Atomic Level Tuning of the Catalytic Properties: Doping Effects of 25-Atom Bimetallic Nanoclusters on Styrene Oxidation

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Abstract:

Atomically precise bimetallic $M_xAu_{25-x}(SR)_{18}$ ($M = Cu$ and Ag , $R = CH_2CH_2Ph$) nanoclusters are investigated as oxide-supported catalysts for the catalytic oxidation of styrene. Their catalytic properties are compared with the case of homogold $Au_{25}(SR)_{18}$ nanocluster. The oxide-supported $M_xAu_{25-x}(SR)_{18}$ catalysts give rise to 42–82% conversion of styrene at 70 °C using (diacetoxyiodo)benzene ($PhI(OAc)_2$) as the oxidant. The Ag and Cu dopants are found to modulate both the activity (i.e. conversion of styrene) and the selectivity to styrene epoxide or benzaldehyde (major products). The $Ag_xAu_{25-x}(SR)_{18}$ clusters exhibit higher activity and benzaldehyde selectivity than the homogold cluster, while the $Cu_xAu_{25-x}(SR)_{18}$ clusters primarily enhance the selectivity to benzaldehyde without significantly changing the activity. The results provide insights into the factors that influence the catalytic activity and selectivity in styrene oxidation.

Keywords: Gold nanoclusters, doping, silver, copper, catalytic oxidation

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1. Introduction

Gold-based bimetallic nanocluster catalysts as well as homogold nanoclusters hold potential in a variety of reactions [1-4], such as catalytic oxidation reactions of CO [5,6], alcohols [7-9], and olefins [10-13] (e.g. propene and styrene). Recent advances in the synthesis of ligand-protected nanoclusters in solution phase have achieved atomic level control of the composition of gold-based bimetallic nanoclusters [14]. A notable example is the attainment of bimetallic $M_xAu_{25-x}(SR)_{18}$ nanoclusters ($M = Ag$ and Cu) [15-17]. Although their structure is similar to that of the homogold $Au_{25}(SR)_{18}$ nanocluster, the bimetallic nanoclusters exhibit different electronic properties due to the substitution of heteroatoms into the gold framework [14-17]. Such effects prompt us that the catalytic properties of bimetallic $M_xAu_{25-x}(SR)_{18}$ would also be changed compared to the $Au_{25}(SR)_{18}$ nanocluster, albeit all of these clusters share the same atomic packing structure.

Previously Tsukuda and coworkers reported that the ligand-off Pd_1Au_{24} nanoclusters on multiwalled carbon nanotubes gave rise to a much better catalytic activity than that of the ligand-off Au_{25} nanocluster in aerobic oxidation of benzyl alcohol to benzaldehyde [18]. Selective oxidation of organic compounds (e.g. alcohol and olefins) with environmentally friendly oxidants (e.g. oxygen, hydrogen peroxide, and (diacetoxyiodo)benzene) is an important direction in green organic catalytic chemistry [19,20]. Konishi et al. reported epoxidation of olefins catalyzed by a manganese-porphyrin complex with dodecanethiolate-protected metallic gold nanoclusters as a co-catalyst and iodosylbenzene (PhIO) as the oxidant [21]. In our previous work, we investigated the catalytic properties of monoplatinum-doped $Pt_1Au_{24}(SR)_{18}/TiO_2$ using $PhI(OAc)_2$ as oxidant in the oxidation of styrene [22]. The Pt-centered $Pt_1Au_{24}(SR)_{18}$ cluster showed much higher catalytic activity and selectivity for benzaldehyde than the $Au_{25}(SR)_{18}$ cluster catalyst.

Herein, we are motivated to investigate the catalytic properties of copper and silver-doped nanoclusters. Compared to the mono-doping cases of Pd and Pt [23,24], the dopants of Cu and Ag typically produce a range of the dopant numbers in $M_xAu_{25-x}(SR)_{18}$ nanoclusters [15-17], but the total number of metal atoms is retained at 25.

In this work we investigate the catalytic activities of the gold-based bimetallic $M_xAu_{25-x}(SR)_{18}$

nanoclusters (where, M=Ag and Au) in the oxidation of styrene using (diacetoxyiodo)benzene (PhI(OAc)₂) as the oxygen source. The PhI(OAc)₂ oxidant is of low toxicity and is a very powerful oxygen atom donor in epoxidation reactions [25].

2. Experimental

2.1. Synthesis and characterization of $M_xAu_{25-x}(SR)_{18}$ ($M=Cu, Ag$) and $Au_{25}(SR)_{18}$

$Cu_xAu_{25-x}(SC_2H_4Ph)_{18}$, $Ag_xAu_{25-x}(SC_2H_4Ph)_{18}$, and $Au_{25}(SC_2H_4Ph)_{18}$ were synthesized according to modified methods [17,26]. The synthesis of $Au_{25}(SC_2H_4Ph)_{18}$ is as follows. Tetraoctylammonium bromide (TOABr, 101.5 mg) and $HAuCl_4 \cdot 4H_2O$ (60.9 mg) were dissolved in THF (10.0 mL) in a three-necked flask. $PhCH_2CH_2SH$ (106 mL) was slowly added to the flask. After the solution turned clear over a period of ca. 0.5 h, an aqueous solution of $NaBH_4$ (58.7 mg, freshly dissolved in 3.0 mL ice-cold nanopure water) was rapidly added at once under slow stirring. After ca. three hours, the reaction was stopped, and THF was removed by rotary evaporation. The black solids were collected and thoroughly washed with MeOH, $Au_{25}(SC_2H_4Ph)_{18}$ was extracted by MeCN, and characterized by matrix-assisted laser desorption ionization mass spectrometry (MALDI-MS) analysis. The syntheses of $Cu_xAu_{25-x}(SC_2H_4Ph)_{18}$ and $Ag_xAu_{25-x}(SC_2H_4Ph)_{18}$ nanoclusters followed a similar procedure as above, except that copper(II) acetate and silver(I) acetate were added in a 1 to 10 copper-to-gold and silver-to-gold ratio.

2.2 Characterization of cluster

The UV-Vis spectra of the nanoclusters (dissolved in CH_2Cl_2) were acquired on a Hewlett-Packard (HP) Agilent 8453 diode array spectrophotometer at room temperature. Matrix-assisted laser desorption ionization (MALDI) mass spectrometry was performed with a PerSeptive Biosystems Voyager DE super-STR time-of-flight (TOF) mass spectrometer. Trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenyldiene]-malononitrile (DCTB) was used as the matrix in MALDI-MS analysis. Typically, 0.1 mg matrix and 10 μ L analyte stock solution were mixed in 10 μ L CH_2Cl_2 , and the mixed solution was applied to the steel plate and then air-dried prior to MALDI analysis.

2.3. Preparation of 1 wt% $M_xAu_{25-x}(SR)_{18}$ /oxides ($M=Cu, Ag$) and 1 wt% $Au_{25}(SR)_{18}$ /oxides

Typically, 1 mg $M_xAu_{25-x}(SR)_{18}$ or $Au_{25}(SR)_{18}$ clusters were dissolved in 5 ml DCM, and 100 mg oxides (TiO_2 , CeO_2 and SiO_2) were added. After stirred 12h at r.t., $M_xAu_{25-x}(SR)_{18}$ /oxides catalysts were collected by centrifugation and dried in vacuum. As shown in the high-resolution scanning transmission electronmicroscopy (STEM) image, the interplanar distance of the TiO_2 support is 0.35 nm (Figure S1 in the Supporting Information), in agreement with the {101} plane of the anatase phase of TiO_2 .

2.4. Typical procedure for styrene oxidation

In a typical reaction, $PhI(OAc)_2$ (0.1 mmol), styrene (0.1 mmol) and 1wt% cluster/oxide catalysts (100 mg, pretreated at 150°C in vacuum for 2h) were mixed in 2 mL acetonitrile. The mixture was stirred under N_2 atmosphere at 70 °C for 10h as indicated in Table 1. The product was obtained after removal of the solvent of the supernatant. The conversion of styrene and yields of styrene epoxide, benzaldehyde and acetophenone were determined by 1H NMR (300 MHz) spectroscopic analysis.

3. Results and discussion

3.1. Characterization of clusters

The three types of nanoclusters (i.e., multiple-atom doped $Cu_xAu_{25-x}(SR)_{18}$ ($x = 0$ to 5) and $Ag_xAu_{25-x}(SR)_{18}$ ($x = 4$ to 8) [17], as well as homogold $Au_{25}(SR)_{18}$ nanoclusters [26] were synthesized following the literature protocols. The nanoclusters were characterized by matrix-assisted laser desorption/ionization (MALDI) mass spectrum (Fig. 1). The MALDI mass spectrum of $Au_{25}(SR)_{18}$ nanocluster exhibits a single intense peak at m/z 7394 ($z=1$), consistent with the calculated formula weight of 7393.72 for $Au_{25}(SR)_{18}$, where $R=CH_2CH_2Ph$ (Fig. 1A); of note, the small peak at 6057 is an inevitable fragment ($Au_{21}(SR)_{14}$) caused by the somewhat destructive MALDI method, i.e., laser irradiation caused the loss of a $Au_4(SR)_4$ unit from the parent $Au_{25}(SR)_{18}$ nanocluster, resulting in some $Au_{21}(SR)_{14}$ fragments [26]. No other peaks were found, indicating the high purity of the $Au_{25}(SR)_{18}$ nanoclusters. The cases of Ag and Cu doping gave rise to a range of x values for $Ag_xAu_{25-x}(SR)_{18}$ or $Cu_xAu_{25-x}(SR)_{18}$ (Fig. 1C-D), but the total number of metal atoms per cluster is preserved at 25, indicating the high stability of the 25-metal-atom structure [13]. As shown in Fig. 1C, the average spacing of the

$\text{Ag}_x\text{Au}_{25-x}(\text{SR})_{18}$ peaks is 89.5, i.e. the atomic mass difference between gold and silver ($M_{\text{Au}} - M_{\text{Ag}} = 197.0 - 107.9 = 89.1$), which suggests that gold atoms are successively replaced by silver atoms with the total number retained at 25. Similarly, in the case of $\text{Cu}_x\text{Au}_{25-x}(\text{SR})_{18}$ (Fig. 1D), the average peak spacing is 133.8 (theoretical $M_{\text{Au}} - M_{\text{Cu}} = 197.0 - 63.5 = 133.5$), which also indicates the substitution of copper for gold atoms; however, the maximum replacement in $\text{Cu}_x\text{Au}_{25-x}(\text{SR})_{18}$ is only up to $x=5$ and is less than the case of $\text{Ag}_x\text{Au}_{25-x}(\text{SR})_{18}$ (where, x up to 8), Fig. 1C-D (insets).

Fig. 1. (A) UV-vis spectra of $\text{Au}_{25}(\text{SR})_{18}$ and the doped nanoclusters, MALDI-MS of the (B) $\text{Au}_{25}(\text{SR})_{18}$, (C) $\text{Ag}_x\text{Au}_{25-x}(\text{SR})_{18}$ ($x = 4$ to 8), and (D) $\text{Cu}_x\text{Au}_{25-x}(\text{SR})_{18}$ ($x = 0$ to 5). The insets in (C) and (D) are the zoom-in spectra. $\text{R} = \text{CH}_2\text{CH}_2\text{Ph}$.

3.2. Catalytic properties of $M_xAu_{25-x}(SR)_{18}$ ($M = Cu$, and Ag) and $Au_{25}(SR)_{18}$ clusters

The $M_xAu_{25-x}(SR)_{18}$ ($M = Cu$, and Ag) and $Au_{25}(SR)_{18}$ clusters were supported onto inorganic oxides (e.g. TiO_2 , SiO_2 , and CeO_2) by impregnation of oxide powders in a dichloromethane (DCM) solution of clusters. The catalytic oxidation of styrene was performed in acetonitrile at 70 °C for 10 h under a N_2 atmosphere, and other conditions are as follows: 0.1 mmol styrene, 0.1 mmol $PhI(OAc)_2$, 100 mg of $M_xAu_{25-x}(SR)_{18}/oxides$ (1 wt% loading of ligated clusters). The conversion of styrene and the selectivities for benzaldehyde, styrene epoxide, and acetophenone were analyzed by 1H NMR. In general, three products (styrene epoxide, benzaldehyde, and acetophenone) were yielded during the catalytic oxidation of styrene by gold nanoclusters (Scheme 1) [27-29]. A typical 1H NMR spectrum is shown in Fig. S2. NMR analysis identified four components in the crude product: the residual styrene which shows signals at $\delta = \sim 5.25, 5.75$ ppm ($-C=CH_2$), and 6.75 ppm ($Ph-HC=CH_2$), styrene epoxide at $\sim 2.83, 3.18$ ppm ($PhCHOCH_2$) and 3.87 ppm ($PhCHOCH_2$), benzaldehyde at 10.02 ppm ($Ph-CHO$) and acetophenone at 2.56 ppm ($PhCOCH_3$). The phenyl groups of the four compounds and another side-product iodobenzene were overlapped from 7.0 to 8.2 ppm. The integrated peak areas and the J - J coupling constants confirm the above assignment. By integrating and normalizing the NMR peak areas, the conversion and selectivity are calculated (averaged over three runs).

Scheme 1. Oxidation of styrene to yield styrene epoxide, benzaldehyde, and acetophenone.

We first compare the three types of clusters supported on TiO_2 . As shown in Table 1 (entries 1-4), the blank test (i.e. using plain TiO_2 in the catalytic reaction) showed a 15.8% conversion of styrene, while the $Au_{25}(SR)_{18}/TiO_2$ catalyst showed a much higher conversion of styrene (58.9%), indicating that gold

clusters are essential in the styrene oxidation reaction. As to the product selectivity, the $\text{Au}_{25}(\text{SR})_{18}/\text{TiO}_2$ catalyst gave a slightly higher selectivity for benzaldehyde (54%) than styrene epoxide (44.3%), with the remaining being acetophenone (1.7%). After doping the gold cluster with silver, the catalytic activity is almost the same as that of $\text{Au}_{25}(\text{SR})_{18}/\text{TiO}_2$, but the product selectivity for benzaldehyde is significantly increased (86.9% over $\text{Ag}_x\text{Au}_{25-x}(\text{SR})_{18}/\text{TiO}_2$ vs 54.0% over $\text{Au}_{25}(\text{SR})_{18}/\text{TiO}_2$). In contrast, the copper-doped clusters gave rise to a reduced activity (41.9%) than that of the homogold catalyst, but the selectivity for the benzaldehyde product is higher (88.3%). Overall, a distinct effect of doping is manifested in that both Ag and Cu doping enhance the product selectivity to benzaldehyde compared to the undoped cluster catalyst.

Table 1. Catalytic performance of cluster/oxide for styrene oxidation (treated in vacuum)

$ \text{Styrene} \xrightarrow[\text{PhI(OAc)}_2, \text{MeCN}, 70^\circ\text{C}]{\text{M}_x\text{Au}_{25-x}(\text{SR})_{18}/\text{oxides}} \text{1} + \text{2} + \text{3} $					
entry	catalysts	conversion (%) ^b	selectivity (%) ^b		
			1	2	3
1	Only TiO_2	15.8	76.1	23.9	trace
2	$\text{Au}_{25}(\text{SR})_{18}/\text{TiO}_2$	58.9	54.0	44.3	1.7
3	$\text{Ag}_x\text{Au}_{25-x}(\text{SR})_{18}/\text{TiO}_2$	60.1	86.9	12.4	0.7
4	$\text{Cu}_x\text{Au}_{25-x}(\text{SR})_{18}/\text{TiO}_2$	41.9	88.3	11.7	trace
5	Only CeO_2	14.1	53.2	46.8	trace
6	$\text{Au}_{25}(\text{SR})_{18}/\text{CeO}_2$	64.2	46.7	51.9	1.4
7	$\text{Ag}_x\text{Au}_{25-x}(\text{SR})_{18}/\text{CeO}_2$	82.1	46.4	53.6	trace
8	$\text{Cu}_x\text{Au}_{25-x}(\text{SR})_{18}/\text{CeO}_2$	66.3	52.9	47.1	trace
9	Only SiO_2	13.3	53.3	46.5	trace
10	$\text{Au}_{25}(\text{SR})_{18}/\text{SiO}_2$	54.5	50.3	48.7	1.0

11	$\text{Ag}_x\text{Au}_{25-x}(\text{SR})_{18}/\text{SiO}_2$	81.5	71.2	28.2	0.6
12	$\text{Cu}_x\text{Au}_{25-x}(\text{SR})_{18}/\text{SiO}_2$	65.7	74.9	24.4	0.7

[a] Reaction conditions: 0.1 mmol styrene, 0.1 mmol $\text{PhI}(\text{OAc})_2$, 100 mg 1wt% loading $\text{M}_x\text{Au}_{25-x}(\text{SR})_{18}/\text{oxides}$, 2 mL acetonitrile, 70 °C, 10 h. [b] The conversion of styrene and the selectivities of benzaldehyde, styrene epoxide, and acetophenone were analyzed by ^1H NMR.

With respect to the CeO_2 -supported $\text{M}_x\text{Au}_{25-x}(\text{SR})_{18}$ and $\text{Au}_{25}(\text{SR})_{18}$ catalysts (Table 1, entries 5-8), the $\text{Ag}_x\text{Au}_{25-x}(\text{SR})_{18}/\text{CeO}_2$ gave a much higher activity (82.1% conversion of styrene) than other catalysts, while the product selectivities are almost the same as the case of the undoped catalyst. No distinct effect in both activity and selectivity was observed for the Cu-doped catalyst.

In the case of SiO_2 -supported catalysts, we again observed that the Ag-doped catalyst gave a much higher activity and an increased selectivity for benzaldehyde compared to the undoped catalyst. Similarly, the Cu-doped cluster offered a distinct increase in the selectivity for benzaldehyde but the increase in catalytic activity is less than that of the $\text{Ag}_x\text{Au}_{25-x}(\text{SR})_{18}/\text{SiO}_2$.

3.3. Insights from the $\text{M}_x\text{Au}_{25-x}(\text{SR})_{18}$ ($M = \text{Cu}, \text{Ag}$) and $\text{Au}_{25}(\text{SR})_{18}$ cluster catalysts

Based on the above catalytic results, the catalytic selectivity is affected by both the oxide support and the metal clusters. TiO_2 prefers benzaldehyde while both CeO_2 and SiO_2 give rise to roughly equal benzaldehyde and styrene epoxide products. The activity of all of the three plain oxides is low (13.3 – 15.8%).

The loading of $\text{Au}_{25}(\text{SR})_{18}$ clusters onto TiO_2 , CeO_2 and SiO_2 gave rise to roughly 50% selectivities for benzaldehyde and styrene epoxide. The TiO_2 -supported $\text{M}_x\text{Au}_{25-x}(\text{SR})_{18}$ ($M = \text{Ag}, \text{Cu}$) catalysts prefer to yield benzaldehyde (Table 1, entries 3 and 4; 86.9% over $\text{Ag}_x\text{Au}_{25-x}(\text{SR})_{18}$, 88.3% over $\text{Cu}_x\text{Au}_{25-x}(\text{SR})_{18}$). This trend is also consistent with the case of $\text{Pt}_1\text{Au}_{24}(\text{SR})_{18}$ (89.9% selectivity for benzaldehyde) [22]. In the case of CeO_2 -supported $\text{M}_x\text{Au}_{25-x}(\text{SR})_{18}$ catalysts, no major difference in the selectivities for benzaldehyde and styrene epoxide is found, indicating a cooperative role of the cluster and the support in affecting the product selectivities, which is reminiscent of the cluster/support interfacial effect, either in terms of charge transfer or the perimeter sites of the interface being the

catalytically active centers. Further insight can be obtained from the case of the catalytic selectivity of SiO₂-supported M_xAu_{25-x}(SR)₁₈ catalysts, in which both Ag- and Cu-doped M_xAu_{25-x}(SR)₁₈ nanoclusters offer distinctly enhanced selectivity for benzaldehyde (Table 1, entries 10-12). It is well known that SiO₂ is chemically inert and does not exhibit any charge transfer to or from the cluster, thus, we rationalize that the perimeter sites of the cluster/support interface should be the catalytically active centers, which can explain the cooperative role of the cluster and the support in tuning the selectivity for product.

With respect to the atomic structure of M_xAu_{25-x}(SR)₁₈ (M=Ag, Cu), both types of dopants were confirmed to reside at the icosahedral surface [15,16], in contrast with the case of Pt doping in which the single Pt atom is located in the icosahedral center [22]. Thus, the above catalytic results indicate that the selectivities for benzaldehyde and styrene epoxide are also affected by the inner icosahedral shell of the M_xAu_{25-x}(SR)₁₈ (both Ag and Cu doping). This insight is in contrast with the previously reported effect of central doping of a single Pt atom in Pt₁Au₂₄(SR)₁₈ for catalytic oxidation of styrene [22].

It has been reported in the literature [21] that the surface thiolate groups on gold nanoclusters can be partially oxidized by oxidants (e.g. PhIO, which is similar to PhI(OAc)₂ in our present work), and that the oxidized thiolates (e.g. in the form of sulfoxide) are eliminated from the cluster surface to generate unprotected gold surface. To test that, we performed IR measurements on the Au₂₅(SR)₁₈ and Ag_xAu_{25-x}(SR)₁₈ catalysts after treatment with PhI(OAc)₂ (Fig. 2). The fresh Au₂₅(SCH₂CH₂Ph)₁₈/TiO₂ catalyst shows IR absorption bands at 2860, 2930 and 2960 cm⁻¹, which are from the aliphatic C-H stretching vibration of the -SCH₂CH₂Ph ligands. Treatment with PhI(OAc)₂ at room temperature or 70 °C did not lead to significant changes except that the 2860 cm⁻¹ band became somewhat weaker (Fig. 2A). A similar result was also observed in the case of Ag_xAu_{25-x}(SCH₂CH₂Ph)₁₈/TiO₂ catalyst (Fig. 2B). Thus, the clusters are quite stable under the oxidation conditions; nevertheless, the IR results do not rule out the possibility that some ligands might be stripped off during the prolonged reaction process.

Fig. 2. IR spectra of (A) the $\text{Au}_{25}(\text{SCH}_2\text{CH}_2\text{Ph})_{18}/\text{TiO}_2$ and (B) $\text{Ag}_x\text{Au}_{25-x}(\text{SCH}_2\text{CH}_2\text{Ph})_{18}/\text{TiO}_2$ catalysts after different treatments.

Spectroscopic evidence for the absorption of alkene on gold nanoclusters during epoxidation was reported in the literature [30]. Experimental and theoretical studies of the catalytic activity of bare gold clusters (Au_{6-10}) [31], as well as model calculations on the oxidation over Au(111) surfaces [32], have also been reported. The role of the support in the oxidation has been studied in the literature [33,34]. Based on the literature and our own results discussed above, we propose a possible catalytic mechanism for the styrene oxidation reaction. First, the cluster/support interface should be the catalytic sites. The ligated clusters or the partially dethiolated clusters adsorb the reactants. The reactant styrene should be absorbed on the gold/support surface, and $\text{PhI}(\text{OAc})_2$ to be activated through weak $\text{Au}\cdots\text{O}$ interaction with the gold surface [21], then oxygen-atom transfers to styrene to yield benzaldehyde and styrene epoxide (Scheme 2). Given the location of Ag (or Cu atoms) at the inner icosahedral surface [35] (Scheme 2, right

panel), after partial dethiolation there is a possibility that the Ag (or Cu) atoms may migrate from the inner icosahedral surface to the outer surface and exchange atomic sites with surface gold, but this chance should be less and future analysis by X-ray absorption spectroscopy [36] may provide further information.

Scheme 2. Schematic illustration of a possible catalytic mechanism of oxidation of styrene catalyzed by gold nanoclusters with PhI(OAc)₂ as the oxidant. The right panel shows the low-energy configuration of Ag₃Au₂₂(SR)₁₈ (the R groups are omitted in the drawing) [35].

4. Conclusion

In summary, we have investigated the catalytic properties of copper or silver-doped bimetallic M_xAu_{25-x}(SR)₁₈ nanocluster catalysts in the selective oxidation of styrene using (diacetoxyiodo)benzene as the oxidant. Both Ag_xAu_{25-x}(SR)₁₈ and Cu_xAu_{25-x}(SR)₁₈ clusters increase the product selectivity toward benzaldehyde. The results indicate that the selectivities for benzaldehyde and styrene epoxide are affected by the inner shell of the icosahedral M_xAu_{25-x}(SR)₁₈ clusters. The atomic level insights into the factors influencing the catalytic activity and selectivity will be useful in mapping out the detailed catalytic mechanism and the new design of selective catalysts.

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Graphical Abstract: