General Synthetic Route Towards Highly Dispersed Metal Clusters Enabled by Poly(ionic liquid)s

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Supporting Information Placeholder

ABSTRACT: The capability to synthesize a broad spectrum of metal clusters (MCs) with their size controllable in a subnanometer scale presents an enticing prospect for exploring nanosize-dependent properties. Here we report an innovative design of a capping agent from a polytriazolium poly(ionic liquid) (PIL) in a vesicular form in solution that allows for crafting a variety of MCs including transition metals, noble metals, and their bimetallic alloy with precisely controlled sizes (~ 1 nm) and record-high catalytic performance. The ultrastrong stabilization power is result of an unusual synergy between the conventional binding sites in the heterocyclic cations in PIL, and an *in-situ* generated polycarbene structure induced simultaneously to the reduction reaction.

INTRODUCTION

Metal clusters (MCs) with dimensions between a single metal atom and nanoparticles of > 2 nm have attracted focused attention.¹ The small size of MCs forces most of, if not all, their constitutional atoms to be exposed to surface. In addition, the size approaches the Fermi wavelength of electrons, resulting in molecule-like characters including discrete energy levels, size-dependent fluorescence, good photostability and in some cases biocompatibility.² However, the extremely tiny size brings synthetic difficulty because such clusters are naturally prone to aggregation and particle growth, driven by high surface energy.³ Some synthetic routes have been developed over the past few years to prepare MCs.⁴ As a popular one, an impregnation-precipitation procedure to physically confine MCs inside a nanoporous support has been described,⁵ but the precise size control of uniformity of tiny pores of the support itself is challenging, not to mention the tedious surface functionalization and retarded diffusion kinetics in such systems. A solution to this problem is to apply, instead of a solid porous support, capping agents, often in large excess, targeting a maximum surface coverage to lower down surface energy and suppress growth.⁶ This simple and scalable method however suffers frequently from a "trade-off", that is covering a highenergy surface which is catalytically or photochemically

active adversely restricts accessibility to active sites. Generally speaking, a "smarter" design of capping agents is constantly pursued to reach an optimal balance or even break such trade-off.

Poly(ionic liquid)s (PILs) are an emerging, powerful class of functional polymers prepared from ionic liquids.⁷ They possess a wide property and application spectrum due to the structural synergy between the ionic liquid component and the macromolecular architecture.8 One particular feature of PILs is their unusual interfacial activity to bind eventually to most surfaces, from bionanomaterials, metals to carbons, serving as a type of universal stabilizer.9 Recently, PILs have also contributed to nanomaterial design by generating unusual inorganic morphologies inaccessible so far in PIL-free synthetic conditions.¹⁰ Herein, we report a further contribution by the construction of high-performance capping agents derived from PILs that can stabilize a bunch of welldispersed, long-term stable MCs of extremely small size (~1 nm) and high catalytic performance. This success relies on the association of the traditional binding power of PILs to metal species, as mentioned previously, with a finely tuned hydrophilicity/hydrophobicity balance, but more significantly the simple in-situ formation of a poly(N-heterocylic carbene) (polyNHC) structure from the polytriazolium chains during the MC formation.



Scheme 1. Schematic illustration of the general procedure toward the synthesis of metal clusters (MCs) stabilized by structurally well-defined P(triaz) (the positions of atoms in the triazolium ring are numerically labeled) vesicles in a dichloromethane and methanol mixture (volume ratio = 2:1). The inset at the bottom middle is a cryo-EM image of a single vesicle. See Figure S9 for an overview.

RESULTS AND DISCUSSION

We started by synthesis of a 1,2,4-triazolium PIL poly(4hexyl-1-vinyl-1,2,4-triazolium iodide) (denoted as "P(triaz)") with pending hexyl substituent along its polytriazolium backbone (Scheme 1 and S1-4). The hydrophilic triazolium iodide ion pair enables the P(triaz) wellsoluble in polar solvents such as alcohols, while the pending hexyl chain expands their solubility/dispersability window to moderately polar solvents such as dichloromethane." The incorporation of these two components of distinctively different features into one repeating unit favors the formation of superstructures in solutions of selective polarity, as discussed later. The triazolium units along the backbone are a key structure motif here, as they will serve as precursors to polyNHC that amplifies their capping power. Compared with common elemental binding sites, e.g., N, O and S, NHCs as strong σ -donators and comparatively weak π -acceptors are more robust to bind metal centers either homogeneously in solution or heterogeneously on metal nanoparticles.^{12,13} Based on these considerations, the reaction medium used here is specifically chosen as a dichloromethane and methanol mixture (volume ratio = 2:1), in which P(triaz) self-assembles into vesicular structures (inset cryogenic electron microscopy (cryo-EM) images in scheme 1, Figure S9) of 40 ~ 250 nm in size and 15 ~ 35 nm in the wall thickness. The vesicular structures are, in comparison to classic polymer core-shell micelles, a favorable support for heterogeneous catalysis, as its thin wall facilitates fast mass diffusion and exposes its both surfaces to contact reactants in solution. Decreasing the alkyl length from hexyl to butyl (Figure S₇) results in a molecularly dissolved PIL in the same mixture solvent, while a PIL with longer alkyl chain, such as decyl (Figure S8), forms irregularly shaped large colloids.



Figure 1. (a) Cryo-EM image of the Pd/P(triaz) hybrid vesicles (dark circle) on a Quantifoil carbon grid. The inset is a cryo-EM image of a single Pd/P(triaz) vesicle. (b) Bright field (BF) TEM image of Pd clusters on a P(triaz) vesicle. Some of Pd clusters are highlighted by white dotted circles. (c) HAADF-STEM image and (d) the corresponding size distribution histogram of Pd clusters.

In a first step, Pd was chosen as an example to demonstrate the effectiveness of our polymer support towards the synthesis of a wide spectrum of high-quality MCs (Scheme 1). Briefly, a light yellow solution of P(triaz) (5 mg) in a 9 mL mixture solution of dichloromethane and methanol (volume ratio = 2:1) was prepared. The color of solution became dark brown right upon adding palladium nitrate (Pd content in solution = 0.5 mg) (Figure Sio), suggesting coordination bonding between Pd (II) and P(triaz). After aging for 20 min, the mixture was subsequently reduced by a methanol solution (0.5 mL) of sodium borohydride (NaBH4, 5 mg) to a light brown solution without any precipitate, indicating Pd cluster formation via reduction and stabilization by P(triaz).

The size and size distribution of Pd clusters were characterized by transmission electron microscopy (TEM) and cryo-EM. The cryo-EM and bright field (BF) TEM images of Pd/P(triaz) show the formation of well-dispersed P(triaz) vesicles and Pd clusters stabilized onto them, respectively (Figure 1a,b and S11&12). The morphology of Pd clusters was characterized by high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) (Figure 1c). The average diameter of Pd clusters is 1.0 ± 0.2 nm (Figure 1d). X-ray photoelectron spectroscopy (XPS) analysis identifies the formed Pd clusters with binding energy at 335.3 and 340.6 eV (Figure S13), corresponding to Pd 3d5/2 and Pd 3d3/2 of metallic Pd, respectively. The variation of Pd loading concentration in the range of $4.8 \sim 14.5$ wt% (with regard to the

P(triaz)) did not change the ultrasmall size of clusters (~ 1 nm) (Figure S14). Despite the ultrasmall size, Pd clusters are uncommonly stable against aggregation upon storage of months. More attractively, the PIL-stabilized Pd clusters can be processed like polymers, *i.e.* solution-cast into a film on a substrate, dried and re-dissolved in solution (Figure S15). This is fundamentally different from common metal nanoparticles, which upon drying often break or become non-dispersible. In a control experiment, the P(triaz)-free metal ion solution upon reduction by NaBH4 contains seriously aggregating metal particles as revealed by TEM image in Figure S16.

To our surprise, the P(triaz) route described here is general towards a large variety of MCs, including transition (*e.g.*, Co, Ni, Cu) and noble metals (*e.g.*, Ru, Rh, Ag, Pt, Au,) and even their bimetallic alloy (*e.g.*, Au-Ni) with loading mass up to 29 wt%. These various types of MCs of averagely 1 nm in size are exceptionally dispersible in liquid-phase (Figure S10), and the representative HAADF-STEM images are collected in Figure 2 (Figure S17 with higher magnifications) and evidenced by XPS and powder X-ray diffraction (PXRD) characterizations (Figure S18-28).

The role of P(triaz) in stabilization and immobiliza-



Figure 2. HAADF-STEM images of various MC/P(triaz) hybrids. Insets are the size distribution histograms of the corresponding MCs. The average size for Co: 0.9 ± 0.2 nm, Ni: 1.0 ± 0.2 nm, Cu: 1.1 ± 0.2 nm, Ru: 0.7 ± 0.2 nm, Rh: 1.1 ± 0.2 nm, Ag: 1.1 ± 0.2 nm, Pt: 0.9 ± 0.2 nm, Au: 1.2 ± 0.2 nm, and AuNi: 1.1 ± 0.2 nm.

tion of MCs triggered our interest. The UV-Vis spectra were firstly recorded to monitor the solution mixing process of P(triaz) and metal ions. Notably, a shift of absorption band of the metal ion/P(triaz) mixture in comparison to individual metal ions or P(triaz) in solution was observed (Figure S29-36). For example, in the Pd(II)/P(triaz) system, compared to the absorption of Pd(II) ion at 209 nm and P(triaz) at 247 nm, new absorption bands at 231 and 295 nm emerged (indicated by black arrows in Figure 3b), indicative of strong affinity between both species in solution that enriches metal ions into the vesicular support. To specify the binding site of P(triaz), proton nuclear magnetic resonance ('H NMR) measurements were employed. As shown in Figure 3c, upon addition of palladium nitrate the C5-proton signal in the triazolium ring (10.6 ppm) shifts to a high-field 10.3 ppm, indicative of its coordinative interplay with Pd(II). A similar trend was observed in other metal ion/P(triaz) mixtures as well (Figure S37&38). The critical step is the addition of NaBH4 to the metal ion/P(triaz) solution. In



Figure 3. (a) Schematic illustration of a Pd cluster (deep violet ball) stabilized by P(triaz) with multi-binding sites, i.e. polycarbene and naked nitrogen sites, the light violet ball represents the component of Pd atoms. (b) The UV-vis spectra monitoring the formation process of Pd/P(triaz) in CH2Cl2 and CH3OH (volume ratio = 2:1). (c) The ¹H NMR spectra record the formation process of Pd/P(triaz) in CD2Cl2 and CH3OH (volume ratio = 2:1). The signal at 8.5 ppm is attributed to NaBH4 as a blank in CD2Cl2 and CH3OH mixture (volume ratio = 2:1). (d) ¹³C NMR spectra of P(triaz), Pd(II)/P(triaz) and Pd/P(triaz) in CD2Cl2 and CH3OH mixture (volume ratio = 2:1). A strong intensive peak at 169.6 ppm appeared in Pd/P(triaz) (shown in a light violet rectangle), which is a typical chemical shift for metal-carbene coordination that has been observed previously. (e) XPS spectra for C1s signals of P(triaz) and Pd/P(triaz). In P(triaz), the C1s spectra could be fitted by the sum of three separated peaks (dotted lines) with 1:1:8 area ratios that correspond to C5 (287.2 eV), C3 (286.3 eV) and eight alkane carbons (284.6 eV) in PIL (the charge of alkane carbons here were corrected to 284.6 eV), respectively. The C5 component in Pd/P(triaz) shifts o.5 eV to lower binding energy (286.7 eV) as compared with that of P(triaz) due to the Pd-carbene complexation. (f) XPS spectra for N1s signals of P(triaz) and Pd/P(triaz) and Pd/P(triaz). In both spectra, the N1s spectra could be fitted by the sum of two separated peaks (dotted lines) with 1:2 area ratios that correspond to the naked nitrogen (N2) and the two nitrogen atoms (N1 and N4) of the triazolium ring.

Pd(II)/P(triaz), the C₅-proton signal with a visible intensity drop could be observed (Figure 3c, highlighted by a light violet rectangle). The C5 protons in the triazolium ring are well-known to be active as carbene precursor even in the presence of weak bases.^{13d} Our observation suggests that in the presence of BH4⁻ as a weak base that extracts protons (The chemical structure of P(triaz) maintained overall integrity in this case (see Figure S39) exception the extraction of part of its C-5 protons), carbenes form and bind the nearby metal species. Through integration of 'H NMR spectra, 33 % of the triazolium units in P(triaz) were calculated to participate in carbene formation, corresponding to averagely one metal atom per 1 triazolium unit. Similar behaviors were found in other metal species with an estimated carbene/metal ratio between 1-2 (Table S1). The carbene-Pd complex formation was further confirmed by ¹³C nuclear magnetic resonance (¹³C NMR) spectra (Figure 3d), in which a new peak appears at 169.6 ppm, typical for metal-carbene coordination.¹⁴ Such new characteristic peaks assigned to metalcarbene complexes were also observed in other MCs/P(triaz) hyrbids (Figure S40). More evidences from the peak shift in XPS spectra of carbons after metalcarbene complex formation were collected in Figure 3e and Figure S41-48. For example, the C5 signal in carbene-Pd complex shifted 0.5 eV to lower binding energy due to the more pronounced nucleophilic characteristic (Figure 3e); this is consistent with previous observation in ionic liquid derived monocarbene to stabilize metal nanoparticles.13f

It is clear that a strongly coordinating support is essential to control over the nucleation and growth of MCs.¹⁵ In this context, native P(triaz) is first of all capable of coordinating with Pd(II) primarily through the naked N2 nitrogen atom. The XPS measurements detected a 1.2 eV shift of N₂ signal from 398.6 eV in native P(triaz) to a high binding energy position (399.8 eV) in the Pd/P(triaz) hybrid (Figure 3f), which is far more stronger than the shifts of N1 and N4 signals (<0.5 eV). Similar phenomena of binding energy shifts have also been observed in other MC/P(triaz) systems (Figure S49-56). The affinity of P(triaz) towards metal ions collects them inside the substrate and brings them closer to the triazolium ring for the subsequent metal-carbene complex generation. An extra function of N2 nitrogen is to facilitate the formation of carbene in triazolium compounds.^{13d} Polycarbene formation by NaBH4 is a concurrent process to the reduction of Pd(II) and serves as in-situ capping agent for Pd clusters. Polycarbene is expected to act as a powerful complexing agent to transition metals, forms a thermodynamically more stable poly(carbene-metal) hybrid and plays a vital role in size control on MCs. It is different from previously reported soluble polymers, nanoporous materials or conventional poly(ionic liquid) supports, in which common elemental binding sites (e.g., N, O and S) are employed for metal nanoparticle stabilization.^{5, 6, 9g,h,} ^{17d} The lack of universal compatibility of these supports to different metals and their relatively mild coordination power make them difficult to apply to a broad spectrum of MCs and to effectively control their size and dispersability simultaneously. In a control experiment using poly[4-hexyl-1-vinylimidazolium iodide] (denoted as PILimidaz, Figure S5&6), in which the C2 position (N-CH2-N) is a weaker carbene precursor in the conditions used here for MC synthesis. The resultant Pd nanoparticles stabilized by PIL-imidaz are larger and broadly distributed in size from 1.5 to 11 nm (Figure S57). The 'H NMR spectra confirmed that after addition of NaBH4, the C2-H signal has only a little shift (<0.2 ppm, Figure S58), indicating the C2-H in the imidazolium ring is more inactive for metal-carbene formation than that in triazolium. This is also quantified by our calculation from its ¹H NMR spectra that for the imidazolium units only less than 5 % in PIL-imidaz participate in the metal-carbene formation (Figure S59). It is clear that the in situ generated polycarbene is required for stabilizing ultrasmall MCs. This role can also not be replaced by analogous monocarbenes; by using the triazolium monomer instead of P(triaz) as stabilizer, the freshly prepared Pd particles aggregate macroscopically in solution (Figure S6o). In fact, it was found that the C₅-proton signal in P(triaz) has a slight decrease (< 8 %) in its integrity right upon Pd(II) addition, although the ¹³C-NMR spectrum detected no metal-carbene signal (Figure 3d). This evidence implies the replacement of the C₅-proton by Pd(II) that forms metal-carbene complex might take place already before NaBH4 addition but in a weak equilibrium. This equilibrium shifts towards the metal-carbene side once the released C5-protons are neutralized by BH4, which serves simultaneously as reductant and base. In a control experiment that replaced NaBH₄ by UV light to reduce Ag(I)/P(triaz) to Ag/P(triaz), it ended up with large Ag aggregate (Figure 61&62), as metal-carbene formation is restricted in the absence of base.



Figure 4. Time course plots of H₂ generation for the methanolysis of ammonia borane (AB) over the Rh/P(triaz) and unsupported Rh-catalysts (Rh/P(triaz)-Free) at 298 K (Rh/AB = 0.01). Inset: the corresponding TOF values of the catalysts.

The P(triaz)-stabilized MC systems were exemplarily tested in a simple assay to evaluate the effect of the new

capping agent on metal reactivity, the liquid-phase methanolysis of ammonia borane (NH3BH3, AB). AB is known as a chemical hydrogen source that releases hydrogen through reaction with water or methanol.¹⁶ Rh clusters were chosen as catalyst, as they are commonly used for this reaction. Under identical experimental conditions, Rh/P(triaz) with a Rh loading of 0.01 mmol (Rh/AB = 0.01) completed the reaction $(H_2/AB = 3.0)$ within 1.16 min at 298 K (Figure 4), *i.e.* a turnover frequency (TOF) value as high as 260 min⁻¹. It is the highest value reported so far among all supported catalysts and capping agent protected catalysts,16,17 including common commercial catalyst Pd/C (Figure S63). By contrast, the PIL-free Rh nanoparticles (4-8 nm in size) required more than 30 min (TOF number of 10 min⁻¹) to complete the reaction (Figure 4). In the case of triazolium monomer-stabilized Rh nanoparticles, the reaction ended up with a lower TOF number of 75 min⁻¹ (Figure S64). Even dendrimers (e.g., polyamidoamine dendrimer with hydroxyl surface group, PAMAM-OH) as the classic high-performance stabilizer for Rh cluster (1.5 \pm 0.3 nm, Figure S65) revealed a TOF number of "only" 141 min⁻¹ (Figure S66). Durability and recyclability of MCs are of high significance for potential catalytic applications. The Rh/P(triaz) catalyst was found to be effective for at least 4 successive additions of AB into the reactor (Figure S67). HAADF-STEM measurements reveal that the size and morphology of Rh cluster remained the same (Figure S68&69). The Rh/P(triaz) catalyst could be also recovered as a solid when dried in N2 atmosphere, washed and re-dissolved in solution for the next run without any activity loss (Figure S70). We assume that this unexpected high catalytic activity and stability can be reasonably attributed to the polycarbenebased capping agent that is used in this work to replace the polyimidazolium-based conventional PILs as well as the dendrimers. The metal-carbene bond might be strong enough that the metal-metal bonding is no more favored, i.e. from a thermodynamic perspective the MCs with surface metal-carbene complex are self-stabilizing. Besides, though the P(triaz) vesicle itself is catalytically inactive to AB (Figure S71), the vesicular form bearing a thin wall is a structural merit, as it enriches active sites necessary for MC stabilization and meanwhile facilities fast mass diffusion in solution. When using non-vesicular P(triaz) in methanol or PIL-butyl in the same dichloromethane/methanol mixture as stabilizers for Rh clusters (particle size: 1.4 ~ 1.8 nm), lower catalytic activity with a TOF number of 112 and 143 min⁻¹, respectively, was observed (Figure S72-75).

CONCLUSION

In conclusion, polytriazolium PILs bearing hexyl side chains spontaneously assembled to nanovesicles and were capable of exerting a strict size control over a broad of MCs of about 1 nm in size. It prominently enhances catalytic performance, *e.g.* the reactivity of the as-synthesized Rh MC/P(triaz) catalyst is currently the best in a model reaction of methanolysis of ammonia borane, being at least 25% higher than the state-of-the-art catalyst.^{17d} The

key to the success of this approach is enhancing the already high stabilization power of PILs by in-situ generated polycarbenes under base addition. This previously undiscovered mechanism in MC stabilization is inspiring to researchers in nanoscience and particle processing. Beyond catalysis, the highly stable, dispersible MCs/PIL covering a broad spectrum of metal species are expected to be potentially also useful in imaging, nanomedicine and magnetism study.

ASSOCIATED CONTENT

Supporting Information.

Supporting Information is available free of charge via the Internet at http://pubs.acs.org."

Experimental sections, Chemicals and instrumentations, additional characterizations, and catalytic data.

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Notes

The authors declare no competing financial interest.

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