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Polyacrylamide-Mediated Silver Nanoparticles for Selectively Enhancing Electroreduction of CO₂ towards CO in Water

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Abstract: Conversion of the greenhouse gas CO₂ to value-added products is an important challenge for sustainable energy research. Here we construct a durably nanohybrid composed of Ag nanoparticles and polyacrylamide for the selectively electroreduction of CO₂ to CO. The nanohybrid exhibits outstanding CO Faradaic efficiency of 97.2 \pm 0.2 % at -0.89 V_{RHE} with a desirable CO partial current density of -22.0 ± 2.3 mA cm⁻², and maintains the CO Faradaic efficiency above 95% over a wide potential range (-0.79 to -1.09 V_{RHE}) and excellent stability during a 48 h prolong electrolysis. We demonstrate that the origins of selective enhancement of CO2 reduction over the nanohybrid stem from the activation of CO2 via hydrogen bond and the low basicity of amide. DFT calculations imply that the synergy of Ag nanoparticles and amide could better stabilize the key intermediate (*COOH) and effectively lower the overpotential of CO2 reduction. These results establish the synergistic effects of organic/inorganic hybrid as a complementary method for tuning selectivity in CO₂-to-fuels catalysis.

Introduction

With the rapid development of the global economy, the enormous fossil fuel consumption has resulted in a sharp increase in the concentration of carbon dioxide (CO₂) in the atmosphere, causing progressively severe environmental problems. How to take full advantage of CO₂ has become a hot spot in the scientific research.^[1] Superior to emission reduction and CO_2 storage, electrochemical conversion of CO_2 is considered as an environmental-friendly and promising route since it can not only reduce CO2, but also convert it into valuable low-carbon fuels such as CO,^[2-4] formic acid,^[5,6] alcohols,^[7,8] and hydrocarbons,^[9-12] etc. However, there are still many challenges to overcome, such as the large overpotential, low durability of electrocatalyst and the competitive hydrogen evolution reaction (HER) in aqueous environment.[13,14] Therefore, designing an efficient electrocatalyst with outstanding activity, selectivity and stability is still desperate.

Various electrocatalysts have been investigated for CO_2 electrochemical reduction reaction (CO_2ER), and among them, metal catalysts have stood out thanks to their good electrical conductivity and stability in aqueous environment.^[15-20] Furthermore, those metal electrocatalysts selective for CO production are more attractive as they exhibit highest energetic efficiencies. Ag is considered as the more promising electrocatalyst relative to Au since it is low-cost and has a comparable CO selectivity.^[21-24] Tremendous efforts have been dedicated to developing and improving the performance of Ag

catalysts for CO₂ER, including regulating the particle size,^[25,26] shape,^[27,28] morphology^[29,30] and defect site^[31,32] of nanostructured Ag. Nevertheless, the activity and selectivity for CO₂ER are still unsatisfactory due to the weak adsorption of CO₂ (or intermediates) and the hydrophobicity on the surface of these well-defined metal catalysts in aqueous electrolyte.

Therefore, some cocatalysts^[33-35] have been employed to modify the metal catalysts to enhance the interaction between the metal catalyst and CO2 or the key intermediates and lower the energy barrier of CO2ER. For example, Gao, et al. constructed an Au-CeO_x interface to stabilize the key intermediates COOH* and thus facilitated CO_2ER .^[36] However, the introduction of metal oxide significantly reduces the electrical conductivity of the electrode and the hydrophobicity remains unsolved. Zhang, et al. improved CO2ER performance by coating the N-doped carbon nanotubes (CNTs) with an overlayer film of polyethylenimine (PEI), which can concentrate CO₂ on the electrode surface.^[6] On the other hand, the key intermediate CO2 ** was presumably stabilized by the N-doped CNTs and the co-catalyst PEI, lowering the activation energy of CO₂ reduction into formic acid. Unfortunately, HER was also promoted to a great extent probably due to the protonation of PEI in the nearneutral aqueous electrolyte.^[37]

Inspired by the synergistic effect in enhancing CO₂ adsorption and activation, we propose herein a strategy to selectively facilitate CO2ER by fabricating a durably organic/inorganic nanohybrid composed of polyacrylamide (PAM) and Ag nanoparticles (NPs). As for the amide group in PAM, the carbonyl group is conjugated with the p orbital occupied by the lone pair on the nitrogen atom, decreasing the electron cloud density on the nitrogen atom and increasing the polarity of the N-H bond. Consequently, the amide group would not be protonated in near-neutral electrolyte and the reactive H atom may form hydrogen bond with the O atom in CO₂, thus enhancing the adsorption of CO₂ and activating CO₂. Meanwhile, the introduction of PAM appropriately improves the hydrophilicity of the electrode surface, which may facilitate the timely diffusion of CO₂ dissolved in the aqueous solution to the electrode surface, thereby contributing to an enhanced CO₂ER controlled by reactant diffusion at high overpotentials. Furthermore, we tried to prepare Ag NPs with large sizes of ~100 nm to alleviate the sensitivity of the catalytic activity to particle size, aiming at enhancing the durability of the hybrid catalyst. Density functional theory (DFT) calculations reveal that the PAM-modified Ag NPs indeed could stabilize the key intermediate *COOH and effectively lower the overpotential of CO₂ER.

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Results and Discussion

The structure and morphology of the PAM-modified Ag NPs (AgNPs@PAM) powder were firstly characterized by SEM and are shown in Figure 1. The large-scale SEM image (Figure 1a) indicates that the hybrid powder has a honeycomb-like macroporous morphology. The partially enlarged SEM image (Figure 1b) further displays that the size of Ag NPs coated with PAM is 100 ± 20 nm. The elemental mapping images (Figure 1d) confirm that the elemental carbon, nitrogen and oxygen in PAM indeed exist in the hybrid catalyst. The XRD patterns (Figure 1e) indicate that Ag NPs in the as-prepared hybrid are the face-centered cubic (fcc) structure since Ag (111), (200), (220), (311) and (222) crystal planes are detected respectively and Ag (111) is the major plane in the crystalline structure. The HR-TEM image (Figure 1c) shows that the lattice distance of Ag NPs is 0.23 nm, which corresponds to the Ag (111) crystal plane and

agrees well with the XRD result. Additionally, the identical FT-IR spectral fingerprints of AgNPs@PAM and PAM (Figure 1f) further confirm the successful introduction of PAM to the surface of Ag NPs. Specifically, peaks observed at ~3412 cm⁻¹ are ascribed to the stretching vibration of N–H.^[38] The doublet peaks at 2975 cm⁻¹ and 2924 cm⁻¹ show the antisymmetric stretching vibration of methyl and methylene and the peaks at 1650 cm⁻¹ and 1572 cm⁻¹ are assigned to the C=O stretching vibration and the N-H bending vibration, respectively. The surface composition of Ag NPs and AgNPs@PAM was further scrutinized by means of the XPS technique. The as-prepared samples show typical Ag metal spectra with peak separation of 6 eV and no Ag₂O residuals (Figure S1). The presence of the N 1s peak at around 400.0 eV (Figure S2) indicates the existence of amide N on the surface of Ag NPs.^[39]



Figure 1. (a) SEM image, (b) partially enlarged image and (c) HR-TEM image of AgNPs@PAM; (d) The elemental mapping images of silver (green), carbon (red), nitrogen (cyan) and oxygen (purple) of AgNPs@PAM; (e) XRD patterns of AgNPs@PAM; (f) FT-IR spectra of PAM and AgNPs@PAM.

The CO₂ adsorption isotherms of Ag NPs, PAM and AgNPs@PAM were measured to determine the CO₂ adsorption ability. As seen in Figure 2a, Ag NPs shows the worst CO₂ adsorption ability (0.2141 cm³ g⁻¹, 1 atm), which is far less than that of PAM (0.5118 cm³ g⁻¹, 1 atm). The much higher adsorption

capacity for the linear polymer implies that PAM is likely to adsorb CO₂ chemically. Under the accumulative effect of Ag NPs and PAM, AgNPs@PAM shows the best CO₂ adsorption capacity (0.5442 cm³ g⁻¹, 1 atm), which is more than 2.5 times larger than that of Ag NPs. Further, the contact angles of a drop

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of water (3 μ L) on the surface of Ag NPs and AgNPs@PAM were measured to evaluate the hydrophilicity of the catalysts (Figure 2b, c). In contrast to the hydrophobic surface of Ag NPs (70.35°), AgNPs@PAM exhibits an appropriate hydrophilic surface property (26.85°) thanks to the introduction of amide groups. Obviously, the hydrophilic surface of AgNPs@PAM is

more favorable for CO₂ER since it can not only ensure a sufficient contact area between the metal electrode and the electrolyte to facilitate the mass transfer,^[34,40] but also accelerate the adsorbed gaseous products to escape the surface of metal electrode.^[41-43]



Figure 2. (a) CO2 adsorption isotherms of Ag NPs, PAM and AgNPs@PAM; Contact angle measurements of (b) Ag NPs and (c) AgNPs@PAM.

To preliminarily evaluate the catalytic performance of AgNPs@PAM, linear sweep voltammetry (LSV) tests were first conducted in N₂- and CO₂-saturated 0.1 M KHCO₃ electrolyte with pH 6.8 at a scan rate of 10 mV s⁻¹ (Figure S3). A clear positive shift of onset potential and enhanced cathodic current are found in the atmosphere of CO₂, indicating that CO₂ is electrochemically reduced over AgNPs@PAM. Electrocatalytic performance of the hybrid catalyst for CO2ER was further investigated by the controlled potential electrolysis in 0.1 M KHCO₃ electrolyte saturated with CO₂. Only CO and H₂ were observed during the overall electrolysis and no liquid phase reduction products was found by ¹H NMR spectroscopy. The contents of PAM in the Ag NPs hybrid catalysts quantified by TGA (Figure S4, Table S1) was first evaluated to determine the optimal ratio. As expected, the CO partial current density (j_{co}) is boosted significantly when the content of PAM continues to increase to 5.34 wt.%. However, both CO2ER and HER (Figure S5) are suppressed (especially for the former) with further increasing the content of PAM to 6.35 wt.% probably due to the deteriorated electrical conductivity of hybrid catalyst (Table S2). Additionally, it should be noted that the excessively enhanced hydrophilicity with further increasing the content of PAM tends to cause the Ag NPs hybrid to be flooded (Figure S6). Taking CO2ER performance and structure stability of catalyst into account, the Ag NPs hybrid with 3.74 wt.% PAM (AgNPs@PAM) was chosen to further explore the role of PAM in selectively enhancing electrochemical conversion of CO₂ to CO. As shown in Figure 3a, the onset potential of CO2ER over AgNPs@PAM (-0.39 V) shifts positively by 100 mV with a CO Faradaic efficiency (FE) of 35.3% compared with Ag NPs without PAM modification (-0.49 V), implying an improved intrinsic activity. With the overpotential increasing, both CO FE and j_{co} (Figure 3a, b) rise rapidly. The AgNPs@PAM hybrid exhibits the maximum CO FE

of 97.2% at -0.89 V with a j_{co} of -22.0 mA cm⁻², while Ag NPs in the absence of PAM only delivers a CO FE of 48% with a j_{co} of -2.1 mA cm⁻² at the same potential. Most impressively, the H₂ partial current density (j_{H2}) over AgNPs@PAM is only -5.5 mA cm^{-2} when the j_{co} reaches -58.5 mA cm⁻² at -1.29 V, providing an attractive catalyst system for the electrochemical conversion of CO₂ into valuable fuels. To make clear the origin of the excellently selective CO2ER over AgNPs@PAM, the catalytic performance of Ag NPs with a similar size of ~ 100 nm (denoted as AgNPs-100, Figure S7) prepared with the aid of surfactant sodium dodecyl sulfate was also evaluated. As seen from Figure 3a, b, the jco over AgNPs-100 is indeed remarkably enhanced at each applied potential compared with that over Ag NPs with the size of ~ 500 nm, but it still lags far behind that over AgNPs@PAM, especially at the high overpotentials. On the contrary, it is interesting to note that the $j_{\rm H2}$ over AgNPs-100 is much higher than that over AgNPs@PAM at potentials \geq -0.79 V. Accordingly, the CO FE over AgNPs-100 reaches the maximum of 90.0% at -0.69 V with a poor j_{co} of -5.8 mA cm⁻², and then drops rapidly as the potential shifts negatively. By contrast, the CO FE over AgNPs@PAM can be maintained above 95% in the wide potential range from -0.79 to -1.09 V, and it is still above 90% when the applied potential increases to -1.29 V. These comparisons fully reveal that PAM plays a crucial role in enabling AgNPs@PAM to simultaneously possess high activity and selectivity at high overpotential. In addition, the maximum CO FEs of the previously reported Ag-based electrocatalysts are summarized in Table S3. These results demonstrate that AgNPs@PAM is a very competitive catalyst for CO₂ER in aqueous solution.

The electrochemically active surface areas (ECSA) of AgNPs@PAM and Ag NPs were measured through the Cu underpotential deposition (UPD) method^[44] and their specific

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activities were obtained via normalizing the j_{co} by the corresponding ECSA. As seen in Figure S8, AgNPs@PAM indeed exhibits an extremely higher specific j_{co} than that of Ag NPs at each operating potential, further confirming that AgNPs@PAM is intrinsically more active than Ag NPs. Tafel analysis was performed to gain insight into the reaction kinetics of CO₂ER over AgNPs@PAM, (Figure S9). The measured Tafel slope for AgNPs@PAM is 133 mV dec⁻¹, which is comparable to the 118 mV dec⁻¹ expected for rate-limiting single-electron transfer from the adsorbed *CO₂ to form the surface-adsorbed *CO₂·.^[45] However, the smaller Tafel slop for AgNPs@PAM relative to our previously reported values for Ag NPs with sizes of ~ 5 nm^[46] also suggests that the introduction of PAM may contribute to the enhancement of the intrinsic activity of Ag NPs.

In addition, the electrochemical stability of AgNPs@PAM was measured at -0.79 V by prolonging the electrolysis. As shown in Figure 3c, the total current density remains stable at ~ -11 mA cm⁻² and the CO FE only slightly declines by ~ 2% after the 48 h electrolysis. This outstanding electrochemical durability could be reasonably attributed to the following two aspects. First, the utilization of Ag NPs with large size could exert a mitigated effect of particle size on CO₂ER activity, circumventing a significant decrease in CO production rate due to the slight agglomeration of Ag NPs during electrolysis (Figure S10). Second, the appropriate hydrophilicity of AgNPs@PAM could accelerate the desorption of CO from the electrode surface, preventing the hybrid catalyst from being poisoned effectively.^[47]



Figure 3. (a) CO FE, (b) j_{co} and (c) j_{H2} over Ag NPs, AgNPs-100 and AgNPs@PAM versus the applied potential; (d) Stability test for CO₂ER over AgNPs@PAM at -0.79 V.

To shed further light on the origin of selectively enhancing CO_2ER over AgNPs@PAM, a set of comparative experiments were conducted in CO_2 -saturated 0.1 M KHCO₃ electrolyte without and with cocatalysts by using the same Ag NPs as working electrode. As seen in Figure 4a, b, the maximum CO FE is only 58.0% over Ag NPs at -0.79 V, while it can be substantially increased to 86.3% at a more positive potential of -0.69 V after addition of 6 mg PAM to the catholyte. Meanwhile,

the j_{co} in the presence of PAM is also boosted significantly and such enhancement effect for CO₂ER is more pronounced at higher overpotentials. Interestingly, HER almost shows an opposite variation trend to CO₂ER, implying that the introduction of a proper amount of PAM is capable of promoting CO₂ER exclusively, and the resultantly increased CO₂ concentration on the surface of Ag NPs could simultaneously suppress HER to some extent (Figure 4c, d). These results further evidently

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indicate that the synergistic effects of Ag NPs and PAM does play a preponderant role in selectively enhancing CO₂ER, which enables the AgNPs@PAM hybrid to show a very competitive CO FE of 97.2% at -0.89 V even though the average size of Ag NPs is as high as ~ 100 nm. For comparison, polyethyleneimine (PEI), a widely investigated cocatalyst for CO2ER [6,48] was also examined to evaluate its ability to tune the reactivity of Ag NPs. As shown in Figure 4d, the j_{H2} appreciably and systematically rises across all applied potentials examined after addition of 6 mg PEI into the catholyte. By contrast, the j_{co} first follows the opposite variation trend to the j_{H2} when the Ag NPs catalyst is not sufficiently activated at low overpotentials (E \geq -0.59 V). Moreover, it can be observed that the onset potential of CO production also shifts negatively from -0.49 V to -0.59 V. Then with the overpotential increase, the Ag NPs catalyst is further activated and PEI starts to exhibit a positive effect on CO₂ER. Accordingly, the change in the i_{co} shows synchronous with that of i_{H2} , contributing to an almost PEI-independent CO FE owing to their similar growth rate. In fact, PEI is positively charged in the CO₂-saturated 0.1 M KHCO₃ electrolyte (pH = 6.8) because of partial protonation at the primary amine N's positions (its conjugate acid $pK_a = 9.5$) (Inset in Figure 4a). Clearly, these protonated amine groups in PEI are more easily reduced than

water molecules (p K_a = 15.8) to release H₂, leading to an improved HER kinetics. In addition, most of the imine groups (its conjugate acid $pK_a = 7$) in PEI are not protonated and would play the same role as amide groups to promote CO₂ER. All in all, the synergistic effect of PEI and Ag NPs can only deliver an increased CO production rate at high overpotentials, but contributes little to the improvement of CO FE. Furthermore, the ability of PEI to boost the j_{co} is obviously inferior to that of PAM at each applied potential. From the results of these comparative experiments, it can be reasonably concluded that the performance of PAM over PEI in facilitating CO2ER, especially in terms of selectivity, is closely associated to the p-π conjugate system of amide group. First, such a unique electron structure makes the conjugate acid of amide have a pK_a of only around -0.5. This lack of basicity ensures that PAM will not be protonated to accelerate the H₂ evolution rate in the catholyte with a pH of 6.8. Second, the enhanced reactivity of N-H hydrogen atoms may be more effective in activating CO₂ or stabilizing the key intermediates formed in CO2ER through the formation of hydrogen bonds compared with those of imine counterpart. Consequently, these two properties and the appropriate hydrophilicity mentioned above underlie the AqNPs@PAM hybrid for selectively enhancing CO₂ER.



Figure 4. (a) CO FE, (b) jco, (c) H₂ FE and (d) jH₂ over Ag NPs electrode in 0.1 M KHCO₃ electrolyte without and with cocatalysts. Inset: partial protonation of PEI.



Subsequently, the *in-situ* ATR-IR and UV-vis spectroscopy were used to verify the ability of PAM to chemically activate CO₂. As shown in Figure 5a, a broad infrared absorption peak centered at ~ 837 cm⁻¹ can be found over AgNPs@PAM in CO₂ atmosphere, which is very close to that reported infrared characteristic absorption peak (~ 839 cm⁻¹) of the reactive intermediate formed by CO₂ bonding with -NH₂,^[49] and the peak at 837 cm⁻¹ will disappear in the absence of CO₂ or PAM. These two observations further confirm the chemisorbing CO₂ taking place over AgNPs@PAM during the electrolysis, and the activation of CO₂ is likely to be achieved through the formation of hydrogen bonds between the active hydrogen atoms in the amide group and the oxygen atoms in CO₂.^[50,51] In addition, the UV-vis spectra of 300 mg L⁻¹ PAM aqueous solution in N₂ and CO₂ atmosphere were measured to further examine the

formation of hydrogen bond between PAM and CO₂. As shown in Figure 5b, the distinct absorption peaks observed around 200 nm in N₂ atmosphere can be assigned to the $n \rightarrow \pi^*$ electronic transition resulted from the p- π conjugate effect of amide group in PAM.^[52] The peak wavelength underwent a 3 nm blue shift after bubbling CO₂ into the PAM solution, which can be attributed to the formation of hydrogen bond between PAM and CO₂. Specifically, the O atom in CO₂ with a strong electronegativity (3.44) causes an inductive effect toward the amide group through the formation of hydrogen bond, which increases the electron cloud density on the nitrogen atom and reduces the liquidity of π electron in the amide group, thereby elevating the energy level of π^* orbit.^[53] Therefore, more energy for electron migration of $n \rightarrow \pi^*$ is needed, leading to the blue shift of the peak wavelength.



Figure 5. (a) In-situ ATR-IR spectra of Ag NPs and AgNPs@PAM purged with N₂ or CO₂ at -0.89 V; (b) UV-vis spectra of PAM aqueous solution in N₂ and CO₂ atmosphere.

To sum up, our results have demonstrated that amide group indeed facilitates the adsorption and the activation of CO₂, which are achieved through the hydrogen bond between the highly active H atom in amide group and the O atom in CO₂. Similar to the common phenomenon that the adsorption energies of reaction intermediates tend to follow linear scaling relations in heterogeneous catalysis, we envision that the key intermediate COOH^{*} could behave as CO₂ to form hydrogen bond with amide group to lower the overpotential of CO₂ER. To this end, DFT calculations were conducted with Ag (111) and Ag (111)@C₄H₉NO models to calculate the free energies of the following reaction mechanistic steps [Equation 1–3] ,^[54] where * denotes an adsorption site and e⁻ is an electron. For the convenience of calculation, isobutanamide (C₄H₉NO), which is similar in structure to the PAM unit, was chosen to model with Ag (111) to describe the Ag NPs-PAM interface.

$\text{CO}_2(g) + * + \text{H}^+(aq) + e^- \rightarrow *\text{COOH}$	(1)
*COOH + H ⁺ (aq) + e ⁻ \rightarrow *CO + H ₂ O (I) *CO \rightarrow CO + *	(2)
	(3)

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Figure 6. The DFT calculated free energy changes of CO formation without isobutanamide (black line) and with isobutanamide (red line)

Figure 6 shows the optimized structures and calculated free energy diagram of CO₂ER over Ag (111) and Ag (111)@C₄H₉NO. Both Ag (111) and Ag (111)@C4H9NO show a largest free energy for the formation of carboxyl (*COOH) species by the initial proton-coupled electron transfer [Equation (1)]. Encouragingly, the corresponding energy cost over Ag $(111)@C_4H_9NO$ is 0.23 eV lower than that over Ag (111). Subsequently, the protonated decomposition of *COOH to *CO [Equation (2)] and the desorption of *CO [Equation (3)] are also facilitated under the synergetic effect of Ag (111) and amide group owing to the spontaneous process. These calculations demonstrate that the overpotential of CO₂ER is indeed reduced via the formation of hydrogen bond between amide group and the key intermediate *COOH, leading to an enhanced CO2ER performance.

Conclusion

In summary, we successfully constructed a durably PAMmediated Ag NPs electrocatalyst for selectively enhancing the electroreduction of CO₂ to CO in water. The adsorption isotherms of CO₂ and the contact angle measurements show that amide group can endow this hybrid catalyst excellent CO2 adsorption capacity and favorable hydrophilicity. The comparative experiments suggest that the exclusive CO2ER enhancement over Ag NPs after introduction of PAM could be attributed to the highly active hydrogen atom and the appropriate pKa value of amide group. The in-situ ATR-IR and UV-vis spectra confirm that the activation of CO₂ is achieved by forming hydrogen bond with the amide group. Further, DFT calculations imply that the overpotential of CO2ER could be further reduced via the same reaction mode between the key intermediate *COOH and amide group. Benefiting from these merits mentioned above, the synergistic catalysis of Ag NPs and amide group contributes an outstanding CO FE of 97.2% ± 0.2 % at - 0.89 V with a desirable j_{co} of -22.0 ± 2.3 mA cm⁻², and the CO FE can even be maintained above 95% over a wide potential window of -0.79 to -1.09 V. Meanwhile, this organic/inorganic hybrid catalyst also displayed an outstanding electrochemical durability during a 48 h prolonged electrolysis thanks to the large size of Ag NPs, showing great potential for practical application in the large-scale production of CO from CO₂ electrolysis. We anticipate that this combined nanoscale and molecular strategy can be extended to other important electrocatalytic reactions and provide a new route for the design of hybrid materials with synergistic catalytic effects.

Experimental Section

Catalyst preparation

The hybrid catalyst composed of Ag NPs and PAM was synthesized by one-pot reaction in water phase. Firstly, 0.03 g PAM and 1.275 g AgNO₃ were dissolved into 100 mL deionized water successively. The above solution was then quickly added into a freshly prepared solution of NaBH₄ (0.275 g in 100 mL H₂O) under vigorous stirring. After stirring the mixture for 2 h at 20 ± 3 °C, the black precipitate was collected by high speed centrifugation of 8000 r·min⁻¹, washed thoroughly with deionized water and dried in a vacuum oven at 60 °C overnight, and then the hybrid catalyst was obtained and denoted as AgNPs@PAM. Notably, the amount of PAM was easily adjustable, and another three contents of 0.015 g, 0.045 g and 0.06 g were also adopted in this work, the asprepared hybrids were named as AgNPs@PAM-15, AgNPs@PAM-45, AgNPs@PAM-60, respectively. Ag NPs (~ 500 nm diameter) without any modifications and Ag NPs (~ 100 nm diameter) prepared with the aid of sodium dodecyl sulfate were synthesized according to our early work.^[55]

Characterizations

To get the crystallographic information of the catalyst, powder X-ray diffraction (XRD) patterns were obtained by using a Rigaku X-ray facility with $Cu_{K\alpha}$ radiation (λ = 1.5406 Å) at 40 kV and 20 mA with the 20-angle



from 5° to 90°. A field-emission scanning electron microscope (FESEM; Nova Nanosem 450) equipped with energy dispersive X-ray spectroscopy (EDX) was used to observe the morphology and elemental composition of the catalyst. High-resolution electron microscopy (HRTEM; Jeol, JEM-2100, 200 kV) was performed to determine the crystal faces and lattice stripes of the catalyst. X-ray photoelectron spectroscopic (XPS) characterizations were performed on a Thermos Scientific Escalab 250Xi instrument with Al Ka X-ray to measure the surface properties of the as-prepared hybrid catalysts. To determine the Ag content of catalyst, the thermal gravimetric analysis (TGA) was performed on a Netzsch STA449F3 at a temperature ramp of 5 °C min⁻¹ under an air flow from room temperature to 900 °C. Fourier transform infrared spectroscopy (FT-IR) data were obtained using a Nicolet Magna-IR 550 spectrometer and the contact angles were recorded using a DataPhysics OCA-30 instrument. The resistivity of as-prepared catalysts was tested using a M-3 Mini type four-probe tester (Suzhou Jingge Electronic Co., Ltd.). The adsorption isotherms of CO2 were obtained at 298 K using a Quadrasorb SI analyser and the catalysts were degassed at 298 K for 10 h prior to the measurement.

The *in-situ* attenuated total reflectance infrared (ATR-IR) spectra were collected by a PerkinElmer Spectrum 100 spectrometer equipped with a liquid nitrogen cooled mercury cadmium telluride (MCT) detector (LingLu Instruments, Electrochem IR) with unpolarized IR radiation at an incidence angle of 55°. The catalysts were compressed into square sheets and placed on the basal plane of a hemi-cylindrical Si prism beveled at 60°. Typically, 64 scans were collected for each spectrum at a resolution of 4 cm⁻¹. An ultraviolet and visible spectrophotometer (UV-vis; Shimadzu UV-2550) was used to collect the absorption curves of PAM aqueous solution saturated with N₂ and CO₂, respectively. Using distilled water as the blank, the different solutions were scanned in the wavelength range of 190 ~ 800 nm.

Electrochemical measurements

All electrochemical experiments were performed in a three-electrode system and the airtight two-compartment electrochemical cell was separated by Nafion 117 cation-exchange membrane. The potential was controlled by a PGSTAT 302N electrochemical workstation (Autolab, Metrohm). 0.1 g as-prepared AgNPs@PAM powder was compressed into square sheet (1 cm × 1 cm) by tablet machine (Keyan, 769YP-10T), which could be directly used as the working electrode by an electrode holder. The Pt mesh (2 cm × 2 cm) and Ag/AgCl (3.5 M KCl) were used as the counter electrode and reference electrode, respectively.

Each compartment of the electrochemical cell contained 35 mL of 0.1 M $\rm KHCO_3$ electrolyte and approximately 15 mL of headspace. The pH of the catholyte was 6.8 after CO₂ saturation. All potentials reported in this paper were measured against an Ag/AgCl reference electrode and converted to the reversible hydrogen electrode (RHE) reference scale using E (vs. RHE) = E (vs. Ag/AgCl) + 0.21 V + 0.0591 × pH. During the electrolysis, the catholyte was magnetically stirred at a rate of 1000 rpm to assist the effective diffusion of the gaseous reactants and products. To minimize the influence of the change of electrolyte during the long-term stability test, 0.5 M and 0.1 M KHCO3 solutions were used as the anolyte and the catholyte, respectively, and Nafion 117 cation-exchange membrane was replaced by AMV anion-exchange membrane. The electrolysis data were collected at the 13th, 36.5th and 48th h intervals during the stability test. The gas products were online monitored by a gas chromatogram (Techcomp 7900) equipped with a thermal conductivity detector (TCD) and a flame ionization detector (FID). The possible liquid products were determined by ¹H NMR spectroscopy (Avancell 500 MHz) with D₂O as the solvent.

Computational methods

DFT calculations were performed using the Vienna Ab-initio Software Package (VASP) with the Perdew-Burke-Ernzerhof (PBE) exchange-

correlation functional,^[56,57] and the electron-ion interaction was treated using the projector-augmented-wave (PAW) method,^[34,58] Wave functions of valence electrons were expanded using plane wave basis sets with a kinetic energy cutoff of 400 eV. The (4×4) periodic slab models with four atomic layers were combined with a 20 Å vacuum layer. Along the z axis, two bottom layers were fixed during the geometry-optimization processes whereas the upper two layers were allowed to relax. The closest-packed faces which are (111) for the fcc structure were considered to be representative reactive surfaces and the (1×1×1) k-point grid was employed. To estimate the enthalpy changes during solvation process implemented in the VASP program, a dielectric constant ε = 80 was used for water.^[59-61]

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Keywords: Nanohybrid • Amide • Ag nanoparticles • CO₂ reduction • Synergistic catalysis

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The polyacrylamide-modified Ag nanoparticles with extraordinary CO_2 adsorption capacity and favorable hydrophilicity were constructed for the selective electroreduction of CO_2 to CO in near-neutral aqueous solution.