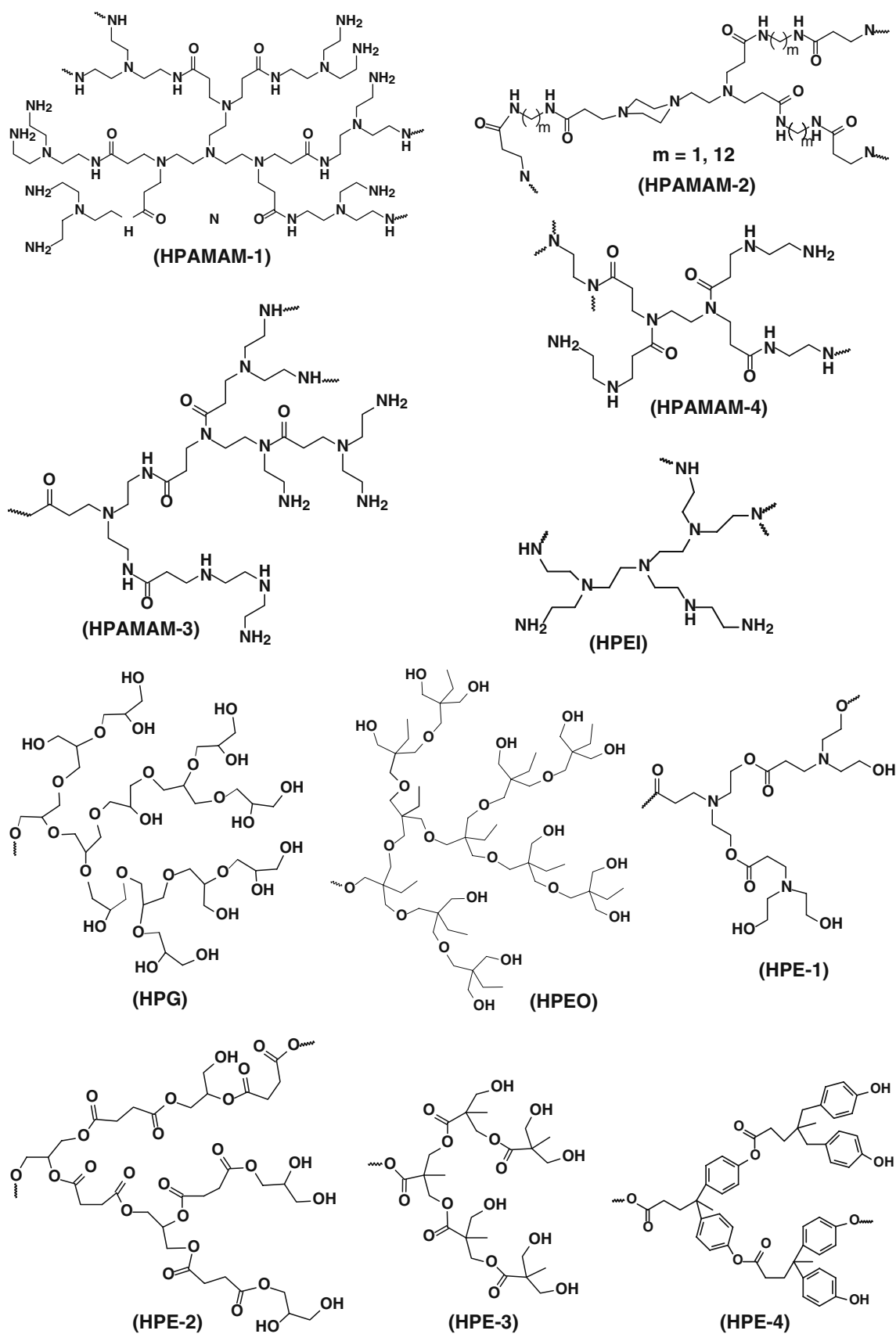


Fig. 4 Chemical structures of HPs used as stabilizers to synthesize nanocrystals. The terminal functional groups might be modified in the real work (see Table 1)

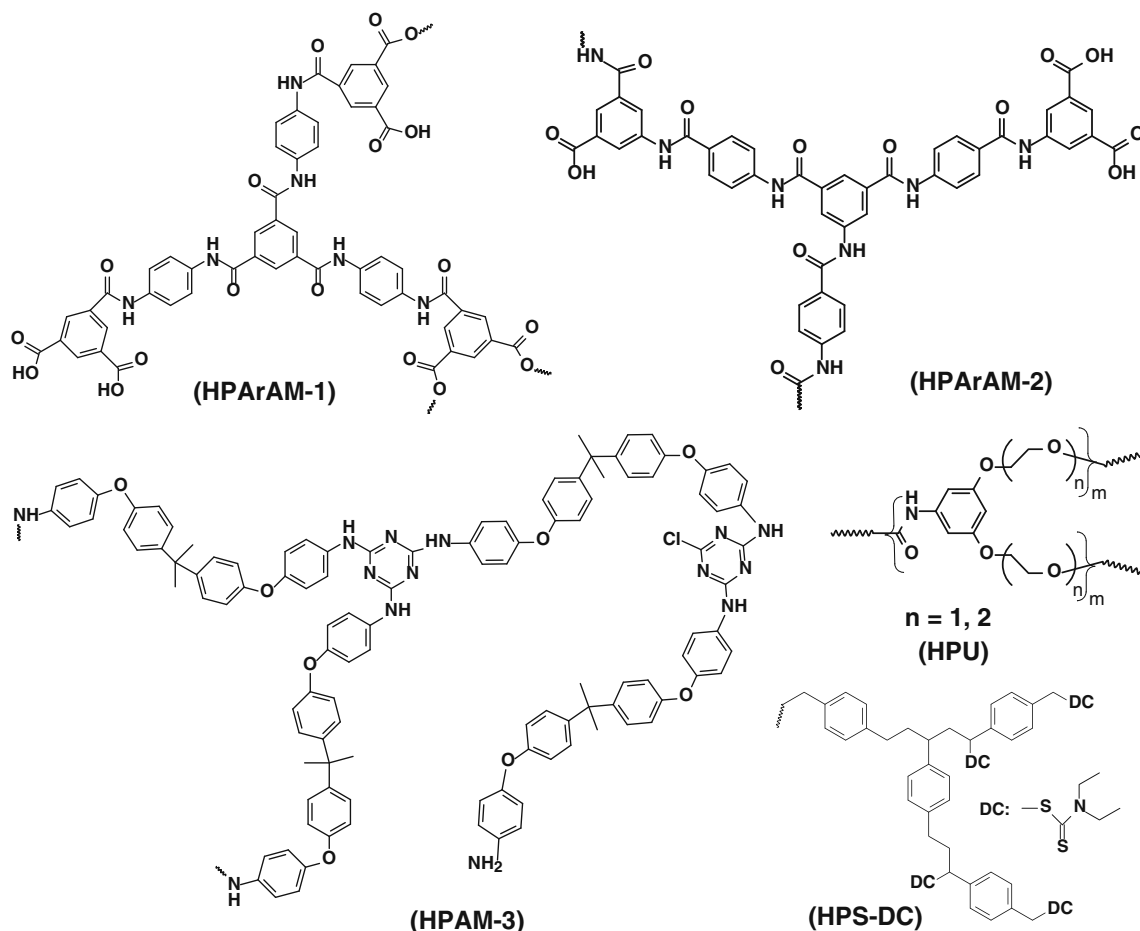


Fig. 4 (continued)

used. Long aliphatic chains were frequently used to modify HPEI. For instance, Mecking et al. prepared Ag NPs using linear alkyl-modified HPEI as the stabilizer [39, 40]. The obtained NHBs can be applied as effective and environmentally friendly antimicrobial surface coatings. Rh NPs have also been obtained and used for the hydroformylation of 1-hexene [41]. Utilizing the same amphiphilic stabilizer, Ag NPs have also been prepared at the interface of water and chloroform using NaBH_4 as the reductant [42], bearing the advantage of easy purification of the resulting NPs because of the insolubility of the reducing agents in organic phase. Alternatively, Ag NPs can be prepared in the fluoruous phase with the stabilizer of HPEI-containing perfluorinated groups [43].

Hydrophilic carbohydrate (e.g., glycidol, gluconic acid, and lactobionic acid) modified HPEI was also employed to synthesize metal NCs (e.g., Ag, Au, Cu, and Pt) in aqueous solution via a two-step process: complexation of core-shell HPs with metal ions and reduction of the ions to zero valent metal by NaBH_4 [44]. The immobilization of carbohydrate cannot only stabilize the NPs much efficiently but also can improve the biocompatibility of the NHBs.

The core-multishell structure made by Marty and co-workers with HPEI as the core, long alkyl chain as the inner shell, and PEG as the outer shell has been used to synthesize in situ Au NPs without an additional reductant [45]. The amphiphilic structure of the shell allows the stabilization of preformed hydrophobic and hydrophilic Au NPs in both water and organic solvents.

Apart from the common solvents, supercritical CO_2 (SCCO_2) due to its non-toxicity, non-flammability, and natural abundance, has been promoted as a sustainable and “green” solvent. SCCO_2 has also been utilized to prepare Pd and Ag NPs with carbonyl-diimidazole-activated carboxylic acid-modified HPEI ($\text{HPEI-CO-C}_{10}\text{H}_4\text{F}_7$) as the stabilizer [46]. The greatest advantage of this method is that reagents do not have to be soluble, but just need to be swollen in SCCO_2 , therefore enables the use of a broader range of polymers and precursors as compared with the classic solution chemistry.

Except for the chemical modifications, non-covalent physical interaction can also be utilized to alter properties of HPEI. Zhu et al. have reported the synthesis of CdS NCs within supramolecular self-assembly nanoreactors con-

Table 1 Overview of NCs prepared by “HPs first” strategy

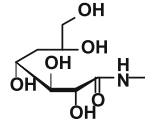
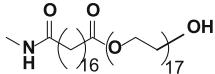
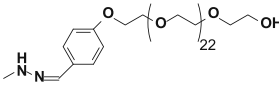
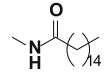
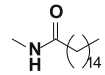
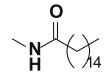
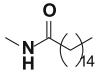
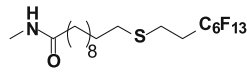
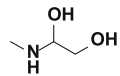
HPs	Mn/ k	Terminal Groups	NCs	Size/ nm	Conditions	Ref
	9.7	-NH ₂	Au	4~7	Water/HAuCl ₄ , NaBH ₄ /r.t.	[28]
HPAMAM-1	9.7/13.8		Au	4~9	Water/HAuCl ₄ ,N -aBH ₄ / r.t.	[29]
	9.7/13.8	-NH ₂	Pt	1.8/1.6	Water/K ₂ PtCl ₆ , NaBH ₄ / r.t./48 h	[30]
	3.8/7.0/6.3		ZnO	3~5	THF/Zn(Cy) ₂ , Ar/ r.t./2 d	[31]
	0.9	-NH ₂	Ag	10~40	Water/AgNO ₃ , NaBH ₄ / r.t./2 h	[32]
	2.5/3.0	-NH ₂	Ag	9.3,10.7/3 .9, 200	Water/AgNO ₃ , NaBH ₄ / r.t./2 h	[33]
HPAMAM-2	1.4/4.0/7.9	-NH ₂	Ag	8.7, 9.6, 10.2	Water/AgNO ₃ , NaBH ₄ / r.t./2 h	[34]
	26	-NH ₂	Ag	4~15	Water/AgNO ₃ /r.t ./24 h	[35]
	140 (Mw)	-N(CH ₃) ₂	Ag, Au	1.4~7.1 3.9~7.7	Water/AgNO ₃ or HAuCl ₄ ·4H ₂ O/r.t ./12 h	[36]
HPAMAM-3	2.7	-NH ₂	Ag	10~30	Water/AgNO ₃ /r.t .	[37]
HPAMAM-4	3.4		CdS	4.2	Water/Cd(OAc) ₂ , Na ₂ S, N ₂ /r.t./49 h	[38]
HPEI	5 (Mw)		Ag	1~2	Toluene/AgNO ₃ , Li[HBET ₃]/r.t.	[39]
	5, 25 (Mw)		Ag	1.2, 2.3	Benzene//AgNO ₃ , H ₂ /r.t.	[40]
	5 (Mw)		Rh	2~3	Toluene/ Rh(acac)(C ₂ H ₄) ₂ , H ₂ /r.t., 1.5 bar/3 d	[41]
	25 (Mw)		Ag	3~5	Toluene(Chlorof- orm)&Water/Ag- NO ₃ ,NaBH ₄ / r.t.	[42]
	4.5		Ag	3.9	---	[43]
						

Table 1 (continued)

HPs	Mn/ k	Terminal Groups	NCs	Size/ nm	Conditions	Ref
	0.6/3.6/9.6 /10.5		Ag, Au, Pt		Water/AgNO ₃ , (HAuCl ₄ ,K ₂ PtCl ₆ ,)NaBH ₄ / r.t.	[44]
	5 (Mw)		Au	6.2	Water/HAuCl ₄ /2 5°C/ a few days	[45]
	5 (Mw)		Pd, Ag	3.3, 6.0	Supercritical CO ₂ /Pd(acac) ₂ ,A -gNO ₃ ,H ₂ /100°C /1.5 h	[46]
	10	-NH ₂	CdS	3	Water-CHCl ₃ /Cd (AC) ₂ ,Na ₂ S/ r.t.,N ₂ / 50 h	[47]
	25 (Mw)	-NH ₂	Au	10-70	Water/HAuCl ₄ /r.t. /16 h or Ethanol/HAuCl ₄ / r.t. /80 h	[48]
	25 (Mw)	-NH ₂	Pt	2.88	Water/K ₂ PtCl ₆ , N ₂ /UV/1 d	[49]
	25~50 (Mw)	-NH ₂	CdS, ZnS, CdS@ZnS, ZnS@CdS, CdS@ZnS @CdS, ZnS@CdS @ZnS	7-53,4-17 ,19-24,23 -35,108-1 85,100-13 0	Water/CdCl ₂ , ZnCl ₂ , Na ₂ S/Icebath	[50]
	25 (Mw)	-NH ₂	SnO ₂	3-3.5	Ethanol/Na ₂ SnO ₃ ,CO ₂ /r.t./>2.5 h	[51]
	25 (Mw)	-NH ₂	Fe ₃ O ₄ @Au	50-150	Water/Fe ₃ O ₄ -PEI -Au _{seed} -PEI,NaO H, iteration of HAuCl ₄ ,NH ₂ OH ,HCl/r.t.	[52]

Table 1 (continued)

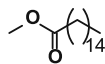
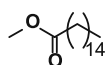
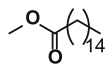
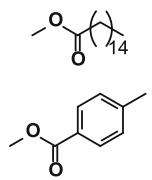
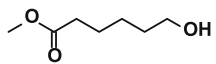
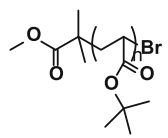
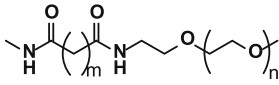
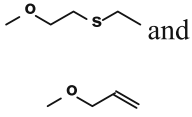
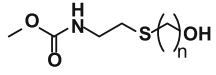
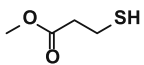
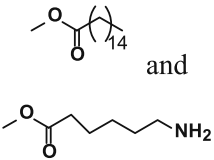
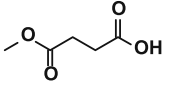
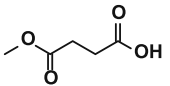
HPs	Mn/ k	Terminal Groups	NCs	Size/ nm	Conditions	Ref
HPG	1.7,4.7		Pd	2.1, 5.2	Toluene/H ₂ or heating to 60°C/PdCl ₂ or Pd(OAc) ₂ /several h	[53]
	2~6		Pd	2.2, 4.9	Toluene/Pd(OAc) ₂ /60°C/overnight	[54]
	3,5.5		Pd	1.2,2.3	Toluene-methol/PdCl ₂ ,NaBH ₄ /r.t./1 h	[55]
	2,4,6,10		Pd	20~400	1.Toluene/PdCl ₂ , CO or H ₂ /overnight 2.Toluene/Pd(OAc) ₂ /60°C/overnight 3.Toluene/Pd(OAc) ₂ , Li[HBET ₃]/r.t.	[56]
	17		Ag	>10 for FFS, clusters for FSF	FFS or FSF	[57]
	--	 n=36,6	Ag	2-3	Water/AgNO ₃ /r.t./UV/1-9 h	[58]
	3,6	 m=10, 16; n=7, 16	Pt	2~3	Water/H ₂ PtCl ₆ ·H ₂ O,NaBH ₄ /r.t./48 h	[59]
	2,8		Au	3.0, 5.1	Water-toluene/H-AuCl ₄ ,NaBH ₄ /r.t./2 d	[61]
	2,5,8	 n=2,6,11	CdSe, CdS		Methol/Cd(NO ₃) ₂ ·4H ₂ O, Na ₂ S/r.t. or Methol/Cd(NO ₃) ₂ ·4H ₂ O, Na ₂ Se, N ₂ /r.t.	[62]


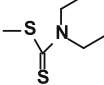
Table 1 (continued)

HPS	Mn/ k	Terminal Groups	NCs	Size/ nm	Conditions	Ref
	1.9		Pt	4.5	Ethanol/HAuCl ₄ , NaBH ₄ / r.t./1 h	[63]
	---	-OH	Au	2.5	Water/HAuCl ₄ ·3H ₂ O, NaBH ₄ , NaOH/r.t.	[66]
HPE-1	---	-OH	Cu	10~150	Water/CuCl ₂ , NaBH ₄ , NaOH, oxygen free/r.t./6 h	[67]
	---	-OH	Ag	10~50	Water/AgNO ₃ , NaBH ₄ /r.t./several h	[68]
HPE-2	2.7	-OH -COOH	Ag	7.7	Ethanol-water/AgNO ₃ , KOH, surfactant, N ₂ /UV	[69]
	---		Ag	2~4	Air-water interface/ AgNO ₃	[70]
HPE-3	---	-OH 	PbS hollow sphere	50~70 10~20 of wall thickness	Water-acetone/Pd-(acac) ₂ , Na ₂ S/25 °C/27 h	[71]
	---		PbS	7.8	Water-acetone/Pd(NO ₃) ₂ , Na ₂ S ₂ O ₃ , Isopropanol/r.t. ⁶⁰ Co gamma-ray DMAc/Ti(iOPr) ₄	[72]
HPE-4	5.1	-OH or -Si(OEt) ₃	TiO ₂	15, 6	1,6-diisocyanato hexane, dibutyltin dilaurate/70 °C under vacuum/2 d	[73]

structured by terminal amino groups of HPEI and palmitic acid via electrostatic interaction [47]. The obtained oil-soluble NCs can be easily transferred to water phase by adding excess triethylamine, due to the break of the interaction between HPEI and palmitic acid. The highlight of this work is that water-soluble HPSs can be used to prepare NCs in the organic phase, and the phase transfer between organic and aqueous phases for NCs can be readily realized.

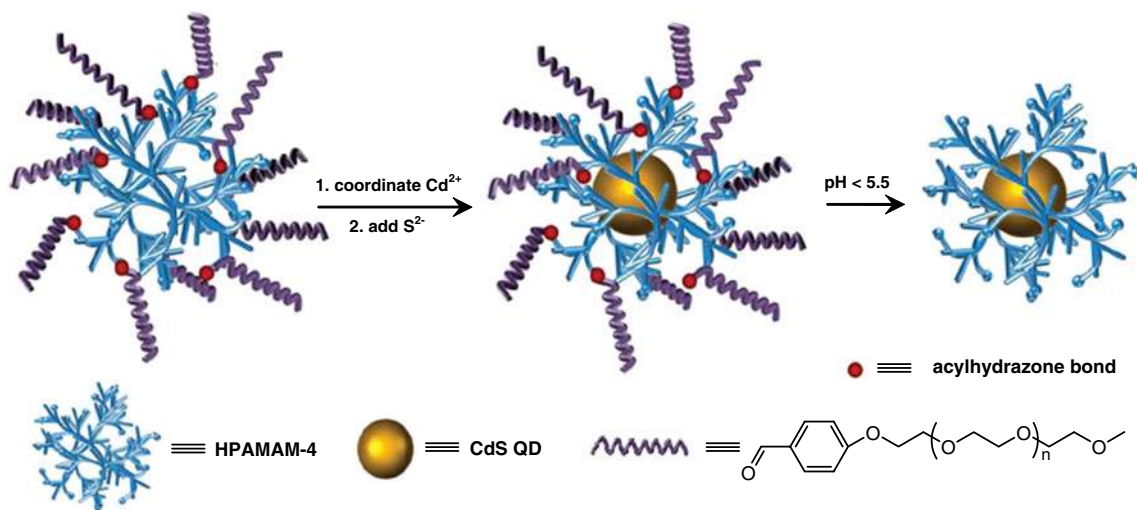
Unmodified HPEI has been used directly as a stabilizer to prepare metal NCs and semiconductor NCs as well. Similar to HPAMAM, the amino groups of HPEI can be utilized as reducing sites to prepare metal NPs. For example, Au NPs have been synthesized at room temperature in aqueous solution of HPEI, which acts as both a stabilizer and a reductant [48]. The NHBs can assemble into a large area of 2D aggregates at the interface of toluene and water through either heating the

Table 1 (continued)

HPs	Mn/ k	Terminal Groups	NCs	Size/ nm	Conditions	Ref
HPArAM-1 ,2	23.8, 42.5, 100.2	-NH ₂ -COOH	Pd	--, 3.5, 2.5	Water, CH ₃ COO- H/PdCl ₂ , NaBH ₄ / r.t. for 48 h and 50 °C for 2 h.	[74]
	23.8, 42.5, 100.2	-NH ₂ -COOH	Pd	2.9, 3.2, 2.8	DMF or DMSO/ PdCl ₂ , H ₂ , N ₂ /r.t./ 53 h	[75]
HPAM-3	5.2 (Mw)	-NH ₂	Ag	7.2	DMSO-water/ AgNO ₃ , NaBH ₄ / r.t./ 40 min	[77]
HPU	--	-OH	Ag ₂ S	4~10	DMF/AgNO ₃ , Thioacetamide/r.t ./3 h	[79]
	--	-OH	Ag	~10	Ethanol/AgNO ₃ , UV irradiation/4,24,2 6 h	[80]
HPEO	2		ZnO	3~6	Toluene/Et ₂ Zn, A r/3 h	[82]
HPS-DC	19.5(Mw)		Ag	3	Water/AgNO ₃ , U V irradiation/0.5 h	[82]

mixture of toluene and suspension of NHBs or adding benzenethiol to the toluene phase at room temperature. Besides, monodispersed Pt NCs can be obtained in the presence of HPEI with the aid of UV irradiation [49].

Preparation of complex semiconductor nano-heterostructures has drawn considerable attention due to the enhanced optical and electrical properties compared to the single-phase semiconductor NPs. CdS and ZnS NPs and their core/shell nano-

**Fig. 5** Preparation of water-soluble CdS QD/HPAMAM-g-PEG nanocomposites with pH-sensitive properties [38]

structures have been prepared in aqueous solution of HPEI [50]. Also as semiconducting materials, SnO₂ NPs have been synthesized with a series of dendritic hosts such as HPEI, PAMAM, and poly(propyleneimine) [51]. Different from other reports that utilize high temperature of reaction condition or moisture-sensitive reagents, Fahlman et al. have utilized simple oxidation of an encapsulated stannate salt via a reaction with carbon dioxide under ambient conditions, obtaining NPs smaller than 10 nm with excellent dispersibility. In addition, HPEI can act as a linkage to attach gold seeds onto magnetite core owing to the electrostatic interaction, then Au shell is in situ grown on the Fe₃O₄ core, obtaining 50–150 nm magnetite–gold core-shell NPs [52]. The coating of gold NPs with the help of HPEI cannot only maintain magnetic properties but also can decrease the aggregation of magnetite NPs.

Hyperbranched polyglycerol (HPG)

HPG consists of a highly flexible aliphatic polyether backbone and lots of terminal hydroxyl groups, imparting its excellent water solubility and PEG-like biocompatibility. Likewise, both modified and unmodified HPGs have been tried as stabilizers to synthesize NCs.

Palmitoyl chloride and palmitic acid were widely used to modify HPG, obtaining an amphiphilic core-shell structure (C₁₆-HPG) of stabilizer. In the presence of C₁₆-HPG, palladium nanoclusters were formed by a reduction of PdCl₂ or Pd(Oac)₂ in toluene with hydrogen or heating [53]. The Pd NPs show excellent stability and catalytic activity in the hydrogenation of cyclohexene [54]. With the similar stabilizer, Frey and co-workers have synthesized Pd NPs from PdCl₂ [55]. Compared with hydrogen reductant, they found that smaller size of NPs could be obtained using NaBH₄ reductant under much more convenient reaction conditions. Interestingly, when carbon monoxide was used as the reductant, shape-selective, thin hexagonal Pd platelets with size of 15 to several hundred nanometers in the other two dimensions were obtained [56]. Besides, poly(ϵ -caprolactone) (PCL) and poly(acrylic acid) have also been used to modify HPG for preparing Ag NPs [57, 58].

Haag et al. constructed various core-multishell architectures with HPG core, C₁₈ inner alkyl shell, and mono-methylated PEG outer shell [59]. Similar to the HPEI-based core-shell stabilizer, the HPG-based core-multishell structure can be utilized to in situ synthesized NPs, as well as dramatically improve the stability of NPs. The obtained Pt NPs were further applied as catalyst in hydrogenation reactions of methyl crotonate and isophorone and the asymmetric hydrogenation of ethyl pyruvate [60].

Apart from building core-shell structure to encapsulate NPs, special elements that can strongly complex with metal ions such as sulfur were introduced to HPG for the synthesis of NPs. For instance, Huang et al. have used thioether-

modified HPG to synthesize Au [61], CdS, and CdSe NPs [62]. Moreover, thermo-responsive Pt NPs have been obtained in a sulfur-contained, three-layer, onion-like polymer containing an outer shell of thermo-responsive poly(*N*-isopropylacrylamide), an inner shell of crosslinked poly(*N,N*-dimethylaminoethyl acrylate), and an HPG core [63].

Besides the modified HPG, very recently we found that an unmodified HPG with high molecular weight (>20 kDa) can also be directly used as a stabilizer to prepare various aqueous NCs including mono- or bimetallic noble metal NCs, magnetic NCs (Fe₃O₄), semiconductor such as ZnS, Ag₂S, PbS, CuS, and CdS and other NCs (e.g., AgCl, AgBr, PbCrO₄, CaF₂, SmF₃, NdF₃, Sm(OH)₃, and Nd(OH)₃) (Fig. 6) [64]. Our synthesis methodology shows remarkably the combined advantages of facile one-pot synthesis protocol, generality for various nanocrystals, low toxicity, or good biocompatibility of NCs, excellent solubility of NCs in both water and organic polar solvents, high stability of NCs, and lots of residual hydroxyl groups useful for further modification, affording enormous opportunities to use the NCs for many technological applications. In addition, water-soluble monometallic (Au, Ag, Pt, Pd, and Ru) and bimetallic (Au/Pt, Au/Pd, and Au/Ru) NPs can also be obtained using HPG as the stabilizer without an additional reductant [65].

Hyperbranched polyester (HPE)

Four types of HPE, HPE-1, 2, 3, and 4, have been utilized to synthesize NPs (Fig. 4). Hyperbranched poly(amine-ester) (HPE-1) synthesized from diethanol amine and methyl acrylate, HPE-2 made from succinic anhydride, and glycidol with terminal carboxyl and hydroxyl groups, have been used as stabilizers to prepare Au [66], Cu [67], and Ag [68, 69] NPs.

Long alkyl-modified HPE-3 with outer alkyl tails and compressed amine-hydroxyl core that can form nanofibrillar micellar structures within a Langmuir monolayer has been used as mediate for the formation of stable Ag NPs by a one-step process [70]. Semiconductor PbS QDs have been widely used for potential photonic materials and Pb²⁺ ion-selective sensors for their property of near-IR light emission. Succinic anhydride-modified HPE-3 has been used to synthesize PbS/HPE-3 nanocomposite, resulting in hollow spheres [71]. PbS NCs of 7.8 nm can also be formed in situ from Pb(NO₃)₂ and Na₂S₂O₃ with the help of ⁶⁰Co gamma-ray irradiation [72].

Metal oxide NPs also play an important role in the field of nanoscience. For instance, the incorporation of TiO₂ NPs in thin films and coatings is especially encouraging, since surface hardness can be thus significantly improved and, on the other hand, self-cleaning and antimicrobial properties can be introduced based on their photocatalytic effect. Hyperbranched aromatic-aliphatic polyester with phenolic end-

groups was utilized to prepare TiO_2 NPs via a sol–gel method, and the NHBs were thermally cured with 1,6-diisocyanatohexane [73]. The thermal properties as well as hardness of the coating have been enhanced in the presence of TiO_2 .

Hyperbranched polyamide (HYPAM)

Hyperbranched aromatic polyamides (aramids) (HPArAM-1), synthesized from p-phenylenediamine and trimesic acid have been used as polymeric stabilizer to in situ synthesize Pt NPs with different reductants and solvents [74, 75]. Another HPArAM-2 obtained from the AB_2 monomer, 5-(4-aminobenzamido) isophthalic acid, was also introduced to enhance the metal-retaining capability of polyamide 6 (PA6) by preparing solution and melt blends of PA6 and HPArAM-2 [76], obtaining a higher Pd content in the NHBs

without aggregation compared with PA6 as support. Karak et al. also did some work on the preparation of Ag NPs with HPArAM-3 as stabilizer [77]. As a comparison, neat linear polyacrylamide (LPAM) and mixtures of LPAM and HPArAM-3 were used as stabilizers to prepare Ag NPs [78], showing that Ag NPs with smaller size and better antibacterial activity could be obtained for the LPAM/HPAM-3-combined system.

Hyperbranched polyurethane (HPU)

Ag_2S NCs and Ag NCs using HPU as a stabilizer have been prepared at room temperature [79, 80]. HPU with hyperbranched polyether polyol synthesized from cyanuric chloride and butanediol as core, copolymer of monoglyceride, 4,4'-diphenylmethane diisocyanate, and PCL diol as shell, has also been utilized to prepare Ag NCs [81].

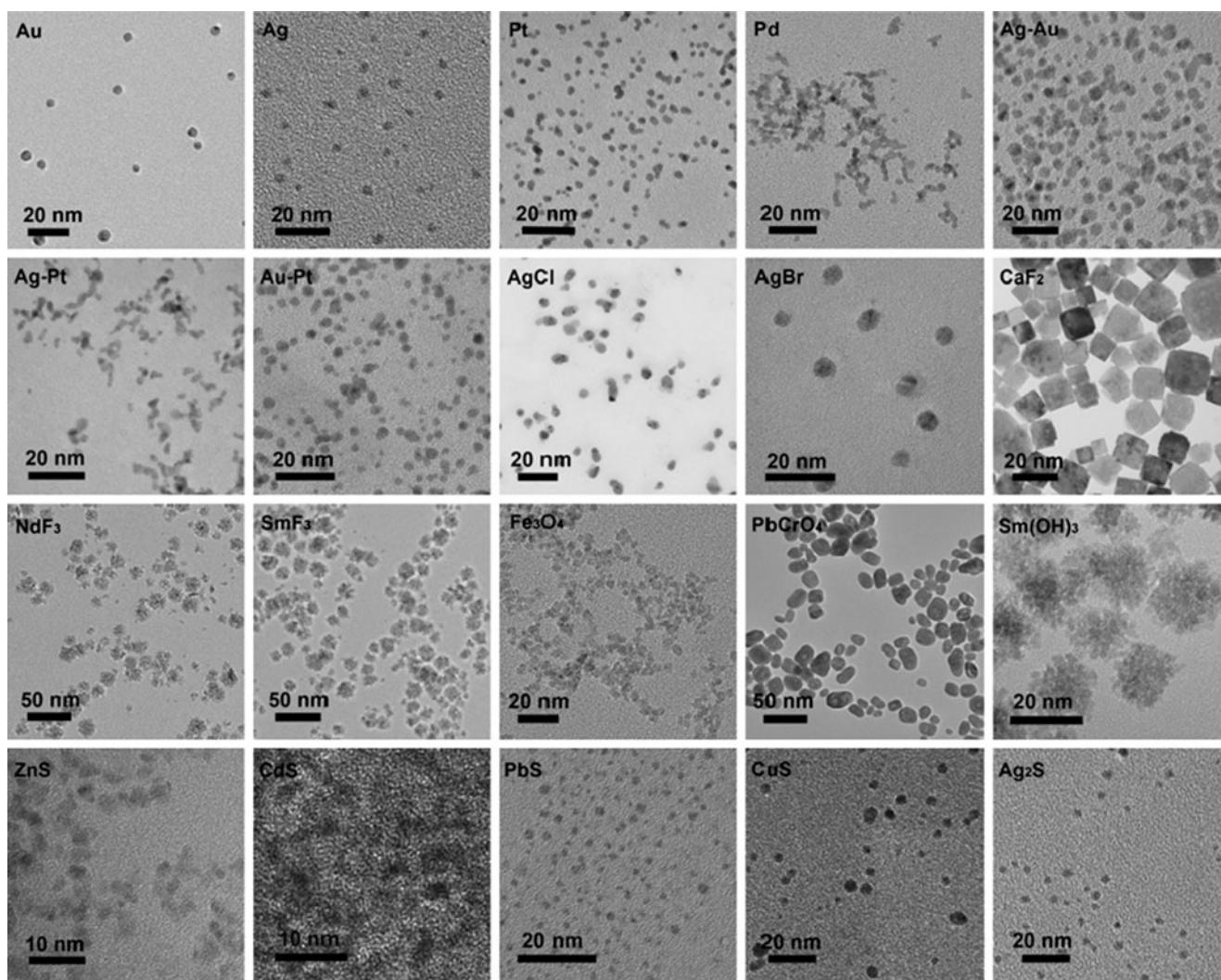


Fig. 6 Representative TEM images of series of NCs prepared with unmodified HPG as stabilizer. Reprinted with permission from [64]

Hyperbranched poly(3-ethyl-3-hydroxymethyloxetane) (HPEO)

Amphiphilic HPEO partially modified by stearate has been used to prepare ZnO NPs by slow degradation of Et_2Zn via exposure to air [82]. HPEO makes it possible to disperse the resulting NPs in apolar solvents, for example in toluene, to yield highly transparent, long-term stable dispersions, making the material highly interesting for coating applications.

Hyperbranched polystyrene (HPS)

Hydrophobic HPS synthesized from 4-vinylbenzyl *N,N*-diethyldithiocarbamate became dispersible in water upon complexation with Ag(I) ions, which could spontaneously form nanospheres, and small Ag NCs evenly distributed on nanospheres generated later via photoreduction of the complexes [83]. The strategy “HPs first” is convenient as well as extensively applicable, obtaining various NCs either oil-soluble or water-soluble. Especially for the NHBs prepared in aqueous phase, excellent water solubility and biocompatibility can be achieved. Additionally, the size of the NCs can be tuned to some extent via adjusting the structure or size of HPs and the reaction conditions. Attentively, HPs own the polydispersibility nature, sometimes resulting in the inhomogeneous properties of NCs, and the size control over NCs is not so precise.

NCs first

Compared with the “HPs first” strategy, “NCs first” allows us to prepare NCs with the traditional methods, affording more uniform dispersibility. Then, the properties of NCs such as solubility, biocompatibility, and surface functionality can be tuned by surface modification with desired HPs. In this regard, in situ growth of HPs onto QD surfaces is of particular interest and significance.

Semiconductor QDs have attracted increasing attention within recent years due to their promising applications in optical devices, solar cells, biosensors, and biological imaging. Unfortunately, the naked QDs cannot be directly utilized in almost all of the applications because their surfaces are susceptible to external environment, which results in their fluorescence quenching and the release of toxic metal ions. Therefore, it is essential to endow the QDs surface with a protecting shell. Recently, we have introduced the in situ anionic ring-opening polymerization (ROP) strategy to graft biocompatible HPG from the surfaces of CdTe QDs (Fig. 7a) [84]. The obtained CdTe@HPG NHBs were evaluated by cell labeling (Fig. 7b). It is found that the biocompatibility and fluorescence biostability of the CdTe QDs are obviously enhanced in comparison with pristine CdTe QDs because of

the envelope of biocompatible HPG. Incidentally, thermo-sensitive, amphibious CdTe NCs have also been obtained by grafting with poly(2-(dimethylamino)ethyl methacrylate) (PDMAEMA) via direct surface-initiated oxyanionic vinyl polymerization [85].

Alternatively, silica NPs possess good water dispersibility, biocompatibility, and surface functionality, which is one of the most popular inert materials for surface protection of QDs. We have reported a one-pot approach for large-scale production of silica-hybridized CdTe QDs (SiO_2 -*h*-QDs) with excellent controllability and high reproducibility (Fig. 8) [86]. The as-prepared water-soluble SiO_2 -*h*-QDs are ultrafine with diameters below 18 nm and show excellent optical stability, favorable biocompatibility, low toxicity, and facile surface functionality compared to the naked CdTe QDs. Meanwhile, their emission and absorption wavelengths can also be tuned by the reaction time because of the growing hybridization mechanism. The resulting SiO_2 -*h*-QDs have accordingly been utilized to blend with polymer such as poly(vinyl alcohol) and poly(methyl methacrylate) obtaining polymer films with simultaneous photoluminescence and enhanced mechanical properties [87]. The SiO_2 -*h*-QDs can also be grafted with multihydroxy HPG by in situ anionic ROP of glycidol [86].

Additionally, HPs-grafted ZnO NPs have been synthesized by surface-initiated self-condensing vinyl polymerization of a styrene-based AB* inimer [88], *p*-chloromethyl styrene, from nanosurfaces of the NPs functionalized with monolayer of ATRP initiators. Magnetic nanoparticles (MNPs) have gained an increasing interest because of their potential applications such as cell separation, magnetic resonance imaging, drug delivery, and so on. However, they tend to agglomerate into large clusters and adsorb plasma proteins in applications causing serious problems. Therefore, it is necessary to modify the surface of MNPs with suitable intermediates. We have reported silica shell-protected Fe_3O_4 NPs, resulting silica-hybridized Fe_3O_4 with stable magnetic properties, excellent dispersibility, and surface polyfunctionality [89, 90]. HPG is then grafted from the core-shell structure via in situ anionic ROP of glycidol. The final nanohybrids have been utilized as supports to load nanocatalysts such as Au, Ag, Pt, and Pd, and organic dyes as well as drugs, which will be discussed for more details in the “Applications” section of this article. HPG has also been grafted from 3-mercaptopropyl trimethoxysilane-modified MNPs [91]. It is found that the immobilization of HPG greatly suppresses nonspecific adsorption of proteins of the MNPs. Neoh et al. have introduced reactive hydroxyl groups to Fe_3O_4 NPs by two-phase ligand exchange between 6-hydroxy caproic acid and oleic acid, and then HPG was introduced with the same method [92]. It is demonstrated that the resulted nanocomposites have superparamagnetic

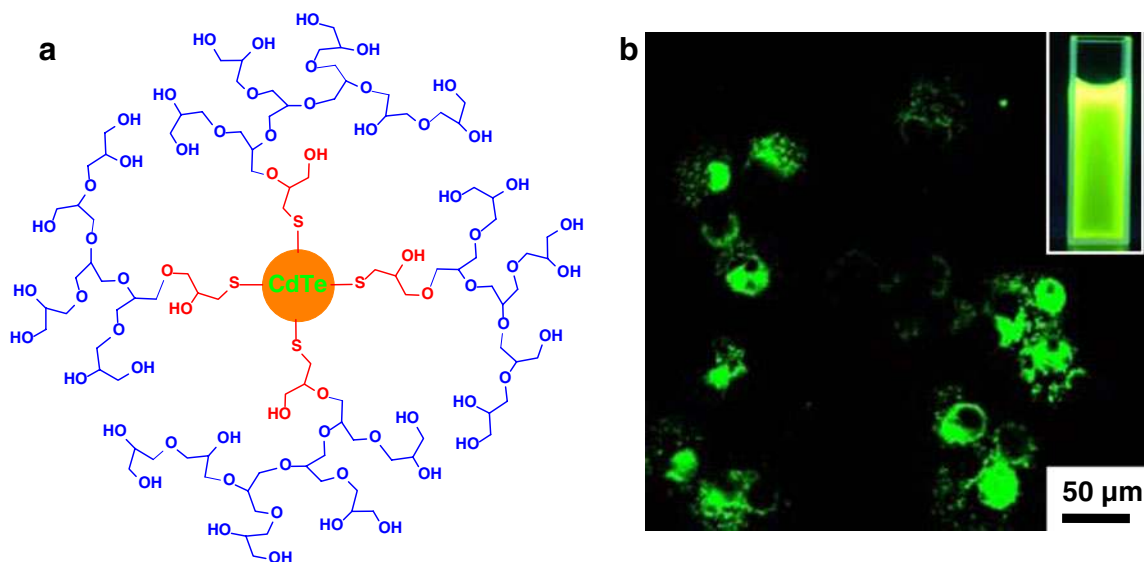


Fig. 7 **a** Structure of CdTe@HPG prepared by surface-initiated in situ ROP of glycidol; **b** confocal microscopy image of A375 cells incubated with CdTe@HPG, and the inset denotes the photograph of aqueous CdTe@HPG irradiated at 365 nm [84]

property, good biocompatibility, and the possibility of a long plasma half-life.

As an important member of 1D nanomaterials, carbon nanotubes (CNTs) exhibit excellent mechanical-, electrical-, and thermal-conductive properties, affording them potential applications in various fields. However, since CNTs usually form stabilized bundles due to strong Van der Waals interactions, they are extremely difficult to disperse in other matrix, which seriously restrict their practical use. HPs have been used to enhance the dispersion of CNTs in other matrices and conjugate fluorescent molecules, taking advantage of their multifunctional, non-entangled 3D structures (Fig. 9). Up to now, several kinds of HPs including HPEO [93], HPG [94, 95], HPU [96], hyperbranched poly(citric acid) [97], hyperbranched poly(ether ketone) [98], etc. have been successfully grafted from the surfaces of CNTs.

The obtained NCs via the “NCs first” strategy normally show uniform dispersibility and high grafting density of HPs. However, the intrinsic properties of the resulting NCs would change more or less due to the harsh chemical reaction. In some cases, for example, the fluorescence of QDs will be quenched during the polymerization. Besides, the HPs that can be used to grow in situ from NCs are quite limited, which is unfavorable for tailoring the structure and properties of resulting NHBs.

Ligand exchange

“Ligand exchange” strategy broadens the scope of optional HPs, at the same time retains the advantages of “NCs first”. QDs are appealing as in vivo and in vitro fluorophores in a

variety of biological investigations due to their unique size-dependent optical attributes, but first of all, QDs should be water-soluble. In the past few years, most of reports concentrated on preparing oil-soluble QDs with small organic molecules or linear polymers as ligands, providing uniform size of QDs. Thus, it is necessary to find proper methods to change the solubility of QDs for further bioapplications, of which ligand exchange with water-soluble HPs is an effective technique.

Nikolic et al. have transferred oil-soluble core-shell QDs (e.g., CdSe@CdS, CdSe@CdS@ZnS), Fe₃O₄, and CoPt₃ NPs into aqueous solution using diethylenetriamine or low molecular weight HPEI-modified PEO (Fig. 10) [99]. Better dispersing effect of NPs was achieved by the HPEI-modified PEO compared with the small molecule-modified PEO. HPEI- and PEG-grafted HPEI was also used for transferring hydrophobic CdSe@CdS@ZnS QDs into an aqueous solution [100]. Different from amphiphilic lipid or polymer coatings, the fluorescence of CdSe@CdS@ZnS QDs is effectively protected from quenching in simulated gastric fluids by using both HPEI and its PEG derivative (PEG-grafted HPEI) [101].

Unlike semiconductor NPs, the quantum-mechanical properties of metallic materials are only observed in atomic clusters. Nie et al. have introduced the ligand exchange method by using HPEI to obtain high-fluorescent and water-soluble Au nanoclusters consisting of only eight atoms [102]. Interestingly, the “as-prepared” fluorescent clusters appeared to be in an oxidized electronic state, so by adding strong reducing agents such as NaBH₄, the fluorescent properties of monodispersed nanoclusters could be tuned. PEG-grafted HPAMAM-3 have also been used to

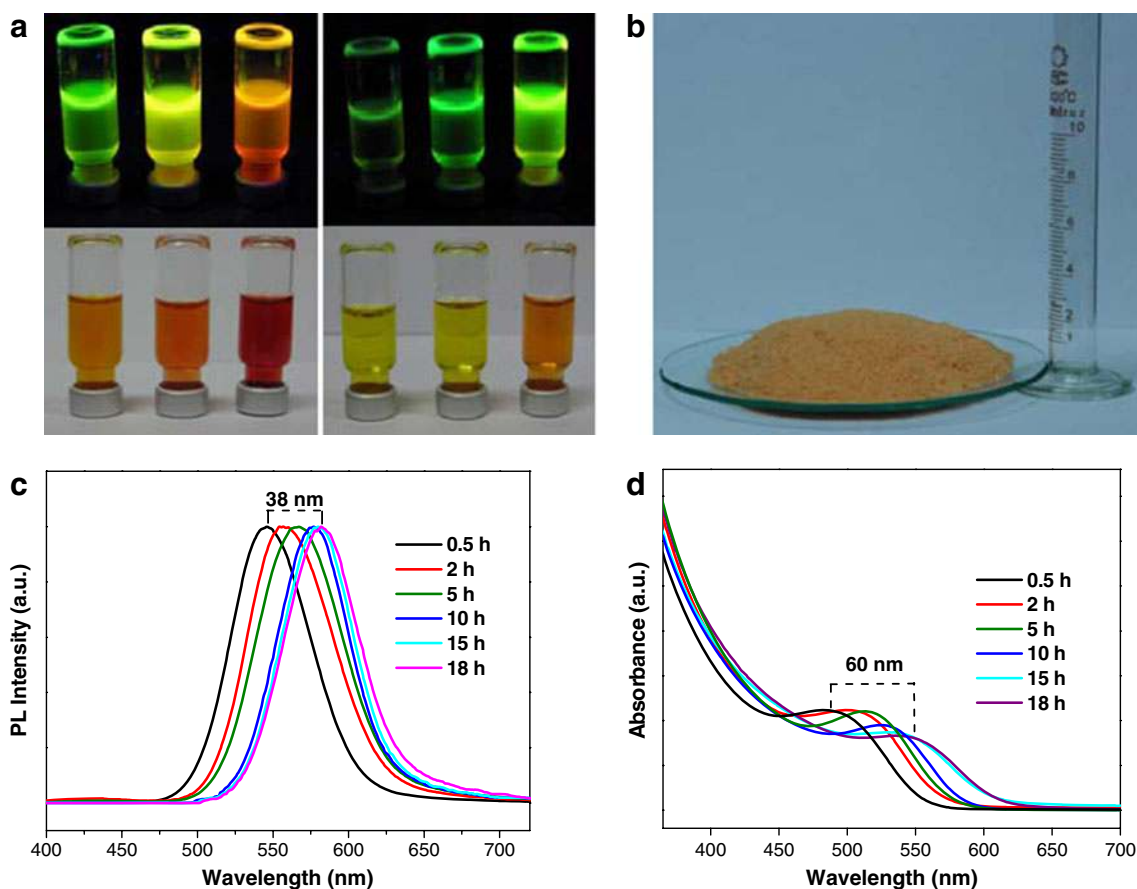


Fig. 8 **a** Photographs of SiO₂-hybridized CdTe QDs in aqueous solution under UV light (365 nm, top) and daylight (bottom). The left three samples were prepared with mercaptopropionic acid (MPA) as ligand at the reaction time of 0.5, 5, and 18 h, respectively, and the right three samples with 1-thioglycerol (TG) as ligand at the reaction

time of 1, 7, and 31 h, respectively, **b** photograph of SiO₂-hybridized CdTe QDs powder obtained in one-batch, and **c** emission as well as **d** absorption spectra of SiO₂-hybridized CdTe QDs with MPA as ligand at different reaction time [86]

transfer three types of hydrophobic NPs, CdSe, Au, and Fe₃O₄, to water phase by utilizing the complexation interaction between the amino groups of HP and the NPs [103].

On the contrary, transferring NCs from water to oil phase using HPs is also possible if necessary. Water-soluble CdTe NCs with methacrylate as ligand are successfully transferred from aqueous phase to oil phase by the attraction of

Fig. 9 **a** Functionalization of multiwalled carbon nanotubes (MWNTs) with HPG and conjugation of fluorescent rhodamine B (RhB) with hydroxyl groups, **b** TEM image of MWNT-g-HPG, **c** confocal fluorescence image of MWNT-g-HPG-RhB [93]

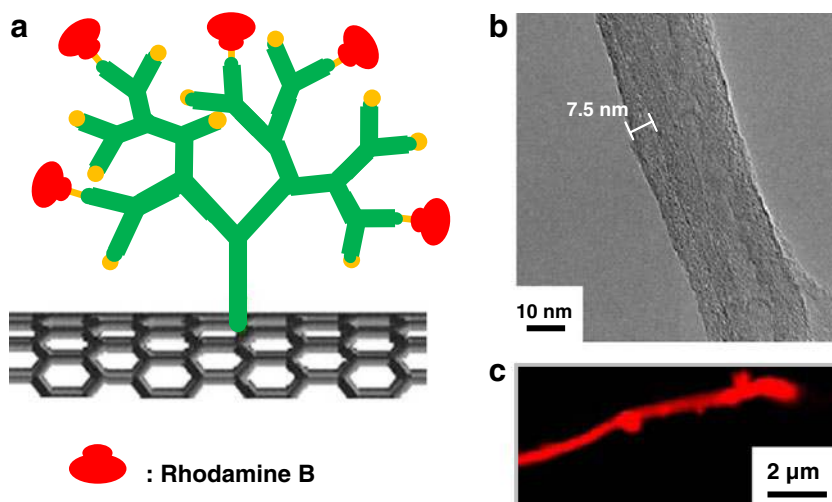
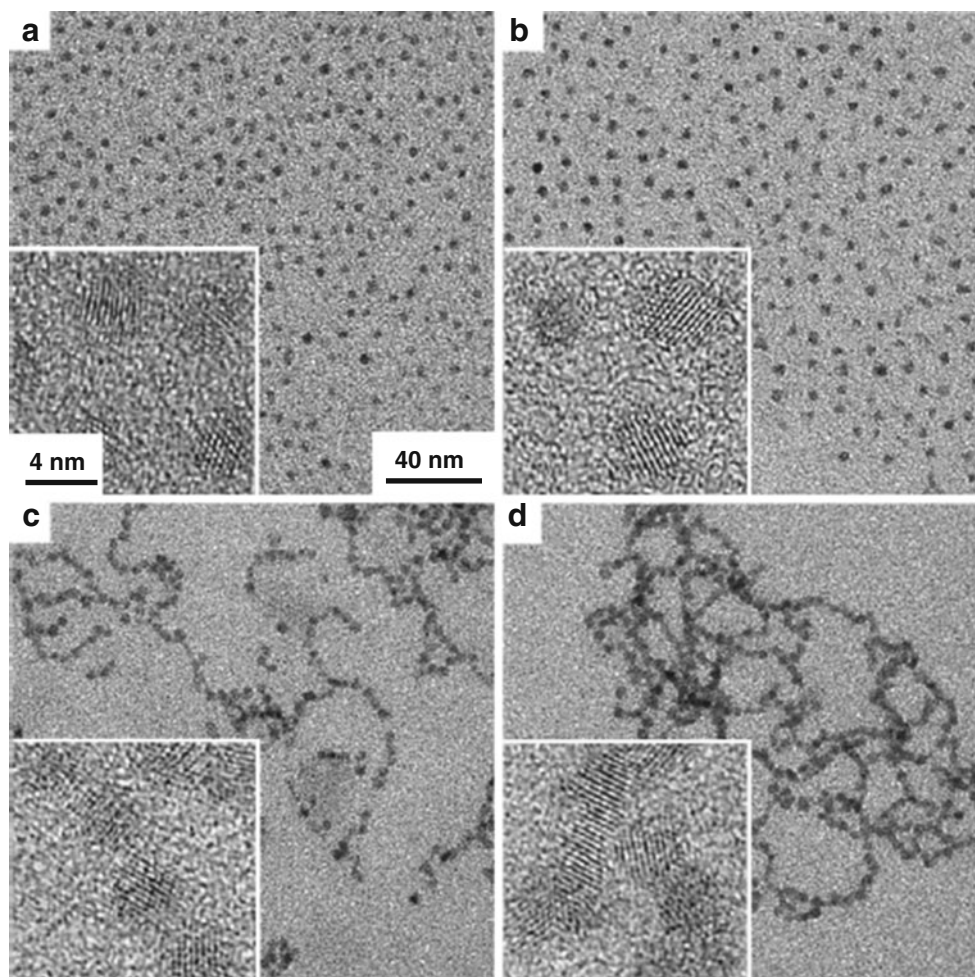


Fig. 10 TEM images of water soluble CdSe@CdS QDs modified with **a** PEO2000–PEI-branched, **b** PEO5000–PEI-branched, **c** PEO2000–DETA, and **d** PEO5000–DETA. Insets show enlargements, 40 nm and 4 nm scale bars in figure (a) apply to all main images and insets, respectively. Reprinted with permission from [99]



amphiphilic HPs composed of hydrophobic hexadecyl shell and hydrophilic HPAMAM-4 core [104]. The liquid/liquid interfacial self-assembly of the QDs can then be achieved by either decreasing the pH value of the aqueous phase or introducing cyclodextrin, obtaining a thin nanocomposites film at the interface of water and chloroform.

Both palmitic acid-modified HPEI and linear PEI have been employed to transfer the citrate-protected 17-nm Au NCs from water into chloroform [105]. Due to the amphiphilic character of HPEI, the CdSe@ZnS QDs and HPEI nanocomposites are also amphiphilic [106]. Thus, the nanocomposites can be easily transferred from oil to water. Liu et al. have obtained a high quantum yield (nearly 100%) CdS NPs using mercaptoacetic acid as a stabilizer in an aqueous solution [107]. Interestingly, they found that the interaction of NPs and HPEI led to the enhancement of the quantum yield of CdS due to the Lewis base nature of HPEI.

Every coin has two sides, and the “ligand exchange” strategy also has some disadvantages such as the incomplete removal of original ligands, change of NC properties during an exchange reaction, and so on. So, each of the

above three strategies has its own merits and demerits requiring careful choice for the most proper one to synthesize the desired NCs in actual experiments and applications.

Action mode of HPs

Generally, the HP stabilizers could play three important roles in the NC synthesis: (a) scaffold for the adsorption of metal ions, (b) cradle for the nucleation, and (c) container/network for the growth of crystals [64]. Thus, to obtain stable NCs, HPs should normally have functional groups that can attract metal ions such as amine groups [28, 29, 51, 100, 102], carbonyl groups [69, 71, 72, 80], hydroxyl groups [53, 64, 65], and thioether groups [61–63, 83]. In addition, core-shell amphiphilic structure made by the modification of HPs can be employed to encapsulate NCs as well. But, we think that the amphiphilicity of HPs is not essential for stabilizing NPs.

Due to the inaccessibility for controlled synthesis of HPs with narrow polydispersity index in a wide range of molar

mass, the molecular weight (MW) effect on the formation of NCs is rarely addressed. Recently, we obtained HPGs with different MWs ranging from 2.2 to 128 kDa via controlled anionic ring-opening polymerization and found that (1) HPG with low MW (<20 kDa) cannot stabilize NCs well, and (2) the size of NCs decreases with increasing the MW of HPG [64]. We think that several macromolecules of HPG, rather than only one, stabilized the NCs. The bigger HPG shall have a better protection (or separation) effect against the contacting and fusion of different particles, resulting in a smaller size of the final NCs.

Different morphology of NCs such as dots, rods, and sheets had been successfully prepared with small molecule ligands [5, 11, 14]. However, such shape control by HPs is rarely reported [55], providing a chance for exploring in the future.

Compared with dendrimers, HPs exhibit different performance in the synthesis of NPs due to their irregular and open structures. First, the maximum loading ions per polymer is often more than a dendrimer with comparable MW because the open structure of HP facilitates the interactions of metal ions with the internal chemical functions [28, 44]. Second, for dendrimers, the surface density of functional groups increases with MW, possibly preventing the metal ions from entering the interior of dendrimer. Alternatively, for smaller generation of dendrimers, the entrapped species become easily dislodged

from the interior due to the relatively open structure. Therefore, the proper size range for NCs growth is between the fourth and sixth generations, which exhibit strong container properties [20]. By contrast, the proper MW range for HPs could be much wider due to the flexible structure (e.g., 22–128 kDa for HPG) [64]. Third, the size of NCs normally increases with the generation of dendrimers, whereas it is reversed for the HP cases.

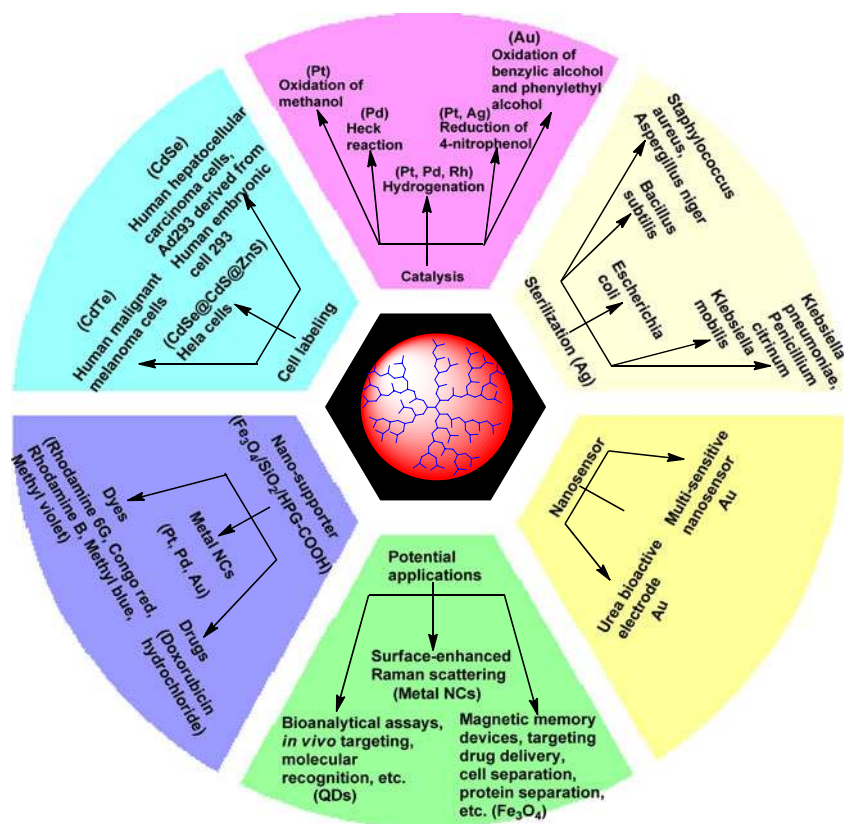
Applications

The application fields of NHBs mainly depend on the specific sorts and properties of NCs. As summarized in Fig. 11, noble metal NCs such as Pt, Pd, and Rh are usually utilized as catalysts, Ag NCs are very effective at sterilization and disinfection, and QDs are capable of bioapplications such as cell imaging, nanosensors, etc.

Catalysis

Noble metal NCs prepared with HPs as stabilizer have been widely used as catalysts due to their large specific surface area and high efficiency. For instance, Pt NPs have been used as catalyst in the hydrogenation of isophorone as well as methyl crotonate [28, 44, 59], asymmetric hydrogenation

Fig. 11 Applications of NC-HP nanohybrids



of ethyl pyruvate [60], and oxidation of methanol [49]. Pd NPs have proved to exhibit catalytic activity in hydrogenation of cyclohexene [46, 53, 54], various unsaturated substances such as benzene, benzylideneacetone, phenylacetylene, diphenylacetylene, and quinoline [74], Heck reaction of 2,3-dihydrofuran and aryl triflate [55]. Rh NPs stabilized by HPEI also show activity in hydrogenation of hexene [41]. Ag NPs exhibit catalytic activity in the reduction of 4-nitrophenol [81].

Thermo-responsive Au NPs have been obtained through the non-covalent interaction between a thermo-responsive HPEI with isobutyramide groups (HPEI-IBAm) and citrate-protected Au NPs [108]. The NHBs are used as catalyst in the reduction of 4-nitrophenol, exhibiting higher reactivity compared with Au NPs without capping polymers. Besides, the catalyst can be recycled due to their thermo-responsive characters, nearly without decrease of activity for six cycles.

Nano-Supports or Reactors

The expensive noble metal catalysts are difficult to be recycled and thus cause huge waste and also contaminate the products. Recently we have developed a novel kind of robust magnetic hybrid based on the carboxylic HPG-functionalized $\text{Fe}_3\text{O}_4/\text{SiO}_2$ and have used it as noble metal nanocatalyst supports for the first time (Fig. 12) [89]. Various noble metal nanocatalysts such as Pt, Ag, Au, Pd have been directly grown on the surface of nanocomposites due to the unique structure and numerous functional groups of HPG. The nanocatalysts not only have high reactivity in reduction of 4-nitrophenol, oxidation of benzylic alcohol and 1-phenylethyl alcohol, and Heck reaction of two typical aryl halides of bromobenzene and iodobenzene with two representative olefins of aryl acid and styrene, respectively, but also can be recycled by an external magnet and reused with no or slightly decrease of reactivity (see Fig. 12e).

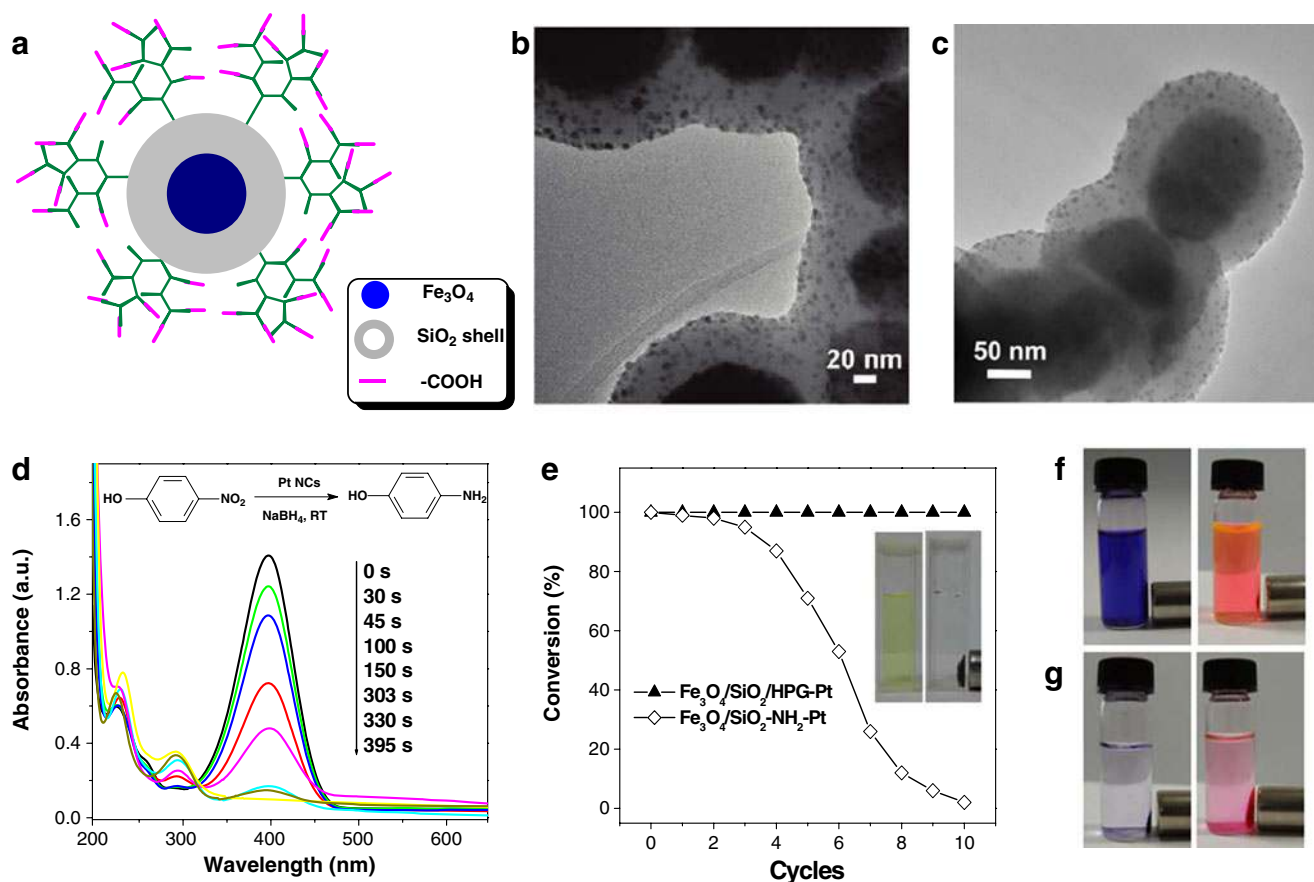


Fig. 12 **a** Structure of $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{HPG-COOH}$, TEM images of Pt nanoparticles on the $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{HPG-COOH}$ supports, newly prepared **b** and after three cycles of catalysis **c**, **d** UV-vis spectra showing the gradual reduction of 4-nitrophenol with $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{HPG-Pt}$ catalyst, **e** conversion of 4-nitrophenol in 11 successive cycles of reduction and magnetic separation with $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{HPG-Pt}$ and

$\text{Fe}_3\text{O}_4/\text{SiO}_2\text{-NH}_2\text{-Pt}$ catalysts, respectively, the inset shows the photographs of the 4-nitrophenol and NaBH_4 solution before adding $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{HPG-Pt}$ catalysts (left) and magnetic separation of catalyst after the reaction (right), and photographs of magnetic separation of methyl violet (left) and rhodamine 6G (right) after adsorption on $\text{Fe}_3\text{O}_4/\text{SiO}_2$ **f** and $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{HPG-COOH}$ **g** [89, 90]

This robust and facilely available magnetic nanohybrid would have promising applications in large-scale catalytic reactions.

Furthermore, the HPG-functionalized magnetic hybrid can be utilized to absorb organic dyes and drugs (Fig. 12f, g) [90], exhibiting very high adsorption capacity for cationic dyes and drugs because of the strong electrostatic attraction between its negative surface groups and the adsorbates. The adsorption capacity can be affected by pH especially at low pH and selectively affected by ionic strength. In addition, the adsorbent can be regenerated in ethanol without serious decrease of its adsorption capacity. Considered the facile fabrication process and its high adsorption capacity, the magnetic adsorbent promises great potential in the adsorptions of dyes from waste water, and drug delivery.

Sterilization

Ag NCs stabilized with various HPs including HPAMAM [35, 36], HPEI [39, 42], and HPAM [77] are widely used as antibacterial substances. Tiller et al. have designed a crosslinked film based on methacryloyl chloride modified HPEI and 2-hydroxyethyl acrylate. The film was subsequently loaded with Ag NPs, additionally modified with PEG [109], providing it microbe-repelling, biocide-releasing, and contact-active antimicrobial properties.

Cell-labeling

The NHBs of HPs and QDs exhibit low cytotoxicity compared with pristine QDs and have been used as cell-imaging agent. The CdTe QDs grafted by HPG have been used to label A375 cells, showing stable and strong fluorescence [84]. Other QDs such as HPAMAM-3 stabilized CdSe and HPEI stabilized CdSe@CdS@ZnS have also been used in cell labeling [100, 103].

Nanosensor

Frey et al. have modified HPG with N-isopropyl acrylamide, obtaining positively charged polyelectrolytes with thermal-responsive properties [110]. Then citrate ligands stabilized and negatively charged Au NPs have been coated with modified HPG through electrostatic interaction, leading to multi-responsive Au NPs with a sharp phase transition upon change of temperature or pH value.

Amino modified HPE-3 has been used as linker between carboxyl modified Au NPs and urease through covalent linkage, obtaining a novel urea biosensor which offered longer shelf life, broader detection range, higher sensitivity, and shorter response time compared with those reported previously [111].

Conclusions and perspectives

Three strategies, coined “HPs first”, “NCs first”, and “ligand-exchange”, have been developed to synthesize NC-HP nanohybrids. Compared with NCs without stabilizers, the HPs-stabilized NCs exhibit better dispersibility and less agglomerations. In contrast to NCs using small molecules or linear polymers as stabilizers, the NC-HP nanohybrids possess more functional groups and have lower cytotoxicity. Moreover, the size and shape of NCs might be controlled by adjusting the structure or molecular weight of HPs. The obtained NC-HP nanohybrids include noble metals, semiconductor NCs, and insulator NCs, etc., showing applications in fields of nanocatalysis, nano-supports, nano-reactors, sterilization, biological labeling, and so forth. We believe that the combination of multifunctional, highly soluble HPs and multifunction of NCs will open an avenue to versatile, robust nanohybrids with tailor-made structures and properties.

As an outlook, the following three aspects are of particular interest, novelty, and importance: (1) synthesis of novel nanohybrids with integrated functions with the linkage of HPs; (2) self-assembly and supramolecular behaviors of NC-HP nanohybrids (through self-assembly or self-organization, different topological structures such as linear chains, cycles, 2D films, 3D spheres and vesicles, dendritic clusters, and macroscopic hydrogels and even fibers, etc. could be accessed); (3) besides the aforementioned 0D and 1D NCs, HPs-grafted 2D nanosheets (e.g., HP-graphene hybrids) that have not been reported yet, affording a more versatile and fascinating platform for fabrication of novel materials, devices, and bio-nano conjugates [112].

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